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ABSTRACTS

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BUREAU OF CHEMICAL ABSTRACTS.

A. PURE CHEMISTRY.

PART II.

General, Physical, and Inorganic Chemistry.

Experimental Test of the Theory of Bohr, Kramers, and Slater. W. BOTHE and H. GEIGER (*Z. Physik*, 1924, 26, 44).—An experimental test of the theory of Bohr, Kramers, and Slater (cf. A., 1924, ii, 433, 509) is suggested. On the basis of the Compton theory of *X*-ray scattering, the simultaneous production of scattered radiation and of the electron associated with it is necessitated. According to the proposed theory, no such simultaneity should be observed. As the scattered radiation and the electron have not the same direction, it should be possible to record their production by two Geiger counters, and to detect any statistical connexion between the two events. S. B.

Extension of Bohr's Correspondence Principle to Small Quantum Numbers. J[illegible] *[illegible] Rev.*, 1924, 24, 463—466).—When an [illegible] om an orbit of quantum number n_2 to o[illegible] of the radiation emitted is an integral (n, [illegible] an frequency of rotation in its orbit duri[illegible] suming that the number of rotations made [illegible] tum level dn is proportional to dn. A. A. E.

1494
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Simultaneous Jumping of Two Electrons in Bohr's Model. P. S. EPSTEIN (*Proc. Nat. Acad. Sci.*, 1924, **10**, 337—342).—A theoretical discussion of the abnormal triplet series in calcium discovered by Russell and Saunders. The series is $1p—mp'$, and the frequencies of the third and of all successive members of the series are greater than the frequency of the normal series limit for the return of an electron to the $1p$ orbit. The excess energy required for the emission of these lines is supposed to be derived from orbital changes of a second electron. The author shows by

consideration of a simplified model that such series are compatible with the principle of correspondence, and are due to the coupling of the electrons within the atom. Such coupling is shown to modify the selection rules so that the azimuthal quantum number of an electron may change by two, or the quantum number of two electrons may simultaneously change by unity. S. B.

Constants of the Rydberg-Ritz Equation. J. H. JONES and J. C. BOYCE (*Proc. Roy. Soc.*, 1924, **A**, **106**, 773—784).

Atomic Force Fields. F. S. BRACKETT (*J. Opt. Soc. Amer.*, 1924, **9**, 237—249).—Regularities have been traced in the variation with atomic number of the energies of inner virtual orbits. These are correlated with changes in the quantum defects for the same elements. The assignment of quantum numbers due to Brackett and Birge is confirmed. S. B.

Relations between the Optical Spectra of Different Atoms of the Same Electron Structure. I. Lithium-like and Sodium-like Atoms. D. R. HARTREE (*Proc. Roy. Soc.*, 1924, **A**, **106**, 552—580).—General theoretical relations of a quantitative nature are given based on the Bohr atom.

Comparison with experimental results on the line spectra of a number of elements is effected by a computation of a quantity known as the "term excess" which is given by the difference between the wave number corresponding with the energy term of the orbit under consideration and the wave number of the corresponding term of the hydrogen-like atom of the same core charge.

The observed values of the "term excess" for sodium-like and lithium-like atoms which remain entirely outside the core agree very closely with a relation of the type indicated by the theory. For orbits which penetrate the core values are found which agree roughly with the values deduced from observed spectra. R. W. L.

Spectra of some Lithium-like and Sodium-like Atoms. D. R. HARTREE (*Proc. Camb. Phil. Soc.*, 1924, **22**, 409—425).—The argument on the interpretation of the experimental results (cf. preceding abstract) is treated in considerable detail. R. W. L.

Optical Constants of Matter. C. G. DARWIN (*Trans. Camb. Phil. Soc.*, 1924, **23**, 137—167).—An analysis of the refraction, reflection, and absorption of light in their relation to the simple phenomenon of scattering without having recourse to any atomic theory, thereby obviating the difficulties that are inherent in the application of the laws of classical thermodynamics to electrons. The results, it is claimed, of this analysis are not to be construed in any sense as in opposition to the classical electron theory; they merely represent an extraction from that theory of the parts which may be regarded without any distrust.

A number of typical results of the application of the analysis now advanced is appended to the paper. R. W. L.

Optical Separations and Atomic Numbers. A. C. MENZIES (*Nature*, 1924, **114**, 861).—The relativity X-ray formula $dv=K(Z-s)^4$

(cf. Millikan and Bowen, A., 1924, ii, 710) has been applied to doublets and triplets generally, and the values of s have been tabulated. The values within the same group are directly proportional to the atomic number, and the slopes of the graphs are very nearly the same for all groups. A. A. E.

Controlled Orbital Transfers of Electrons in Optically Excited Mercury Atoms. R. W. Wood (*Proc. Roy. Soc.*, 1924, **A, 106**, 679—694).—The fluorescence of mercury vapour has been studied. The exciting radiation was from a water-cooled mercury arc. The atoms are primarily excited by absorption of the line at 2536 Å., and an electron is thereby raised to the $2p_2$ orbit. It is raised to higher levels by subsequent absorption of other lines, and the fluorescent light indicates the return path of the electron to the $1S$ orbit. Addition of nitrogen and other gases has remarkable effects on the phenomena. Nitrogen causes the excited vapour to absorb 4046 ($2p_3$—$2S$) strongly, and an intense emission of 5461 ($2S$—$2p_1$), and also other changes. Many other effects of mixtures are recorded. S. B.

Anomalous Zeeman Effects. W. Heisenberg (*Z. Physik*, 1924, **26**, 291—307).—To explain the phenomena of the complex Zeeman effects and other phenomena due to the coupling of several electrons, it is necessary to introduce a further quantum restriction on the value of the coupling energy. S. B.

Spectral Theory and the Origin of the "Nebulium" Lines. S. Rosseland (*Nature*, 1924, **114**, 859—860).—A theoretical consideration of the possibility that the nebulium spectrum may be due to helium. The assumption of a metastable state of hydrogen would harmonise with observations on nebulæ, but the nebular lines can scarcely be ascribed to a molecular compound of hydrogen and helium. A. A. E.

Sommerfeld's and Landé's Rules for Classification of Terms and Zeeman Patterns in Spectra. W. M. Hicks (*Phil. Mag.*, 1924, [vi], **48**, 1036—1048).—Contains a suggested change in form of the enumeration of species of term types and the rules for predetermination of Zeeman patterns, and the discussion of the evidence for and against a rule, accepted by Landé, supposed to give the ratios of the separations in multiplets. C. W. B.

Doppler Effect in Canal Rays from Hydrogen, Oxygen, and Nitrogen. H. Krefft (*Ann. Physik*, 1924, [iv], **75**, 75—107).—Canal rays generated in one chamber were passed into another containing gas at a lower pressure than the first, as in the method of Wien (*Physikal. Z.*, 1910, **11**, 377), producing light by collision, and the Doppler effect of this was studied in relation to the potential difference across the discharge tube. Contrary to previous reports, no limiting velocity was found. The relation of the velocities of the extinction maxima are discussed and also the effect of changing the gases in the chambers. By the use of an electromagnetic field, it is shown that the spark lines of oxygen and nitrogen are

produced from singly positively charged atoms, whilst the arc and series lines probably originate from neutral atoms. With the highest velocities, indications of doubly charged oxygen atoms are obtained. L. J. H.

Series Regularities in the Spark Spectrum of Nitrogen. C. C. KIESS (*Science*, 1924, 60, 249).—Lines in the red and infra-red regions of the arc spectra of metals in air have been identified as spark lines of nitrogen. The sensitive lines result from combinations of a triple P term with an S term, another triple P term, and a five-fold D term. The series regularities given in a table are of odd multiplicity (quintet system) and therefore belong to the spark spectrum of nitrogen. A. A. E.

Fine Structure of the Helium Line 5876 Å. L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1924, 26, 57—58).—The relative intensities of the two components of the yellow helium line 5876 Å. are 1 : 6. If the line is a normal doublet of the type 2π—3δ, the relation should be 1 : 2. It is concluded that the line is probably either an intercombination of two singlet terms or a multiplet of a new type. S. B.

Structure of the Iron Spectrum. II. O. LAPORTE (*Z. Physik*, 1924, 26, 1—22).—A continuation of previous work (A., 1924, ii, 364). Septet terms have been identified, and their intercombinations with the fundamental d-term of the iron spectrum. Additional triplet and quintet terms have been found. Complete tables are given. A quarter of the total number of iron lines have now been assigned orbital transitions. S. B.

Pole Lines occurring in the Interrupted Arc Spectra of Silver, Gold, and Copper. H. LOWERY (*Phil. Mag.*, 1924, [vi], 48, 1122—1131).—Spectroscopic observations have been made of the silver, gold, and copper arcs produced under conditions similar to those of Hemsalech and the Comte de Gramont (A., 1922, ii, 176, 410). In the regions studied, 5220 to 3380 Å., a number of lines have been found in the neighbourhood of the fixed pole which readily fall into two classes according as they cease abruptly at the end of the initial stages of the arc flash or tend to pass on into the intermediate and final stages. Most of the lines have been identified with previously observed arc and spark lines, but a number of them do not seem to have been previously recorded. Lists of the "new" lines occurring in the region 5220 to 3380 Å. are given. C. W. B.

Spark Spectrum of Cæsium. L. A. SOMMER (*Ann. Physik*, 1924, [iv], 75, 163—181).—The spark spectrum of cæsium has been carefully measured from 3268—7280 Å. The series lines of the arc spectrum were measured at the same time: $2p_2-2p_1=554{\cdot}038$ cm.$^{-1}$, in good agreement with Meissner's value (A., 1921, ii, 565). The series lines of the spark spectrum (Cs^+) are evidently too widely spaced for three or more members of the same series to be included in the region studied. Two groups of lines (51) have

been analysed for constant differences and can be arranged into a scheme similar to that of Landé for neon (A., 1921, ii, 669) and to that obtained from an analysis of the lines of xenon. These analogies afford qualitative confirmation of the Sommerfeld–Kossel displacement law. L. J. H.

M-Series of Tungsten. R. Thoraeus (*Z. Physik*, 1924, **26**, 396—399).—The wave-lengths of the *M*-series of tungsten have been measured. The measurement of such long wave-lengths was made possible by the substitution of a red celluloid window in the *X*-ray tube, in the place of a metal foil. S. B.

Series Limit Absorption in Sodium Vapour. G. R. Harrison (*Physical Rev.*, 1924, **24**, 466—477).—As the wave-length decreases, the transmission of sodium vapour rises to a maximum at 2465 Å., decreases regularly to a minimum at the series limit 2414 Å., and returns to its former value at 2200 Å. Eighteen similar curves were obtained for different vapour densities. The results, however, do not permit determination of the precise variation of atomic absorption with wave-length. A. A. E.

Absorption and Dispersion of Thallium Vapour. A. L. Narayan, D. Gunnaiya, and K. R. Rao (*Proc. Roy. Soc.*, 1924, **A, 106**, 596—601).—Thallium vapour in the non-luminous state absorbs lines of the sharp and diffuse series and the $1,\pi_2$ orbit is the ground-orbit of the valency electron. At about 900°, a large number of bands of diffuse and complex structure make their appearance, which are attributed to Tl_2 molecules. The infra-red absorption shows no selectivity in the region 0·9 μ to 1·35 μ, and therefore $1,\pi_2—1,\pi_1$ is not the single-line spectrum of the metal. The work of Geisler and of McLennan on the anomalous dispersion exhibited at 5350·6 Å. has been confirmed. Anomalous dispersion is, however, more prominent at 3775·7 Å. R. W. L.

Relative Absorbing Powers of the *L*-Levels for Radiation of Varying Wave-length. H. W. B. Skinner (*Proc. Camb. Phil. Soc.*, 1924, **22**, 379).—Measurements of the absorbing power were made by a new method, which consists in recording photographically by a Seeman spectrograph the relative intensities of the fluorescent *L*-spectrum of cerium excited by the *K*-radiations of copper, molybdenum, and silver.

The results are held to confirm the work of Robinson (cf. A., 1923, ii, 818) on the relative absorbing powers of the *L*-levels, and to indicate that the λ^3 (λ=*X*-ray wave-length) law is invalid when applied to individual *L*-levels. R. W. L.

Methods of Estimating the Successive Ionisation Potentials of any Element. D. R. Hartree (*Proc. Camb. Phil. Soc.*, 1924, **22**, 464—474).—By assuming that for different elements the quantum numbers of the normal orbit of each of the first 18 electrons captured by a bare nucleus are independent of the atomic number, an analysis is advanced of the corresponding terms representing the energies of the normal orbit for different atoms of the same

electronic structure. It is shown that, assuming the quantum numbers of the term corresponding with the normal orbit, there are four methods which may be used to estimate the value of this term from which the ionisation potential may be evaluated. Approximate values of the successive ionisation potentials of oxygen, iron, and silver are given in tabular form, together with detailed illustrations of the method of calculation. R. W. L.

Negative and Doubly-charged Positive Ions in Argon. H. A. BARTON (*Nature*, 1924, **114**, 826—827).—Singly-charged, positive, atomic argon ions are first detected when an accelerating potential of about 17 volts (uncorr.) is applied to electrons striking the atoms, and doubly-charged positive atomic ions at 45 volts. The result is contrary to the assumption that the critical potential of 34 volts at which the first part of the blue spectrum appears corresponds with the production of doubly-charged ions. Since negative ions originate in that part of the tube where impacting electrons have just sufficient energy to excite the atoms, it would appear that for argon it is a necessary and sufficient condition for the capture of an electron that the atom should first be in an excited state. A. A. E.

Nature of the Ions in Air and in Carbon Dioxide. H. A. ERIKSON (*Physical Rev.*, 1924, **24**, 502—509).—The mobility curves obtained are explained by assuming that ionisation involves the detachment of an electron from a molecule, leaving a positive, unimolecular ion which soon attaches itself to a neutral molecule forming the final, unstable, bimolecular, positive ion, whilst the electron almost immediately joins a neutral molecule forming a stable, negative, unimolecular ion. Dissociation is considered to play only a small part. It is concluded that single molecules singly charged, positively or negatively, all have about the same mobility which is independent of mass and molecular volume, and that a singly-charged cluster of two or more molecules, not forming a single molecule, has a smaller mobility. A. A. E.

Measurement of Critical Potentials of Gases. E. G. DYMOND (*Proc. Camb. Phil. Soc.*, 1924, **22**, 405—408).—It is suggested that these potentials will be more accurately obtained if, instead of plotting the current–voltage curve, as is the usual practice, the differential of this curve be plotted. An experimental method of directly obtaining this value is outlined, and has been tested with helium. The results obtained are essentially preliminary, but much greater sensitivity than with the usual method is promised. L. F. G.

Conditions for Statistical Equilibrium between Atoms, Electrons, and Radiation. P. A. M. DIRAC (*Proc. Roy. Soc.*, 1924, **A.**, **106**, 581—596).—The principle that every process occurring in an assembly in thermodynamic equilibrium is exactly balanced by the reverse process occurring to the same extent is applied to the general case of n-body encounters, both radiative and non-radiative processes being considered. Reaction equilibrium con-

ditions are obtained involving the probabilities of the direct and reverse processes. It is shown that the van't Hoff isochore is of universal validity even for radiative processes and with relativity mechanics.

From Planck's law of radiation it is deduced that every process by which radiation is emitted is stimulated by external radiation of the same frequency, the ratio of stimulated to spontaneous emission being independent of the nature of the process, and inversely proportional to the cube of the frequency. The analysis is extended to the deduction of formulæ for the degree of ionisation of a gas which differs but slightly from those advanced by Saha and Fowler. R. W. L.

Statistical Theory of Dissociation and Ionisation by Collision, with Applications to the Capture and Loss of Electrons by α-Particles. R. H. FOWLER (*Proc. Camb. Phil. Soc.*, 1924, **22**, 253—272).—In a previous analysis (cf. A., 1924, ii, 221) on the basis of the classical Bohr–Thomson theory of ionisation by collision, the author ignored the interactions in the core of any atom entered by an α-particle. The limitations inherent to these premises are obviated in the analysis now advanced.

Formulæ are given for the frequency relations between the general 2- and 3-body collision processes of dissociation and recombination in a perfect gas. For ionisation and its reverse, the formulæ take a simple form. The results are applied to an investigation of the theory of the capture and loss of an electron by swift α-particles in which the effects of the general field of the atom are included. Rutherford's V^5-law for the equilibrium ratio $[H^{++}]/[He^+]$ is a necessary consequence simply of the classical formulæ for the distribution in velocity of the δ-particles ejected by α- or β-particles of given velocity. R. W. L.

Photoelectric Thresholds of Elements. R. HAMER (*J. Opt. Soc. Amer.*, 1924, **9**, 251—257).—The maximum wave-lengths able to stimulate the photoelectric activity of a number of common elements have been measured. The metallic surfaces were only roughly prepared, and the values are regarded as preliminary estimates. S. B.

Calculation of the Fall of Potential in the Ion and Electron Gas Emitted from Glowing Metals. M. VON LAUE and N. SEN (*Ann. Physik*, 1924, [iv], **75**, 182—188).—Mathematical. L. J. H.

Ionic Mobilities in Gaseous Mixtures. L. B. LOEB and M. F. ASHLEY (*Proc. Nat. Acad. Sci.*, 1924, **10**, 351—355).—The mobilities of ions have been measured in mixtures of air and ammonia in varying proportions, with the intention of testing the view that a gaseous ion is surrounded by a cluster of neutral molecules. The results were indecisive. S. B.

Slow Corpuscular Radiations from Salts. T. VOLMER (*Z. Physik*, 1924, **26**, 285—290).—A number of salts have been found to emit positively charged particles at comparatively low temper-

atures (about 450°). Determinations of e/m have now shown that these particles consist of atoms of the metal which is a constituent of the salt. The salts studied were halides of cadmium, copper, zinc, lead, and calcium. S. B.

Soft X-Rays and Secondary Electrons. J. A. Becker (*Physical Rev.*, 1924, **24**, 478—485).—The velocity distribution of photo-electrons excited by soft X-rays has been analysed by a method similar to that used for β-rays. The following critical potentials were obtained: aluminium, L_3, 70 volts; L_1, 80 volts; silver, N_1, 134 volts; M_6, 365—370 volts. The following characteristic lines in the N spectrum of tungsten were observed: N_3—O_5, 410 volts; N_2—O_4, 482 volts; N_1—O_3, 560 volts; N_5—O_3, 305 volts; N_4—O_2, 312 volts. The results are in agreement with Bohr's theory. A. A. E.

Electron Emission Excited by α-Rays. A. Becker (*Ann. Physik*, 1924, [iv], **75**, 217—275).—Aluminium, silver, and gold were bombarded with α-rays in a vacuum. Ten electrons per α-particle are emitted if the velocity of the latter is $1{\cdot}5\times10^9$ cm./sec., and more, up to 20 per α-particle, for higher velocities, independently of the nature of the metal and the direction of the bombardment, *i.e.*, whether perpendicular or oblique. The average velocity with which the electrons leave the surface is independent of the metal, the direction, and the velocity of the exciting α-rays. The distribution of the velocity follows the Maxwell law of random distribution about the value 2 volts, but it is not possible to say whether there is a definite upper limit. The direction of emission is also distributed at random according to the same law. These results are compared with those obtained in the related phenomena of thermionic and δ-ray emission, the laws of which are similar, but not identical. All three are probably due to the same fundamental mechanism. L. J. H.

Radioactive Constant of Niton. I. Curie and C. Chamié (*J. Phys. Radium*, 1924, vi, **5**, 238—248).—The life constant of radium emanation has been determined by a new method. In principle, equal quantities of emanation are sealed into two bulbs, and the activity of one bulb is immediately noted. The time is then taken during which the combined activity of the two bulbs falls to the same value. The period of half-life is thus obtained directly. The corrections required in practice are described. The activity measured was the γ-ray activity of the emanation, filtered through 12 cm. of lead. Preliminary experiments showed that this activity obeyed the simple logarithmic decay law, and that, therefore, no radiation from the active deposit was interfering. The half-life period of niton is given as 3·823 days ($\lambda=7{\cdot}554\times10^{-3}$ per hour) with a probable error of 0·05%. S. B.

Number of β-Particles from Radium-*E*. K. G. Emeléus (*Proc. Camb. Phil. Soc.*, 1924, **22**, 400—404).—By means of an electrical counter, the numbers were measured of α- and of β-particles from a source of radium-*D*, -*E*, and -*F*, of which the quantities of

the last two were nearly in their equilibrium ratio. After correcting for reflection of β-particles at the source, the numbers were approximately equal, although no great accuracy is claimed for this result. According to previous work on their absorption (Meitner, A., 1915, ii, 663), the β-particles from radium-*D* would not be recorded under the experimental conditions. The observed β-radiation was therefore due to disintegration of radium-*E*, and since this was in equilibrium with radium-*F*, of which one atom is assumed to give one α-particle on disintegration, it follows that about one β-particle is emitted per disintegrating atom of radium-*E*. This result does not agree with that of Moseley (A., 1912, ii, 1024), who found that one atom of radium-*E* appeared to emit little more than half a β-particle. L. F. G.

Decay of Radium-*E*. L. Bastings (*Phil. Mag.*, 1924, [vi], **48**, 1075—1080).—No appreciable difference has been detected between the decay constant of those radium-*E* atoms ejecting fast β-particles and the average radium-*E* atom. A value of the decay constant of radium-*E*: $\lambda=0{\cdot}139_0\pm0{\cdot}000_1$ day^{-1} has been obtained corresponding with a half-period of $4{\cdot}98_5$ days. C. W. B.

Electron Emission from Adsorbed Films on Tungsten. K. H. Kingdon (*Physical Rev.*, 1924, **24**, 510—522).—Measurements were made of the electron emission from tungsten filaments covered more or less completely with films of oxygen, thorium, cæsium, cæsium and oxygen, and of thoria in the presence of nitrogen. A. A. E.

β-Ray Spectrum of Radium. O. Hahn and L. Meitner (*Z. Physik*, 1924, **26**, 161—168).—The β-ray spectrum of radium, carefully purified from disintegration products, has been examined. Three groups of rays have been identified with the disintegration of radium itself with the He-values 1037, 1508, and 1575. The differences between the energies of these correspond with the differences between the energies associated with the *K*, *L*, and *M* levels in the atom. It is concluded that their emission is caused by absorption of nuclear γ-radiation of wave-length $6{\cdot}6\times10^{-10}$ cm. S. B.

High Energy Groups in the Magnetic Spectrum of the Radium-*C* β-Rays. C. D. Ellis (*Proc. Camb. Phil. Soc.*, 1924, **22**, 369—378).—Recent determinations (Ellis and Skinner, A., 1924, ii, 85) having indicated that whilst the relative values of the energies of radium-*C* β-rays as determined by Rutherford and Robinson (A., 1913, ii, 899) are accurate, their absolute values are low. The absolute energies of the β-ray spectra have now been determined to an estimated accuracy of 1 in 300 and a probable accuracy of 1 in 1000, using the standardised technique of Ellis and Skinner (*loc. cit.*).

It is concluded that the greater portion of this spectrum is due to the conversion according to the quantum relation of certain high-frequency monochromatic γ-rays in the *K*, *L*, *M*, *N* . . . levels of the radium-*C* atom, and a good agreement is reached between the

values calculated for the energy of the γ-rays necessary to excite the radium-*C* β-rays, and those observed by Bohr and Coster (A., 1923, ii, 110).

Further analysis of the spectrum indicates that γ-rays of up to 2×10^6 volts show no fresh absorption phenomena, which, it is held, indicates that the seat of the γ-ray emission lies in the nuclear electronic system but is distinct from the disintegration electron, and whilst neither the disintegration electron nor the α-particle is actually concerned in the γ-ray emission, strong γ-ray emission is more likely to be followed by instability of the electronic system than of the α-particle system.

A nuclear level system of radium-*C* is advanced provisionally.

R. W. L.

β-Ray Spectrum of Mesothorium. II. D. H. Black (*Proc. Roy. Soc.*, 1924, **A.**, **106**, 632—640).—A repetition of the work of v. Baeyer, Hahn, and Meitner (*Physikal. Z.*, 1912, 264) using much more accurate methods of focussing the β-rays.

It is concluded that the electrons are emitted from the various energy levels in the atom by nuclear γ-rays, and that the γ-rays arise through energy transitions in the nucleus. R. W. L.

γ-Rays and Atomic Disintegration. L. Meitner (*Z. Physik*, 1924, **26**, 169—177).—Radioactinium and actinium-*X*, in undergoing an α-ray change, emit a number of distinct, nuclear, monochromatic γ-rays. Radium only emits one type of γ-ray. α- and β-ray changes may be divided into two classes, those accompanied by γ-ray emission, and those unaccompanied by radiation. The number of types of monochromatic γ-rays emitted, and their frequencies, increase with the magnitude of the nuclear disturbance causing them. The α-ray changes of ionium, polonium, and thorium-*C*, and the β-ray changes of uranium-X_1, radium-*E*, and thorium-*C* are free from γ-ray emission. S. B.

Large Quantum γ-Rays from the Active Elements of the Thorium Family. J. Thibaud (*Compt. rend.*, 1924, **179**, 1052—1054; cf. A., 1924, ii, 717).—A study of the β-spectra excited photoelectrically by γ-rays from mesothorium. From lead, for example, are obtained β-corpuscles with energies 491·5, 571·3, 706, 819, 873·5 kilovolts. These are mostly from the *K* level of electrons, and are excited by γ-rays of 580·7, 795·2, 908·2, 962·7 kilovolts. The first of these is probably from thorium *C*+*C*″.

W. E. G.

Experiments with an α-Particle Counter. E. V. Appleton, K. G. Emeléus, and M. A. F. Barnett (*Proc. Camb. Phil. Soc.*, 1924, **22**, 434—453).—Experiments carried out with the aim of elucidating the action of an α-particle counter of the Rutherford and Geiger type (cf. A., 1908, ii, 555 and *Proc. Roy. Soc.*, 1908, **A.**, **81**, 141) are described. The results are discussed, and some consequential points bearing on the accuracy of enumeration of the particles are considered. L. F. G.

Emission of Nitrogen and Hydrogen in the Infra-red. A. H. PFUND (*J. Opt. Soc. Amer.*, 1924, 9, 193—196).—The infra-red emission spectrum of hydrogen has been studied with a vacuum tube 150 cm. in length. A preliminary experiment with nitrogen confirmed the observation of Coblentz of maxima in the band at about 1 μ (maxima found at 0·59, 0·68, 0·78, 0·90, 1·06, and 1·20 μ). With hydrogen in the tube a maximum was detected, in spite of much continuous radiation from the walls of the tube, at 7·40 μ, corresponding with the first number of a new infra-red series of hydrogen, expressed by $\nu=N(1/5^2-1/m^2)$. The Brackett series was well developed. S. B.

Band Regularities in the Secondary Hydrogen Spectrum. O. W. RICHARDSON and T. TANAKA (*Proc. Roy. Soc.*, 1924, **A**, **106**, 663—678).—Selective intensity changes in the secondary hydrogen spectrum observed in thermionic tubes (see this vol., ii, 13) have led to the recognition of a *P*, *Q*, *R* associated system of bands in this spectrum. The initial and final moments of inertia of the molecule for the emission of the lines in question are found to be several times greater than the moments of the molecules emitting the Fulcher hydrogen bands, or the helium band spectrum. It is suggested that the molecule responsible is abnormal, and may possibly be H_3. S. B.

Second Positive Nitrogen Bands. E. HULTHÈN and G. JOHANSSON (*Z. Physik*, 1924, **26**, 308—322).—The structure of the nitrogen bands at 3536, 3755, and 3805 Å. has been studied. They fall into an "energy level" scheme in which there are five initial and twelve final levels. S. B.

Structure of the Second Positive Group of Nitrogen Bands. P. LINDAU (*Z. Physik*, 1924, **26**, 343—370).—The lines of the second positive bands of nitrogen have been classified according to the modern theory of band spectra. S. B.

Effect of Argon on the First Positive Band Spectrum of Nitrogen. R. C. JOHNSON (*Phil. Mag.*, 1924, [vi], **48**, 1069—1074).—Traces of nitrogen in high-pressure argon show the first positive band spectrum in a considerably modified form. This consists in a selection of a few only of the band heads of the various groups, and the general effect is that found in the afterglow spectrum. Quantitative investigations are described which indicate that there is an energy displacement towards the more refrangible end of each band group. This also is similar to the conditions of the afterglow. It is suggested that all the phenomena hitherto regarded as peculiar to the electrical conditions obtaining in the afterglow may be reproduced in high-pressure argon. The bearing of these facts on the nature of the afterglow spectrum is discussed. C. W. B.

Origin of the Mercury Band Spectrum. A New Band of Mercury. E. HULTEN (*Compt. rend.*, 1924, **179**, 528—530).—The feeble band spectrum exhibited by mercury in a Geissler tube is increased in intensity by passing a current of hydrogen at a pressure

of 1 mm. through the tube. Air, however, appears to have the opposite effect. If no current of gas is passed, the bands disappear as the intensity of the electric current increases. This is attributed to the evaporation of the moisture in the tube, and the author infers that his observations accord with the hypothesis of a compound of the metal with hydrogen. A new band composed of feeble lines between the more intense lines of the band 4017 Å. was observed.
H. J. E.

Absorption Spectrum and Specific Heat of Chlorine Dioxide. H. MAYER (*Z. physikal. Chem.*, 1924, **113**, 220—234).—The absorption spectrum of chlorine dioxide determined by Käbitz (*Diss.*, Bonn, 1905) can be described in terms of five series. The ratio of the velocity of sound in chlorine dioxide to the velocity in air at 20° is 0·6148 at one atmosphere pressure and 0·6214 at 0·1 atmosphere. From these results, C_v for chlorine dioxide is calculated to be $7·5 \pm 0·5$.
M. B. D.

Influence of the Deformation of Ions on Optical and Chemical Constants. III. H. KORNFELD (*Z. Physik*, 1924, **26**, 205—222; cf. this vol., ii, 16).—The theories developed by Bonn and Heisenberg have been applied to the calculation of the infra-red frequencies of the carbonate ion, with a double negative charge.
S. B.

Tesla-luminescence Spectra. IV. Hydrocarbons containing a Single Benzene Nucleus. W. H. MCVICKER, J. K. MARSH, and A. W. STEWART (*J. Chem. Soc.*, 1924, **125**, 1743—1750).—In continuation of previous work (A., 1924, ii, 712) the spectra of thirteen further substances are described. These spectra are constitutional properties somewhat sensitive to minor changes, but showing broad resemblances between related compounds. No clear relationship can be traced between the nature of the substituents and the lengths of the spectra emitted or the distance towards the visible region to which they extend, but if attention be confined to substances having saturated side-chains, a rough relationship exists between the molecular weight and the wave-lengths to which the spectra extend in the ultra-violet. Relative brightness also appears constitutive. Both increase in the mass of the substituents and in unsaturation of the side-chain appear to damp down the spectrum.
L. J. H.

Phosphorescent Properties of the Rare Earths in Alkaline-earth Phosphors. I. R. TOMASCHEK (*Ann. Physik*, 1924, [iv], **75**, 109—142).—A detailed description is given of the phosphorescence spectra of the oxides of the rare earths in diluents of the oxides, sulphides, etc. of the alkaline-earths. The spectrum studied is that of the after-glow, excitation being effected sometimes by the light from the iron arc, sometimes by that from the carbon arc, and sometimes by bombardment with cathode rays. Scandium, yttrium, lanthanum, gadolinium, and aldebaranium give no "after-glow" in the visible region. Theoretical conclusions are deferred to a later paper.
L. J. H.

Luminescence of Phosphors under Magnetic and Electric Fields. E. RUPP (*Ann. Physik*, 1924, [iv], **75**, 326—336).—If a phosphor (ZnSCuα or ZnSMnα) has been excited by ultra-violet light and is exposed, whilst the luminescence is fading, to a very powerful magnetic field (more than 20,000 gauss), a temporary increase in the luminescence results, weaker, but analogous to the results with an electric field (cf. Schmidt, *ibid.*, 1923, [iv], **70**, 161). The phenomenon is directly explicable on Schmidt's theory. Under the influence of the magnetic (only) field, the light is partly polarised perpendicularly to the lines of magnetic force. This shows that the emission process in the phosphor centre is directly influenced by the field. The atomic magnetism of the metallic atoms of the phosphor may influence the result. Apart from this, the influence of a magnetic field (switched on or off) is similar to that of the electric field, because this is created by the movement of the electrons in the changing (magnetic) field. Electric fields of 2000 and 4000 volts are equivalent to magnetic fields of 20,000 and 45,000 gauss, respectively, and the latter to a rise in temperature (after correcting for that due to the electric field itself) of 4°. L. J. H.

Measurement of Fluorescence of Solids. A. GYEMANT (*Z. Physik*, 1924, **26**, 223—234).—A simple method for estimating the intensity of fluorescent light is described. The intensity is compared with a radioactively excited "standard." To measure the intensity of a source of ultra-violet light, the fluorescence it excites in screens containing different surface concentrations of the fluorescing substance are matched with the "standard." The hardness of the constituents of a beam of *X*-rays can be estimated similarly, by using absorbing screens of various thicknesses, to absorb successively the different wave-lengths. S. B.

Polarisation of Fluorescence from Dye Solutions. III. W. L. LEWSCHIN (*Z. Physik*, 1924, **26**, 274—284).—It was shown by Weigert (*Verh. d. Phys. Ges.*, 1920, **23**, 100) that the fluorescent light from solutions of dyes is partly polarised. The present paper considers the effects of temperature, wave-length of exciting light, and concentration of the dye. Increase of temperature decreases the degree of polarisation. The influence of wave-length is not the same for all dyes, but in some instances the degree of polarisation increases for longer wave-lengths. Increase of concentration of the solutions always decreases the polarisation. S. B.

Striking and Breaking Potentials for Electron Discharges in Hydrogen. O. W. RICHARDSON and T. TANAKA (*Proc. Roy. Soc.*, 1924, **A**, **106**, 640—662).—A systematic study has been made of the discontinuous increments in the current passing through a thermionic tube filled with hydrogen when the exciting potential is gradually raised. With a pressure of less than 1 mm. of mercury and the electrodes about 2 cm. apart, three types of discharge have been observed as the potential is raised. These are accompanied by sudden increases in current and by characteristic luminosity

phenomena. The breaking potential is less than the striking potential and probably has a simpler physical significance. The potentials at which these changes occur depend on several factors. They fall to a constant value as the electron emission from the cathode is increased. They change with the gas pressure, having a minimum value for about 1 mm. pressure. The breaking potentials diminish with decreasing electrode separation, but the value is approximately constant for distances less than 1 cm. It is concluded that the value to which the minimum breaking potential converges for small electrode distances is the ionisation potential of the gas. Sources of error and corrections are indicated, and an approximate value of 14·5 volts is obtained for the first ionisation potential of hydrogen. This supports the estimates of Olmstead and of Horton and Davies against the higher value of 17·1 volts obtained by Franck. Oscillations in the exciting circuit decreased the striking potentials by 0·1 volt, but left the breaking potentials unchanged. The ionisation of hydrogen at exciting potentials of about 16 volts is probably expressed by $H_2 \longrightarrow H_2^+ + e$. This view is supported by the weakness of the Balmer lines and the intense development of the secondary hydrogen spectrum in the luminosity. Contrary to the observation of Horton and Davies, the continuous spectrum of hydrogen could not be obtained at lower potentials than the secondary spectrum. S. B.

Dielectric Polarisation in Pure Compounds and Mixtures. L. Ebert (*Z. physikal. Chem.*, 1924, **113**, 1—27).—The dielectric constant ϵ of a substance is an indirect function of the polarisability, which is proportional to the moment produced per c.c. by the action of an electric field. The specific polarisation π is $(\epsilon-1)/(\epsilon-2)$, and the molecular polarisation P is equal to $\pi.M/d$, where M is the molecular weight and d the density. For large values of ϵ, P depends principally on the molecular volume. The molecular polarisation may be divided into components which depend on the structure of the molecule. The electron polarisation P_E within the atoms is, in general, identical with the molecular refraction, and is responsible for absorption in the extreme ultra-violet. The polarisation within the molecule is due to polarisation of the atoms P_A, of the ions P_I, or of the radicals P_R, the corresponding absorption region being the long-wave infra-red. Finally, there is the orientation polarisation of the whole molecule P_O, the absorption region extending from wave-lengths of a few mm. to those of several dm. P_A, P_I, or P_R can only be determined indirectly from the difference between P and P_E, where P_O is very small, that is, in gases and liquids with symmetrical molecules. P_A is small for non-polar compounds, for example, paraffins, but large for typically polar compounds. Only the sum P_A+P_O can be exactly determined. A qualitative idea of the magnitude of P_O, and also of the manner and the extent of the association between the dipoles can, however, be obtained. Large values of P_O, and hence large moments, indicate a lack of symmetry in the molecule which may be made up of several dipolar groups. Large values, for

instance, are found in the case of derivatives of water and ammonia. In simple molecules, the magnitude of P_0 is related to the value of the Kerr constant. In liquid mixtures, no uniform behaviour is to be expected, because of the different degrees of association between the components. The moments of dual ions and salt dipoles are relatively much greater than those of aliphatic dipoles or water. M. S. B.

Kerr Effect in Gases. G. Szivessy (*Z. Physik*, 1924, **26**, 323—342).—The Kerr effect has been studied for sulphur dioxide, ammonia, and carbon dioxide. The magnitude of the electrical double refraction is proportional to the square of the electrical field imposed. The Kerr constant is proportional to the pressure of the gas, and inversely proportional to the wave-length of the light. Kerr constants are given for sulphur dioxide, $1{\cdot}67\times10^{-10}$ (17·3°); for ammonia, $0{\cdot}59\times10^{-10}$ (17·9°); and for carbon dioxide $0{\cdot}24\times10^{-10}$ (17·5°). S. B.

Molecular Coefficients of Refraction. F. Eisenlohr and L. Schulz.—(See i, 17.)

Optical Activity. Copper Salts of Malic Acid. E. Darmois (*J. Phys. Radium*, 1924, [vi], **5**, 225—237).—The acidity and optical activity of solutions of copper oxide in malic acid have been studied. It is concluded that such solutions contain only an acid malate of copper and a basic malate. Mixed malates containing copper and alkali metals have also been prepared and are being investigated. S. B.

Mutarotation. IV. Solution Volume and Refraction Constants of α- and β-Methylglucoside. C. N. Riiber.—(See i, 8.)

Determination of Constitution by Spectroscopic Methods. Constitution of Amino-acids. I. H. Ley and F. H. Zschacke. —(See A., 1924, i, 1341.)

Colour and Constitution. IX. F. Kehrmann.—(See A., 1924, i, 1326.)

Co-ordination Positions of the Oxygen Atom. J. Piccard (*Helv. Chim. Acta*, 1924, **7**, 800—802).—From the nature of the additive products of ethers with triphenylmethyl, the view is put forward that the oxygen atom has a co-ordination number of four, and not three as previously suggested (A., 1922, ii, 212), and that the co-ordination positions are at the peaks of a regular tetrahedron. On this view, the angle between the atoms H—O—H in water is slightly greater than 109° 28′, the deviation from the value for the regular tetrahedron being due to the slight repulsion of the hydrogen atoms. This value is in agreement with Eucken's calculation (cf. *Jahr. Radioaktiv. Elektronik*, 1920, **16**, 408). H. T.

Electronic Theory of Valency. IV. Origin of Acidity. T. M. Lowry (*Trans. Faraday Soc.*, 1924, **20**, 13—15).—A restatement of the author's views on acidity (cf. A., 1924, ii, 447). S. S.

Suggestions for a Magnetic Theory of Valency. A. P. LAURIE (*Trans. Faraday Soc.*, 1924, **20**, 1—10).—Electrons arranged in shells about the atom are each supposed to move in a small orbit, so that they may be regarded as small magnets termed magnetons. The interaction of the magnetic fields is used to account for the formation of polar and non-polar bands, and the structure of hydrates and of ice. The connexion between the Bohr and Langmuir atom models is discussed in terms of this hypothesis. S. S.

Compressibility of Methyl Ether and Molecular Weight of the Gas. T. BATUECAS (*Compt. rend.*, 1924, **179**, 565—567).—Corresponding values of pressure and volume of a known quantity of gaseous methyl ether were made, the results being represented by using the formula $pv=a-bp$. From these, the calculated value of $1+\lambda$ was found to be 1·0270 and the molecular weight of the gas 46·044 (cf. Baume, A., 1908, ii, 372), which is in excellent agreement with modern physico-chemical determinations. H. J. E.

Determination of Molecular Fields. III. From Crystal Measurements and Kinetic Theory Data. J. E. JONES (*Proc. Roy. Soc.*, 1924, **A**, **106**, 709—718; cf. *ibid.*, 441 and 463).—Calculation of the potential energy and interatomic distances in cubic crystals of argon, potassium chloride, and calcium sulphide. W. E. G.

Influence of the Deformation of Ions on Optical and Chemical Constants. II. W. HEISENBERG (*Z. Physik*, 1924, **26**, 196—204).—The methods developed in an earlier paper (A., 1924, ii, 434) have been applied to calculate the stability and heats of formation of triatomic ions and molecules. S. B.

Secondary Electrons Produced by Hard X-Rays in Light Elements. H. FRICKE and O. GLASSER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 441—447).—A corollary of the theory of A. H. Compton (*Physical Rev.*, 1923, **21**, 483; 1924, **23**, 439) for the scattering of *X*-rays consists in the prediction and quantitative description of a type of secondary electrons, "recoil electrons," which result from the passage of *X*-rays through matter. The correctness of this prediction is tested by a determination of that fraction of the ionisation of *X*-rays in air for which the recoil electron emission is responsible. The actual experimental method consists in a comparison of the ionisation currents produced by *X*-rays, 0·180 Å. and 0·115 Å., in small ionisation chambers made of different light elements and their salts. A description of the details of the experimental technique has already appeared (Fricke and Glasser, *Amer. J. Roentgenol.*, 1924, **11**, 435). The experimental data furnish a direct determination of the ratio of two ionisation effects, one due to the photoelectric effect of the rays, and the other to the scattering process. The value of this ratio can also be calculated from Compton's theoretical coefficient and known experimental data. For carbon, the observed and calculated values are in fair agreement. J. S. C.

Compton and Duane Effects. J. A. BECKER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 342—346).—According to Compton's quantum theory explanation of the scattering of *X*-rays, the wave-lengths of the scattered rays should be slightly longer than those of the incident rays by an amount varying with the scattering angle. The effect has been photographically verified by several observers. Duane, however, has been unable to detect the effect using an ionisation chamber method. He finds instead a shift of the lines dependent on the material of the scattering body, which he attributes to the emission of tertiary radiation. Experiments are described to test whether the incompatibility of these results is due to the differences of intensity in the incident *X*-rays used by the observers. The rays scattered by aluminium through 100° were photographed. The Compton effect was verified, and indications of a Duane effect were obtained at the lowest intensity of incident radiation that could be employed. S. B.

Precision *X*-Ray Spectrometers. J. C. HUDSON (*J. Opt. Soc. Amer.*, 1924, **9**, 259—301).—The technique of *X*-ray wave-length measurements is described. Both the photographic and the ionisation methods are included, with especial reference to the apparatus developed by Siegbahn and by Duane. *X*-Ray wave-length tables are appended. S. B.

Structure of Graphite. J. D. BERNAL (*Proc. Roy. Soc.*, 1924, **A**, **106**, 749—773).—Measurements by the method of the rotating single crystal, by the ionisation spectrometer, and from Laue photographs give results agreeing with the hexagonal lattice proposed by Hull (*Physical Rev.*, 1917, **10**, 661), but disagreeing with the lattice proposed by Debye and Scherrer (A., 1917, ii, 437). The unit cell contains four carbon atoms; their probable positions are considered, and it is deduced that the atoms of carbon in graphite lie in planes of successive nets of hexagons superposed so that half the atoms in one net lie normally above half the atoms in the net beneath, whilst the other half lie normally above the centres of the hexagons in this net. Alternate nets lie atom for atom normally above the others. The complete structure is thus essentially that of Hull, but with all the carbon atoms lying in the cleavage plane, as in the Debye and Scherrer model. This agrees well with the more recent views of Bohr on the structure of the carbon atom. Artificial and natural graphite are identical in structure. L. F. G.

Precision Crystal Measurements on Alkali and Ammonium Halides. R. J. HAVIGHURST, E. MACK, and F. C. BLAKE (*J. Amer. Chem. Soc.*, 1924, **46**, 2368—2374).—The film on which the crystal powder is mounted is calibrated by mixing the latter with a standard substance with which it is not miscible at the ordinary temperature (*e.g.*, sodium chloride); the position of the lines for the latter can then be calculated and compared with the observed. The presence of small amounts of isomorphous impurities has only a negligible effect on the length of the side of the crystal unit, the observed values for which were: ammonium chloride $3{\cdot}866\pm0{\cdot}002$,

bromide 4·047±0·002, and iodide 7·244±0·003; potassium chloride 6·280±0·003, bromide 6·578±0·003, and iodide 7·052±0·003; rubidium chloride, 6·571±0·004, bromide, 6·868±0·004, and iodide, 7·325±0·004; cæsium chloride, 4·110±0·002 Å. S. K. T.

Crystal Structure of Tetragonal Lead Monoxide. R. G. Dickinson and J. B. Friauf (*J. Amer. Chem. Soc.*, 1924, **46**, 2457—2463).—The unit cell of red (tetragonal) lead monoxide contains 2 molecules; its dimensions are $a=5·01$ Å., $b=c=3·99$ Å. The oxygen atoms are at (0, 0, 0), ($\frac{1}{2}$, $\frac{1}{2}$, 0), and the lead atoms at (0, $\frac{1}{2}$, 0·24), ($\frac{1}{2}$, 0, 0·24). S. K. T.

Optical Properties of Calamine. P. Sève (*J. Phys. Radium*, 1924, [vi], **5**, 249—256).—The dispersion of the optic axes and the double refraction of calamine have been studied photographically in the visible and the near ultra-violet. The plane of the optic axes crosses at 3270 Å., for which wave-length the crystal is pseudo-uniaxial. The order of the interference produced by the passage of parallel light through a plate of calamine in the direction of the acute bisectrix has a maximum at 5200 Å. As the order of interference is almost constant over a wide range in the visible, the use of calamine as a material for half-wave plates etc. is suggested. S. B.

Structure of Chromium. H. Collins (*Chem. News*, 1924, **129**, 331—334).—Speculative. A. R. P.

Reflection of X-Rays by Barytes. S. K. Allison (*Amer. J. Sci.*, 1924, **8**, 261—276).—The axial ratios of barytes ($BaSO_4$) have been remeasured by an *X*-ray ionisation spectrometer; $a:b:c$ is given as 0·8148 : 1 : 1·3131. The unit cell is a rectangular parallelepiped of dimensions 4·449, 5·448, and 7·170 Å., containing 2 mols. of barium sulphate. The units of structure are arranged at the equivalent points of the space group V_h^{13}. S. B.

Nitrogen and Uranium. P. D. Foote (*Nature*, 1924, **114**, 789).—As a pure speculation regarding the origin of the nitrogen obtained by Hillebrand and by Ramsay from uraninite, it is suggested that the uranium nucleus may contain nitrogen nuclei, since the atomic weight of the former is almost exactly an integral multiple of that of the latter. A. A. E.

Rarity of the Inert Gases on the Earth. F. W. Aston (*Nature*, 1924, **114**, 786).—It is considered probable that the apparent rarity of the inert gases—as compared with the abundance predicted by their positions on the mass-number curves—is in fact real. In collisions of bodies resulting in the formation of a solar system, such atoms unconstrained by chemical combination would collide and rebound indefinitely, gravitating towards the larger masses, *e.g.*, the sun. A. A. E.

Applications of Röntgen Crystal Analysis to Questions of Structure of Organic Compounds. H. Mark.—(See i, 1.)

Electronic States of the CN Molecule. R. S. Mulliken (*Nature*, 1924, **114**, 858—859).—A brief survey of recent work on

the CN bands. The substance which above 2000° can be excited thermally to the emission of the bands must be represented by CN; the red and violet bands respectively correspond with electronic resonance potentials of 1·78 and 3·18 volts. The equilibrium concentration of CN at low temperatures must be extremely small, very much smaller than that of $(CN)_2$, but presumably increases with rise of temperature, probably more rapidly than that of $(CN)_2$, until above 2100° it becomes sufficient for appreciable absorption and emission of the violet CN bands. At much higher temperatures, *e.g.*, in the carbon arc, the CN bands are very intense. A. A. E.

Absorption Spectra of Mixed Metallic Vapours. S. Barratt (*Nature*, 1924, **114**, 827).—Band spectra peculiar to mixtures of magnesium (and calcium) with alkali metals have been obtained, indicating the existence of molecules of volatile alloys in the vapours. Further, the development of lines of the series $1S—md$ in the absorption spectra of rubidium and cæsium vapours has been observed, although this is in contravention of the selection principle.

A. A. E.

Absorption Spectrum and Constitution of Sulphur Vapour. Predissociation of Molecules. V. Henri and M. C. Teves (*Nature*, 1924, **114**, 894—895).—The ultra-violet absorption spectrum of sulphur has been studied between 100° and 1000°, at 0·5—53 mm., the measurements being accurate to 0·02—0·1 Å. When only S_8 and S_6 molecules were present, there is general absorption between 2700 Å. and 2300 Å., no structure being observed. At higher temperatures, a band spectrum of S_2 molecules is obtained, the intensity and number of the bands being determined by the partial pressure of the S_2 molecules. This spectrum is divisible into three distinct portions: (*a*) 3700—2794·2 Å., bands with fine structure; the rotational movement of the molecule is quantised. The distance between the nuclei of the two sulphur atoms is computed to be 0·7 Å. in the normal, and 0·73 Å. in the activated S_2 molecule. (*b*) 2794·2—2592 Å., narrow, continuous bands without fine structure. The change, involving the disappearance of the quantised rotation of the S_2 molecule, is abrupt. (*c*) 2592—2475 Å., broad, continuous bands; again the change is abrupt, and the distance between the nuclei becomes greater than before. The second change involves an increase in internal energy corresponding with the resonance potential of sulphur vapour (4·78 volts). It would therefore appear that before that state is reached in which the valency electrons have jumped into higher orbits, a molecule can be modified internally in that the atoms are driven apart, the bonds weakened, and greater reactivity is displayed. It is proposed to denote this preliminary change by the term "predissociation." Thus for each molecule there may be distinguished the following states in which it can be activated: normal, predissociated, resonance, ionised, and dissociated. A. A. E.

Constitution of Phosphoric Acid. I. Frößchl (*Rad. Acad. Sci. Zagreb*, 1923, **228**, 16—37).—The author determined the mol. weight

of orthophosphoric acid in aqueous solutions by measurements of boiling point elevation. The following values were found: for solutions containing 1—6·5% of phosphoric acid, 137·2; 7—12%, 125·9; 14—27%, 115·7. The curve representing the molecular weights shows discontinuities at 7 and 13% of phosphoric acid. In order to account for the different behaviour of the hydroxyl groups in phosphoric acid, the author supposes that in the acid $P(OH)_5$ ("protophosphoric acid"), three hydroxyl groups have an acid character, one is amphoteric, and one basic. In this case, compounds of the protophosphoric acid with other strong acids must be expected. Derivatives of such compound acids occur at natural minerals (apatite, wagnerite, dahlite) and have been obtained by Weinland and Alfa (A., 1898, ii, 217; 1899, ii, 594). Some new derivatives have been prepared by the author. Alcoholic solutions of phosphoric acid with solid sodium hydrogen carbonate yield a very hygroscopic *substance* with the empirical composition Na_2CO_3,H_3PO_4. It is decomposed readily by water, yielding carbon dioxide. When potassium sulphate is dissolved in concentrated phosphoric acid and the solution poured into alcohol, a crystalline *precipitate*, $2K_2SO_4,H_3PO_4$, is formed. If hot phosphoric acid is saturated with potassium sulphate until crystals appear on cooling, and then precipitated with alcohol, *crystals* with the composition K_2SO_4,H_3PO_4 separate. Ammonium sulphate treated in a similar way yielded a *substance* corresponding with the formula $(NH_4)_2SO_4,NH_4H_2PO_4$. The same behaviour as with phosphoric acid may well be expected with other hydroxides containing more than one hydroxyl group, as, for instance, aluminium, uranium, and osmium. The peculiarities of some organic substances (aldehydes, ketones) may be better understood if the different character of the hydroxyl groups present is assumed. S. S. M.

Distribution of Atoms in Mixed Crystals. G. TAMMANN (*Ann. Physik*, 1924, [iv], **75**, 212—216).—A reply to Borelius (*ibid.*, 1924, **74**, 216) summarising the arguments for and against a "normal" distribution of the atoms in mixed crystals. The "normal" distribution of two kinds of atoms in mixed crystals is that for which, when mixed as completely as possible, the symmetry corresponds with that of the two end members of the series. The total lattice may be thought of as divided into two partial lattices, the first corresponding with one atomic species and the second with the other. Such an arrangement can be attained from random distribution only if the atoms are free to change places, which may not be the case at low temperatures. Hence there is often a difference between mixed crystals obtained from the molten state (by cooling) and those obtained from solution (by removal of solvent). Interference *X*-ray figures should be very sensitive to slight deviations from the "normal" distribution, whilst the limits (of concentration) of chemical action should not. L. J. H.

Experimental Investigation of the Lattice Structure of some Alloys. S. HOLGERSSON and E. SEDSTRÖM (*Ann. Physik*, 1924, [iv], **75**, 143—162).—The structure of palladium–gold and

palladium–copper alloys was studied by the röntgenographic method of Debye and Scherrer. The former series showed a face-centred cubic lattice. The variation of the lattice parameter with atomic concentration may be represented by a smooth curve convex to the concentration axis. In the latter series, a compound, PdCu, is indicated, this having a centred-cubic lattice ($a=2{\cdot}988\times10^{-8}$ cm.). Except in the immediate neighbourhood of the compound, where mixed lattice structure is found, the whole series has a face-centred cubic lattice. L. J. H.

Molecular Dimensions of "Celluloid." V. P. Barton and F. L. Hunt (*Nature*, 1924, **114**, 861).—Experiments on the thickness of films indicate that the diameter of the molecular complex of "celluloid" is not greater than 10 Å. A. A. E.

Index of Refraction of Calcite for *X*-Rays. C. C. Hatley (*Physical Rev.*, 1924, **24**, 486—501).—By using the wedge method, the index of refraction of calcite for molybdenum $K\alpha_1$ rays is $\mu=1-(2{\cdot}03\pm0{\cdot}1)\times10^{-6}$, which agrees well with the value given by Lorentz's dispersion formula. The wave-length of the rays, after correction, is 0·70772 Å. A. A. E.

Coloration of Rock Salt by Radium. P. Ludewig and F. Reuther (*Z. Physik*, 1924, **26**, 45—53; cf. *ibid.*, 1923, **18**, 183).—The coloration of rock-salt specimens by radium has been quantitatively examined. Colour changes were still slowly progressing after 137 days' exposure to 40 mg. of radium. Blue rock-salt passes into a colourless state after 1 day's exposure, and then becomes yellow. S. B.

Coloration of the Alkali Halides by *X*-Rays. P. L. Bayley (*Physical Rev.*, 1924, **24**, 495—501).—Cæsium, rubidium, and calcium fluorides, cæsium, rubidium, potassium, sodium, lithium, silver, barium, beryllium, and calcium chlorides, cæsium, rubidium, and potassium bromides, potassium, sodium, cadmium, and mercury iodides, and potassium silicate assume a coloration when exposed to *X*-rays, but no correlation appears to exist between the colour and the position of the element in the chemical table. Halite, coloured amber, has an absorption band from 0·3μ to 1·3μ, with a maximum at 0·46μ. Sylvite, coloured purple, has a similar band with a maximum at 0·55μ. The conditions of fading of the colorations were investigated. A. A. E.

Optical Properties of Crystals of certain Cyanoplatinates. I. A. Pochettino (*Atti R. Accad. Sci. Torino*, 1924, **59**, 133—141).—Crystals of magnesium, yttrium, and erbium cyanoplatinates exhibit double refraction which increases in absolute magnitude as the wave-length of the light diminishes from $\lambda=0{\cdot}660$ to $\lambda=0{\cdot}470$, but decreases as the wave-length falls from 0·440 to 0·410. With change in λ from 0·455 to 0·445, the uniaxial magnesium cyanoplatinate crystals show a sudden change in the sign of the double refraction, whereas with the biaxial yttrium and erbium cyanoplatinate crystals the plane of the optical axes undergoes a rotation of 90°. T. H. P.

Photochemical Properties of Stannous Iodide. P. FREUNDLER and Y. LAURENT (*Compt. rend.*, 1924, **179**, 1049—1051).—When prepared from solutions of stannous chloride and potassium iodide, the precipitated stannous iodide consists of a mixture of red and yellow modifications, excess of stannous chloride favouring the production of the red modification, and excess of potassium iodide that of the yellow. On exposure to sunlight, the yellow form is changed into the red modification, the reverse change taking place in the dark. When potassium iodide is used, the red form is at once produced if the mixture is heated on a water-bath. When, however, sodium iodide is used, excess of stannous chloride favours the production of the yellow form, which is the stable modification at 100°. The use of sodium iodide greatly reduces the oxidation of the mixture on exposure to air. The presence of traces of tin possibly influences the iodine content of marine plants. W. H.-R.

Pseudo-complexes. A. SCHLEICHER (*Z. anorg. Chem.*, 1924, **140**, 371—378).—A theoretical discussion, in which it is shown that, from a study of the crystal structure of compounds, a distinction must be drawn between true complex compounds having characteristic crystal properties and a high order of symmetry and pseudo-complexes having no characteristic crystal structure of their own and possessing a lower order of symmetry. The formation of both classes of complexes is, however, due to the co-ordination power of the atoms, but the crystal lattice of the pseudo-complexes can be regarded as a growth of the simple molecule of the compound by reason of a definite symmetry of the molecule of lower order and according to certain crystallographic laws analogous to those controlling the formation of twinned crystals. The crystal symmetry of sodium and cæsium chlorides, calcium fluoride, cuprous oxide, zinc sulphide, graphite, and calcium carbonate is derived from the above considerations. A. R. P.

Nature of the Martensitic Structure [of Steel]. F. SAUERWALD and G. JACKWIRTH (*Z. anorg. Chem.*, 1924, **140**, 391—398).—By the method already outlined (A., 1924, ii, 863) it is shown that the martensitic structure of steel is always oriented in the same way as the original γ grain boundaries and that the slip planes are similarly oriented. It would therefore appear that the needle-like structure of martensite is caused by slip phenomena induced by the hardening process (quenching) the steel has undergone and that martensite cannot be regarded as a distinctive phase in the structure of steel. [Cf. *B.*, 1925, 42.] A. R. P.

Metal Crystals. I. E. GRÜNEISEN and E. GOENS (*Z. Physik*, 1924, **26**, 235—249).—The elastic constants of zinc and cadmium have been determined from extension experiments etc. carried out at different crystallographic orientations on large single crystals. Zinc and cadmium show, probably on account of their large axial ratios, an unusually large elastic anisotropy. S. B.

Metal Crystals. II. E. GRÜNEISEN and E. GOENS (*Z. Physik*, 1924, **26**, 250—273).—The velocities of sound in zinc and

cadmium crystals, determined from their elastic constants (see preceding abstract), have been used to calculate the specific heats of these metals by Debye's method. The specific resistances of the crystals at the temperature of liquid air have also been measured.
S. B.

Relation between the Mechanical and Piezo-electrical Properties of a Rochelle Salt Crystal. F. C. ISELY (*Physical Rev.*, 1924, **26**, 569—574).—Stress–strain curves have been obtained for 20°, 22·5°, and 30°, and curves showing the variation of charge with stress for 16—35°. The temperature of maximum piezo-electric response is 22·25°. A. A. E.

Dielectric Anomalies in Rochelle Salt Crystals. J. VALASEK (*Physical Rev.*, 1924, **24**, 560—568).—Residual charge and fatigue effects for a Rochelle salt condenser have been studied; it is supposed that at −20° there is a loosening of the water ions sufficient to permit a slight motion with reference to the salt molecules, whilst above 25° there is further loosening. There is an apparent evolution of heat commencing at 24° and persisting to 54°, when a considerable absorption of heat takes place. A. A. E.

Metastability of Elements and Compounds as a Result of Enantiotropy and Monotropy. VIII. E. COHEN and W. D. HELDERMAN (*Z. physikal. Chem.*, 1924, **113**, 145—156).—By means of the electrical adiabatic colorimeter (cf. *ibid.*, 1924, **112**, 141), measurements have been made of the intermediary heats of solution between various concentrations of the two forms of ammonium nitrate, III and IV, at the transition temperature 32·3°. The difference in these two values for the two modifications, between corresponding pairs of concentrations, gives the heat of transition, which is thus found to be 4·99 cal. per g. According to Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1916, **51**, 581) it is 4·66. The latter value is attributed to the employment of a metastable mixture of the two modifications instead of the pure form. [Cf. A., 1924, ii, 449.] M. S. B.

Atomic Weight of Antimony. P. F. WEATHERILL (*J. Amer. Chem. Soc.*, 1924, **46**, 2437—2445).—Antimony trichloride, prepared by the action of chlorine on pure antimony in a vacuum, was dissolved in an aqueous solution of pure tartaric acid and the resulting solution quantitatively precipitated with silver nitrate solution. From the ratio $SbCl_3 : 3Ag$, the atomic weight of antimony was found to be $121{\cdot}748 \pm 0{\cdot}00086$. S. K. T.

Variation of the Molecular Weight of Mercury with Temperature. A. JOUNEAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1293—1305).—The molecular weight of mercury through the temperature range −40° to 320° was calculated from previously known cryoscopic and surface tension data and from Clapeyron's law and Trouton's rule. The values obtained change regularly with the temperature, independently of the method of calculation, and range from 280 at low to 200 at the higher temperatures. From the Eötvos–Ramsay–

Shields formula, the critical temperature of mercury was found to be 1552°. H. T.

Determination of Molecular Weight by Aid of the Gas-Interferometer of Haber and Löwe. E. BERL and F. RAU (*Ber.*, 1924, **57**, [*B*], 1829—1834).—A current of dry air, free from carbon dioxide, is saturated with (*a*) the vapour of the pure solvent and (*b*) the vapour from the solution of the substance under investigation in the same solvent, and the difference of the vapour tension in the two cases is measured by means of the Haber–Löwe gas-interferometer. The instrument is calibrated with the aid of solutions of azobenzene. Benzene is the most suitable solvent. H. W.

Electrical Properties of Liquid Sulphur. D. H. BLACK (*Proc. Camb. Phil. Soc.*, 1924, **22**, 393—399).—The relative conductivities of liquid sulphur between 130° and 200° were determined and compared with changes in the viscosities over this range. Conductivity increases to a maximum at about 160°, then falls to a minimum at about 185°, and thereafter increases. This behaviour thus agrees approximately with the known viscosity changes, which exhibit a minimum and a maximum at 150—160°, and at about 200°, respectively. The specific resistance at 163° was found to be $7{\cdot}5\times10^{10}$ ohms, approximately. Evidence is given that the conduction is electrolytic in nature. *E.M.Fs.* of polarisation were observed qualitatively (cf. Threlfall and Brearley, *Phil. Trans.*, 1896, **A**, **187**, 57). L. F. G.

Method for the Determination of the Specific Heat of Metals. W. U. BEHRENS and C. DRUCKER (*Z. physikal. Chem.*, 1924, **113**, 79—110).—A method similar to Pirani's (A., 1913, ii, 102) has been employed for the determination of the specific heat of metals. A thin wire is heated to constant temperature in a vacuum and its resistance measured, by means of a Wheatstone's bridge arrangement, before and immediately after the addition of a definite quantity of electrical energy. Making use of the previously determined temperature coefficient of the resistance of the wire, the temperature, and thence the specific heat, may be calculated from the change in resistance. Values for the specific heat of zinc ranging from 0·0921 at 5° to 0·0992 at 225° have thus been found. The value of α/c, the ratio of the relative temperature coefficient to the specific heat, has also been determined for different temperatures by allowing the heating current to pass through a similar wire kept at the ordinary temperature, and measuring only the difference of the relative change of resistance in the two wires at different temperatures of the experimental wire. By this means the dependence of specific heat on temperature and previous thermic treatment may be studied. Zinc, however, shows no anomalies in the value of α/c between 0° and 225°, although the work of previous investigators shows that there is probably a transition point between 100° and 200°.

The advantages claimed for this method are: the smallness of the amount of material and of the energy additions necessary, the

rapidity of the operation, the possibility of measurement over small temperature intervals, and the great degree of exactitude attained. M. S. B.

Latent Heats of Fusion. II. Palmitic Acid and Benzene. K. STRATTON and J. R. PARTINGTON (*Phil. Mag.*, 1924, [vi], **48**, 1085—1089; cf. A., 1922, ii, 258).—The latent heats of fusion and the molecular depressions of freezing point (with mesitylene as solute) have been determined for carefully purified palmitic acid and benzene. For palmitic acid of setting point 62·25°, L=51·03 g.-cal. per g.; E for 100 g. solvent=43·13. For benzene of setting point 5·85°, L=29·92 g.-cal. per g.; E for 100 g. solvent=51·39. The results remove the larger discrepancies between the observed and calculated values of E in the case of palmitic acid which are given in the literature. C. W. B.

Density and Diffusion Measurement by Interferometry. C. BARUS (*Proc. Nat. Acad. Sci.*, 1924, **10**, 349—351).—A continuation of previous results (A., 1924, ii, 385). S. B.

Relation between the Volume of a Substance at Absolute Zero and its Critical Temperature. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **140**, 379—383).—From theoretical considerations the equation v_0M/T_K=constant is deduced, where v_0M is the molecular volume of a substance at the absolute zero and T_K is its critical temperature. The value of this constant has been determined for a large number of organic and inorganic compounds and for the gaseous elements from data already published. The figures obtained appear to show that the relationship holds approximately only for "ordinary" substances (cf. van Laar, *Z. anorg. Chem.*, 1918, **104**, 57; 1922, **120**, 203) and that the deviations vary in magnitude according to the extent that the substance differs from the "ordinary." A. R. P.

Density of Zirconium and Hafnium Oxides. G. HEVESY and V. BERGLUND (*J. Chem. Soc.*, 1924, **125**, 2372—2375).—Carefully purified zirconium dioxide and hafnium dioxide, prepared from the sulphates and ignited at 1000°, had d^{20} 5·73 and 9·67, respectively. The determination of d for a mixture of the two oxides affords a ready and accurate means of determining the percentage of hafnium dioxide present, which is given by the formula $x=(d-5{\cdot}73)/0{\cdot}0394$. It is necessary to prepare the mixture from the sulphates and by exactly the same methods. The values for d found for oxides otherwise prepared is lower and presumably less accurate. C. I.

Density of Gaseous Methyl Ether. T. BATUECAS.—(See A., 1924, i, 1280.)

Vapour Pressures of Monatomic Substances. A. C. EGERTON (*Phil. Mag.*, 1924, [vi], **48**, 1048—1054).—On the basis of the thermodynamic vapour pressure formula a linear equation $\log p=-a/T+b$ closely represents the variation of vapour pressure with temperature of a solid with monatomic vapour, and a vapour

pressure determination at a single temperature should suffice to determine the course of the whole curve. C. W. B.

Vapour Pressures of Rochelle Salt, the Hydrates of Sodium and Potassium Tartrates, and their Saturated Solutions. H. H. LOWRY and S. O. MORGAN (*J. Amer. Chem. Soc.*, 1924, **46**, 2192—2196).—The vapour pressures of the hydrates of sodium and potassium tartrates and Rochelle salt, and of their saturated solutions, have been determined for the temperature interval 15—40° by a static method. The graphs of t_w against t, where t_w is the temperature at which the vapour pressure of water is equal to the vapour pressure of the substance, or its solution, at t, may be represented by the linear equation: $t = at_w + b$, a and b being constants. The results of van Leeuwen (A., 1897, ii, 397) are confirmed. Reproducible values for the vapour pressures of Rochelle salt, or its solution, cannot be obtained if the latter has been previously heated, at any time, above 40° (cf. *loc. cit.*). S. K. T.

Kinetic Theory of Vaporisation. S. C. BRADFORD (*Phil. Mag.*, 1924, [vi], **48**, 936—947).—The kinetic theory has been applied to obtain a quantitative expression for the vapour pressure of liquids in the form: $p = 56{\cdot}47Te^{-3{\cdot}306\sigma VA^{1/3}/T\delta' d}/(\Phi_s d^{1/2}A)$. Φ_s is the co-volume, $\delta' \times 10^8$ the nearest distance of approach of the centres of two molecules of the liquid, A is an arbitrary constant to allow for molecular association of the liquid. Vapour pressures calculated by means of the formula agree very well with the values observed at given temperatures and become equal to 1 atmosphere at the boiling points of the liquids. Edser's formula, $\sigma = K\delta/4$, may be used to calculate the cohesion of liquids with considerable accuracy. C. W. B.

Corresponding Temperatures of Solids. A. BRODSKY (*Compt. rend.*, 1924, **179**, 498—500).—The results obtained by Michaud from experiments on specific heat and entropy (A., 1920, ii, 532) are susceptible of deduction from the theory of specific heats. From the simplest Einstein formula it can be shown that Michaud's "corresponding temperature" depends on the nature of the substance considered, and a further deduction shows that the values of the specific heat for similar values of the corresponding temperature are independent of the nature of the substance. Absolute zero being a corresponding temperature for all bodies, the additivity of the specific heats at this temperature is consistent with the consequences of the Nernst theorem. At higher temperatures than those dealt with, the deductions do not hold in the case of specific heats at constant volume. H. J. E.

Corresponding Temperatures of Solids. H. LAFUMA (*Compt. rend.*, 1924, **179**, 684—686).—A claim for priority against Brodsky (cf. preceding abstract). T. H. P.

Dependence of Coefficient of Expansion of Liquids on Temperature and Chemical Structure. J. J. SASLAWSKY (*Z. physikal. Chem.*, 1924, **113**, 111—130).—From the expression for

the density of liquids $\delta_l=\delta_k(1+2\cdot73\sqrt{T/T_0})$, where $T_0=1\cdot05\,T_k$ (T_k is the absolute critical temperature), T is the observation temperature, and δ_l and δ_k are the densities at the observation and critical temperatures, respectively (cf. A., 1924, ii, 452), a formula for the expansion coefficient has been deduced, $\beta=1\cdot365/(\sqrt{T/T_0}+2\cdot73T)$. This formula has been tested by the experimental data for a number of liquids at temperatures extending from −90° to +200°. The deviations of the experimental values of β from the calculated values are greatest in the case of the alcohols, and for these, contrary to the general behaviour, the experimental value is the smaller one. For other liquids, deviations are small and of approximately the same relative magnitude and may in part be due to inaccuracy in the experimental data. In general, therefore, the expansion coefficient does not depend on the nature of the liquid, but is a simple function of the critical and observation temperatures, and will be the larger the lower the value of the critical temperature. For an ideal liquid, β will reach a minimum value of $1\cdot365/3\cdot73T_0$ at absolute zero, and will approach an infinite value at the critical temperature, owing to the passage from liquid to vapour. The deviations observed in the alcohols cannot be due to association, since other liquids considered to be associated do not exhibit the same behaviour. M. S. B.

Coefficient of Expansion at Low Temperatures. G. Borelius and C. H. Johansson (*Ann. Physik*, 1924, [iv], **75**, 23—36).—Measurements have been made of the coefficients of expansion of copper, cadmium, and zinc between 100° and 300° Abs. by means of the double-mirror dilatometer. W. E. G.

Diffusion of Mercury and Iodine Vapours through Nitrogen. J. M. Mullaly and H. Jacques (*Phil. Mag.*, 1924, [vi], **48**, 1105—1122).—The diffusion coefficients of the vapours of mercury and of iodine have been determined by placing the free elements at the opposite ends of a closed glass tube containing nitrogen. An iodide deposit appears as a narrow ring across the axis of the tube. The gradient can be calculated from the known vapour pressures of mercury and iodine, the distance of the deposit from the ends of the tube, and the partial pressures of mercury and of iodine over the mercury iodides formed. Further, weighing and analysing the deposits after a time interval enable absolute values for the diffusion coefficients to be calculated. Thus, in nitrogen at 9·78 mm. of mercury and 19·4°, $D_{IN}=5\cdot80$ cm.^{2}/sec. and in nitrogen at 5·65 mm., $D_{HgN}=17\cdot3$ cm.^{2}/sec. To compensate for the large difference in vapour pressure between iodine and mercury either the tube can be constricted or an iodine compound such as cæsium tri-iodide can be used. C. W. B.

Diffusion of Hydrogen into Air, measured by the Interferometer U Gauge. C. Barus (*Proc. Nat. Acad. Sci.*, 1924, **10**, 447—452; cf. A., 1924, ii, 385).—A modified form of the apparatus previously described has been employed to determine

the coefficient of diffusion of hydrogen into air. The equations for the calculation of this coefficient from the experimental data are given. The mean value of a (diffusion coefficient a^2), obtained with tubes of different lengths and diameters is 1·014 cm./sec. This is considerably higher than the usually quoted value (a=0·81). J. S. C.

Precision Method for the Determination of Diffusion Coefficients in any Solvent. II. E. COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1924, **113**, 157—159).—The diffusiometer previously described (A., 1923, ii, 130) has been tested with reference to the exactness of the measurement of the height of the diffusion layer when the lubricants used for the plates have different viscosities. The influence of the viscosity is not appreciably greater than the errors of experiment. M. S. B.

Technique and Theory of Measuring the Diffusion of Coloured Substances. R. AUERBACH (*Kolloid-Z.*, 1924, **35**, 202—215).—Diffusion in sufficiently dilute gelatin jellies proceeds parallel with free diffusion in water, and such jellies can be used for studying the degree of dispersion of solutions of the technical dyes. The diffusion of aqueous solutions containing 1 g. per litre of the colouring matter into solid jellies containing 4% of a "medium hard" gelatin has been measured at 20° for a period of 24 hours. The results are expressed in terms of the distance between the meniscus of the gelatin and the point where the colour of the diffused layer matches a solution of one-tenth the concentration of the original solution. By the use of Einstein's formula, the radius of the particles expressed in terms of $\mu\mu$ is found to be $0{\cdot}127/D$, where the diffusion coefficient D is expressed in terms of sq. cm. per day. Thus a connexion between the size of the particles of the dyes in solution and the value $l_{1/10}$ defined above has been traced in the form of a graph. This graph intersects the vertical co-ordinate at the value $\mu\mu$=1·75, whence it is inferred that a 4% jelly is no longer permeable to particles having a diameter greater than 3·5 $\mu\mu$. The method, however, is very useful for the study of colloidal solutions containing smaller particles, including the majority of dye solutions. Since the value $l_{1/10}$ involves an aliquot ratio of the original concentration, it is independent of variations in the purity of the substance and many other sources of error are eliminated by adopting this method. J. F. B.

Stokes-Einstein Law for Diffusion in Solution. (MISS) C. C. MILLER (*Proc. Roy. Soc.*, 1924, **A**, **106**, 724—749).—The diffusion constants, D, of iodine in a number of organic solvents and in aqueous solutions of ammonium bromide and ammonium iodide were determined. The viscosity coefficients, Z, were also measured. If the Stokes–Einstein equation were applicable under the conditions obtaining, DZ should be constant for the various solvents; this, however, was not observed with organic solvents. The variability of DZ was apparently not connected in any simple way with the colours of the iodine solutions, nor with the following properties

of the solvents—molecular weight, molecular volume, density, viscosity, or dielectric constant. *DZ* was found to be fairly constant for bromide solutions, but for iodide solutions the product increased almost linearly with the concentration of the salt. For fifteen organic solvents and twenty-four aqueous solvents, the relative values of *DZ* lie between the limiting values derived from the Stokes–Einstein and the Sutherland (*Phil. Mag.*, 1905, [vi], **9**, 781) equations, respectively. The temperature coefficient of diffusion increases rather irregularly as *D* decreases. On the average, *DZ* scarcely increases with rising temperature to the extent required by the Stokes–Einstein equation. L. F. G.

Experiment on Solid Diffusion and its possible Bearing on the Structure of Solid Solutions. F. C. Thompson and W. H. Dearden (*Trans. Faraday Soc.*, 1924, **20**, 84—85).—Copper diffuses into pure gold and silver at 650° more rapidly than into a solid solution of these two metals. With silver, well marked zones similar to Liesegang's rings are formed. These results support the view that in solid solutions the added atoms are accommodated in spaces in the original lattice and do not replace atoms in the lattice itself. S. S.

Binary Liquid Mixtures. O. Faust (*Z. physikal. Chem.*, 1924, **113**, 482—489; cf. A., 1922, ii, 423).—The deviations from the simple mixture law of the vapour pressures recorded in the literature for 50% acetone–chloroform mixtures at temperatures of 20—90° show an approximately linear variation with temperature, and extrapolation shows that this deviation would vanish at about 150°, at which temperature complex formation must cease. The relation of this result to those obtained for the gaseous phase by Schultze (A., 1913, ii, 676) is discussed. The molecular heats of vaporisation of mixtures of acetone with chloroform and of ether with chloroform are found to be greater than the values required by a simple mixture law, combination of the molecules of the two being indicated. For mixtures of benzene with ethylene dichloride the simple mixture law is obeyed, but for mixtures of carbon disulphide with acetone the values lie below those calculated, this effect being due to depolymerisation of complex molecules. In the case of the system acetic anhydride–water, the latent heat of the (stable) complex, acetic acid, is far below that calculated from the values for its components. G. M. B.

Influence of Proximity to the Critical Solution Temperature on the Volume. N. Perrakis (*Compt. rend.*, 1924, **178**, 703—705).—The densities of mixtures of *o*-cresol with ethyl alcohol and of phenyl ether with ethyl alcohol have been studied, and curves are given showing the dependence of the volume on the composition. For the first pair, the curve is pseudo-parabolic, and similar to that for mixtures of acetic acid and benzene, the components of which are also completely miscible. For the second pair, the components of which are only completely miscible near the critical temperature, the curve is complex, with a well-marked rectilinear portion. This

behaviour is supposed to be entirely due to the proximity of the critical point, and not to the existence of definite chemical compounds. L. L. B.

Solubility of Benzoic Acid in Benzene and in Toluene. J. CHIPMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 2445—2448).—The solubility of benzoic acid in benzene and in toluene has been determined at various temperatures. Graphic methods for the interpolation of the experimental data are described. The heats of solution calculated from Mortimer's expression (A., 1922, ii, 621) indicate a transition point near 95°, but no evidence of this is afforded by the cooling curves. S. K. T.

Determination of the Solubilities of Sparingly Soluble Substances. I. Solubility of Magnesium Oxide in Water. H. REMY and A. KUHLMANN (*Z. anal. Chem.*, 1924, **65**, 1—24).—The solubility of magnesium oxide in water free from carbon dioxide has been determined by evaporating a volume of the saturated solution and weighing the residue, by conductometric titration with standard acid, and by Kohlrausch's conductivity method. The values obtained by these methods agree fairly well, being 0·40, 0·39, and 0·35 millimol. per litre. A. R. P.

The Salting-out Effect. K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 1—65).—The influence of salts on the solubility of neutral substances may be expressed by equations of the form $\log s_o/s_n = k \cdot c_n$ or $s_o/s_n - 1 = k'c_n$, where s_o is the solubility in water, s_n is a salt solution of concentration c_n, and k (or k') is a constant independent of c_n, but varying with the temperature and the nature of the salt and of the neutral substance. The present work is an investigation of the causes of this variation. From the solubility, the activity coefficient, f, has been found for quinol, quinone, succinic acid, and boric acid in various salt solutions, and the equation $\log f = k \cdot c$ is on the whole confirmed. From the solubility data at different temperatures, the heats of solution have been calculated.

The causes of the variation in k with the nature of the substances salted out and of the ions are discussed with reference to Debye's views (A., 1920, ii, 356) on the nature of the cohesive forces, the structure of the univalent alkali and halogen ions being brought into relation with the structure of the corresponding inactive gases. It is probable that k must decrease with increasing size and polarisability of the ions forming the salt, and that the variation from potassium chloride to cæsium chloride will run parallel to that from potassium chloride to potassium iodide. This parallelism can be effaced by the influence of chemical affinity between the ions and the neutral substance, the sign of the ionic charges being determinative for this. The attraction of the water also affects the absolute value of k, and, owing to the great solvent power of water, k, which for gases is chiefly negative, will in solution be chiefly positive, answering to an increased activity of the neutral substance. The hydration of ions is touched on, and the view expressed that none

of the ions K^+, Rb^+, Cs^+, Cl^-, Br^-, I^- is hydrated. Attention is directed to the effacing influence on the forces of cohesion involved by hydration of ion or neutral molecule, but the view that hydration plays the leading part in the salting-out process is rejected.

In agreement with deviations from the mentioned parallelism, as far as regards quinol and quinone it is shown how the reducing qualities of the former and the oxidising power of the latter cause an increased attraction of the former to positive ions and of the latter to negative ions, whereby the importance of chemical affinity for the determination of the activity in concentrated solution, even where no chemical action occurs, is made clear. A special interpretation is found for the salting-out effect in the case of boric acid. Directions are given for the practical application of solubility data to the correction of measurements with the quinhydrone electrode in salt solutions. L. L. B.

Adsorption of the Two Stereoisomeric Hydrobenzoins on Charcoal. P. H. HERMANS (*Z. physikal. Chem.*, 1924, **113**, 385—388).—The fact that *r*-hydrobenzoin is more easily adsorbed by charcoal from solution in water or alcohol than its stereoisomeride, notwithstanding its greater solubility, is explained by assuming that the planes of the benzene rings lie on the adsorbing surface whilst the hydroxyl groups are attracted by the solvent. The case is compared with that of the adsorption of fumaric and maleic acid from aqueous solutions. G. M. B.

Absorption of Salts by Storage Tissues. W. STILES (*Ann. Bot.*, 1924, **38**, 617—633).—From a study of the ions absorbed and excreted from tissue surrounded by salt solutions, it is inferred that the absorption of salts is not a simple process of diffusion through a cell membrane. Accordingly, all data obtained by plasmolytic methods are open to considerable doubt. O. O.

Effect of Hydrogen-ion Concentration on Compound Formation and Adsorption of Dyes by Mordants. R. E. MARKER and N. E. GORDON (*Ind. Eng. Chem.*, 1924, **16**, 1186—1188; cf. A., 1923, ii, 616).—The adsorption of dyes (methylene-blue, crystal-violet, orange-II, and metanil-yellow) by inorganic gels (ferric and aluminium hydroxides and silicic acid) depends on the p_H of the solution. The acid dyes are adsorbed from acid solutions (low p_H), all three gels, but particularly the ferric and aluminium hydroxides, taking up orange-II and metanil-yellow very readily from solutions of p_H about 2·3. Basic dyes, on the other hand, are adsorbed from alkaline solutions (high p_H). Crystal-violet is very readily adsorbed by ferric and aluminium hydroxides at p_H 11, and methylene-blue by all three gels at p_H 12, but only weakly by the silica. Both ferric and aluminium hydroxides yield crystalline salts with orange-II. W. A. S.

Surface Tension of "Tetralin," "Decalin," and Lubricating Oil. L. GRUNMACH and G. SCHWEIKERT (*Z. physikal. Chem.*, 1924, **113**, 432—440).—The surface tensions of a lubricating oil and two substitutes have been determined by a method involving measure-

ment of the capillary rise between two plates and by the capillary wave method. "Tetralin," d^0 0·9766, γ 3·493 mg./mm. at 18·3°. "Decalin," d^0 0·9026, γ 3·210 mg./mm. at 18·8°. Lubricating oil, d_0 0·9327, γ 3·171 mg./mm. at 19·8°. G. M. B.

Molecular Structure of Thin Films. VI. N. K. ADAM and J. W. W. DYER (*Proc. Roy. Soc.*, 1924, **A**, **106**, 694—709); cf. A., 1921, ii, 488; 1922, ii, 687; 1923, ii, 539, and *Proc. Roy. Soc.*, 1922, **A**, **101**, 452).—Five long-chain alcohols examined formed both condensed and expanded films. The area of cross-section of the chain is near that of long-chain acids, being about 20·4 sq. Å.; the area of the CH_2·OH group is 21·6 sq. Å. Acetates of three long-chain alcohols gave condensed and expanded films; the area of the Me·CO·OCH_2· group is 23 sq. Å. Two long-chain methyl ethers were prepared and formed very unstable films; the methyl group on the oxygen apparently weakens the attraction of the molecule for water. Linolenic and clupanodonic acids, containing 3 and 5 double bonds, respectively, behave similarly to oleic acid, previously examined. Arachidic acid and some derivatives were prepared; they gave results in harmony with those already found for other members of the same series. The transition between "allotropic" condensed films of carbamide derivatives is examined more closely than hitherto; transition temperatures increase with length of carbon chain. Condensed film allotropy is exhibited also by hexadecyl- and octadecyl-acetamides; here the closer packing is with the low-temperature films, the reverse of the behaviour of the carbamide derivatives. The typical properties of condensed films of very long-chain compounds, *i.e.*, more than 27 carbon atoms long, are not so marked as with shorter-chain compounds. In pentaerythrityl tetrapalmitate, the four chains attached to a common centre through polar groups should be normally directed to the corners of a tetrahedron, but when present in films are oriented perpendicular to the surface. The application of a comparatively large compressive force is necessary before close packing occurs; this is ascribed to the resistance of the valency linkings in the central group of carbon atoms to deviation from their normal directions. L. F. G.

Micro Determination of Molecular Weights by the Method of K. Rast. W. S. SSADIKOW and A. K. MICHAILOW (*Biochem. Z.*, 1924, **150**, 368—371).—An examination of the applicability of Rast's micro camphor method of determining molecular weights (A., 1922, i, 421). Results are sometimes variable even when the substance is soluble in camphor. J. P.

Cryoscopic Measurements with Nitrobenzene. II. Variation of Molecular Depression with Water Content. F. S. BROWN and C. R. BURY (*J. Chem. Soc.*, 1924, **125**, 2219—2226).—Cryoscopic measurements were made with the water content kept constant by the presence of salt hydrate pairs (T., 1923, **123**, 2037). Washburn's equation, in which the depression is set proportional to the sum of the mol. fractions of the solutes,

fits the data accurately for benzil and some other solutes, whilst the equation of van't Hoff agrees less satisfactorily. L. J. H.

Anomalous Rotatory Dispersion. F. Bürki (*Helv. Chim. Acta*, 1924, **7**, 759—762).—The criterion for anomalous dispersion put forward by the author (*cf.* A., 1924, ii, 218) shows that, contrary to the views of Lowry and Dickson (A., 1915, ii, 660), the menthyl α-phenylcinnamate, 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl β-phenylethyl ketone, and menthyl α-acetyl-β-phenylbutyrate behave anomalously. H. T.

Dimensions of Ions in Aqueous Solutions. K. Jabłczyński (*Rocz. Chem.*, 1923, **3**, 362—376).—The limiting values for the volume occupied by a dissolved electrolyte, that is, the sum of the volumes of the anion and cation, have been calculated from measurements of densities of solution. It is shown that the values are practically identical in each case with the sum of the volumes of the ions in the solid state as calculated by W. L. Bragg (A., 1920, ii, 537) by his *X*-ray method. Measurements show that, in the case of the halogen acids and lithium bromide and iodide, the volume of the undissociated molecule is equal to the sum of the volumes of the component ions; in other cases, a difference is found. The volume of the bromine ion is twice and that of iodine three times as great as those deduced from Bragg's measurements. Those of hydrogen, lithium, sodium, and silver ions are almost identical. The volumes of some compound ions such as ammonium and hydrazine were found to be practically identical with those of methane and ethane, respectively; the volumes of methylamine and trimethylamine ions are also close to the calculated values, but the volumes of anions do not show additive properties.

The relation between the volume of an ion in solution and its mobility is expressed by the Stokes–Einstein equation $lw^{1/3}=K_1$, the theoretical value for K_1 being 102·77. Experimentally, however, greater values are found, and this is attributed to the effects of hydration; thus a lithium ion carries 12, sodium 5, potassium 0·6 mol. H_2O; rubidium, cæsium, and ammonium are not hydrated. These figures are in good agreement with those obtained from cryoscopic and ebullioscopic measurements (Jablczyński and Kon, T., 1923, **123**, 2953). Taking hydration into account, the new value of K_1 becomes 207·9, or twice the value calculated from Stokes' equation; it is suggested that for ions this should have the form $3\pi\eta v$.

G. A. R. K.

Activity Coefficients of Dilute Aqueous Solutions of Hydrogen Chloride, Thallous Chloride, and Lead Nitrate. M. Randall and A. P. Vanselow (*J. Amer. Chem. Soc.*, 1924, **46**, 2418—2437).—Accurate determinations of the freezing points of solutions have been made with a modified Adams' apparatus (A., 1915, ii, 222), all dissolved air and other gases being removed from the solutions by prolonged evacuation. The activity coefficients of hydrogen chloride, thallous chloride, and lead nitrate derived from the data agree with the values obtained by other methods,

but not with the values given by the equation of Debye and Hückel (A., 1923, ii, 724; cf. A., 1924, ii, 306). S. K. T.

Physico-chemical Investigations on Uric Acid. R. STERN (*Biochem. Z.*, 1924, **150**, 535—541).—The spontaneous transformation of a solution of sodium monourate on keeping for 4 days into a colloidal sol showing opalescence, increased viscosity, and a tendency to double refraction is described. J. P.

Dissolution of Substances in Mixed Liquids with Special Reference to Colloids. E. W. J. MARDLES (*J. Chem. Soc.*, 1924, **125**, 2244—2259).—The solvent action on colloidal substances, such as tannic acid and cellulose acetate, of various binary mixtures of liquids suspected of forming molecular complexes with each other has been investigated, together with some of the physical properties (viscosity, surface tension, etc.) of the sols produced. The presence of the colloid greatly exaggerates any abnormality of the composition–viscosity (etc.) curve. In general, molecular simplification increases the solvent action, but where the components are themselves associated, the effect of complex formation may be masked by the molecular dissociation of the component liquids. [Cf. *B.*, 1925, 1.] L. J. H.

Physical Differences between Sols and Gels of Agar. E. HATSCHEK and R. H. HUMPHRY (*Trans. Faraday Soc.*, 1924, **20**, 18—22).—Sols and gels containing 3% or more of agar show optical differences, the gel scattering light much more effectively. The electrical conductivity of agar solutions containing 2% of copper sulphate is 1—2% greater in the gel than in the sol at the same temperature; the same result was obtained by the use of direct and alternating currents. It is suggested that in the gel condition the segregation of a phase rich in agar leaves a less viscous phase which contains most of the electrolyte and has a greater conductivity than the viscous sol. S. S.

Influence of Anions on the Coagulation of a Negative Colloidal Sol. D. C. HENRY and V. A. MORRIS (*Trans. Faraday Soc.*, 1924, **20**, 30—36).—From a study of the coagulation of a gold sol by a series of sodium salts, it is found that the anion exerts a definite stabilising effect. The order of the anions is oxalate > HPO_4'' > CO_3'' > OH' > citrate > HCO_3' > Br', I', acetate, valerate > butyrate, CNS' > SO_4'' > Cl', benzoate. The order is not that of the Hofmeister series nor that of the effectiveness of the anions in the coagulation of positive sols. S. S.

Velocity of Coagulation of Colloids of the Second Order. C. K. JABŁCZYŃSKI (*Bull. Soc. chim.*, 1924, [iv], **35**, 1286—1292).—Smoluchowski's equation (A., 1917, ii, 297) has been derived and experimentally confirmed for the velocity of coagulation of colloids of the second order, although the processes taking place in the coagulation of colloids of the two types are essentially different. This relationship also holds in the presence of protective colloids. Vigorous stirring has no influence on the velocity of coagulation. H. T.

Slow Coagulation of Colloids of the First Order. C. K. JABŁCZYŃSKI (*Bull. Soc. chim.*, 1924, [iv], **35**, 1277—1286).—Smoluchowski's equations (A., 1917, ii, 297) for the coagulation of colloids of the first order have been confirmed by observations on the slow coagulation of ferric hydroxide and arsenious sulphide. The method used depends on the absorption of light by the hydrosol, the absorption being measured by passing the light through crossed Nicols and finding the angle through which one had to be rotated to give equal illumination with the standard. If α denotes this angle then log tan α—log tan $\alpha_0 = Kt$. This equation is shown to be identical with Smoluchowski's. Two new methods for the derivation of his equation are described. H. T.

Ageing of Metal Hydroxides, and the System Chromium Hydroxide–Chromite–Sodium Hydroxide. R. FRICKE and O. WINDHAUSEN (*Z. physikal. Chem.*, 1924, **113**, 248—260).—Both amorphous chromium hydroxide and crystalline aluminium hydroxide (prepared by dilution of 5*N*-sodium aluminate to 3*N* and shaking in the absence of air) when added to a solution of sodium hydroxide, dissolve to an extent which depends on the amount of solid phase present. This agrees with the results obtained by Müller (A., 1923, ii, 71) and is attributed to the inhomogeneity of the hydroxides. The rate of solution of these hydroxides is extraordinarily slow in spite of the very large surfaces exposed. The possible causes for this behaviour are discussed, since the explanation given by Müller for amorphous chromium hydroxide cannot be applied to crystalline aluminium hydroxide. M. B. D.

Protection and Precipitation of Gold by Proteins. R. ZSIGMONDY and E. JOËL (*Z. physikal. Chem.*, 1924, **113**, 299—312).—The influence of gelatin on the stability of a colloidal gold sol depends on the concentration of the protein. As the concentration diminishes, it shows a protective action, later a coagulating effect, and finally becomes indifferent. The colour changes characteristic of these stages with fine and coarse gold hydrosols, with and without sodium chloride, have been tabulated. The results are explained on the assumption that several protein molecules may be combined with a gold particle or that gold particles may be adsorbed on the surface of a particle of the protective colloid. M. B. D.

Antagonism between Dyes and Inorganic Salts in their Absorption by Storage Tissue. C. E. T. MANN (*Ann. Bot.*, 1924, **38**, 753—777).—Using thin slices of mangold tissue, the absorption of methylene-blue, neutral-red, and orange-G, respectively, has been followed in simple solution and in solutions containing the chlorides of ammonium, magnesium, aluminium, and lanthanum. In simple solution, the dyes are absorbed in the order: neutral-red > methylene-blue > orange-G at a time when equilibrium is being approached. This absorption is explained on the ultra-filtration theory of the nature of the plasma-membrane. The chlorides of aluminium and ammonium in 0·1*N*-solution have nearly the same effect, which is greater than that of magnesium

chloride. The presence of a salt in the solution of the dye antagonises the intake of the dye by the living tissue, and the magnitude of this antagonism is a function of the valency of the cation and its concentration. The antagonistic action between electrolyte and methylene-blue is stronger than that between the same electrolyte and neutral-red. The results obtained support Kahho's colloid precipitation theory of the plasma membrane (A., 1922, i, 94). O. O.

Hydration of Molecules and Ions. R. FRICKE (*Kolloid-Z.*, 1924, **35**, 264—274).—A summary, with bibliography of recent work. E. M. C.

Water Fixation in Colloids. A. KUHN (*Kolloid-Z.*, 1924, **35**, 275—294). E. M. C.

The Colloid-chemical Theory of Water Fixation in the Organism. M. H. FISCHER (*Kolloid-Z.*, 1924, **35**, 294—302). E. M. C.

Water Fixation in Colloids, from the Medical Point of View. H. SCHADE (*Kolloid-Z.*, 1924, **35**, 302—309). E. M. C.

Water Metabolism and Pharmacological Action. H. HANDOVSKY (*Kolloid-Z.*, 1924, **35**, 309—313). E. M. C.

Retention of Water in Soils. G. WIEGNER, R. GALLEY, and H. GESSNER (*Kolloid-Z.*, 1924, **35**, 313—322).—The properties of clay suspensions are determined by the nature of the "stabilising" cations associated with the ionised surface molecules of silicic acid. Clays with a single stabilising ion show a gradation in properties through the series Li, Na, K, and NH_4, Rb, Cs, and H; the stability of the clay depends on the hydration of the cation. A lithium clay is lyophilic, bulky, viscous, and insensitive towards electrolytes, whilst a cæsium clay is lyophobic, sensitive to electrolytes, and has a less viscous. The alkaline-earths show a similar series. The flocculating powers of salts follow the hydration of their cations. When more than one cation is present, base exchange plays an important part in the coagulation process and takes place the more readily the higher the hydration of the stabilising ion and the lower that of the coagulating ion. E. M. C.

Influence of Solvent on the Equilibrium of Isomerides. O. DIMROTH (*Annalen*, 1924, **438**, 58—67; cf. A., 1911, ii, 31; 1913, ii, 763).—A theoretical paper, polemical against Smits (A., 1915, ii, 750; 1917, ii, 232; "Die Theorie der Allotropie," Leipzig, 1921, pp. 80—100, 138, 368—473). The isomerism of benzoylformaldehyde hydrazone and of acetaldehyde phenylhydrazone is discussed. C. H.

Dynamics of the Malonic Ester Equilibrium. A. SKRABAL and A. MATIEVIC (*Monatsh.*, 1924, **45**, 39—41).—The velocity of hydrolysis of malonic esters has been measured in aqueous alcoholic solution at 25° with hydrochloric acid as catalyst. The ester equilibrium has been calculated from the data. For methyl

malonate, $K=4\cdot2$ (cf. Palomaa, A., 1918, ii, 435). For ethyl malonate, $K=2\cdot4$. The results are compared with those for oxalic esters (A., 1919, ii, 57, 144). F. M. H.

Equilibrium in the Alcohol–Ether Reaction at 130° and 275°. R. N. PEASE and C. C. YUNG (*J. Amer. Chem. Soc.*, 1924, **46**, 2397—2405).—The equilibrium $2EtOH \rightleftharpoons Et_2O+H_2O$ has been investigated at 275° with alumina as catalyst, and at 130° with sulphuric acid–ethyl alcohol mixture as catalyst. The value of K $(=[Et_2O][H_2O]/[EtOH]^2)$ is $0\cdot66\pm0\cdot1$ at 275° and $8\cdot0\pm0\cdot2$ at 130°, representing the conversion of 62% and 85% of alcohol, respectively. With the help of previously published data, the heat of the reaction is shown to be 7100 cals., the free energy change in the reaction and the free energy of formation of ether vapour at 25° are −3210 cals. and −35,900 cals., respectively (cf. A., 1924, i, 363). S. K. T.

Dual Ions and Internal Salts. A. THIEL (*Z. physikal. Chem.*, 1924, **113**, 53—54).—Polemical against Blüh (A., 1924, ii, 658). Blüh's view of the behaviour of helianthin has long ago been discarded. The formula $\overset{\lceil\quad\rceil}{NMe_2}\cdot R\cdot SO_2Na$ for the internal salt is impossible from the chemical point of view. Dual ions and internal salts are always "charge isomerides," the charges in the former being free, whilst in the latter they are bound by internal compensation of valencies. M. S. B.

Ionisation Constant of Hypochlorous Acid. F. G. SOPER (*J. Chem. Soc.*, 1924, **125**, 2227—2231).—Dilute solutions (10^{-4} to 4×10^{-3}) of hypochlorous acid have been distilled at 25° and the ratio of the concentration in the distillate to that in the original solution has been found to be constant=2·69. In this connexion, the conclusions of Noyes and Wilson (A., 1922, ii, 692) are criticised. From the value of the ratio and the concentration of hypochlorous acid in the distillate obtained from solutions of sodium hypochlorite, the hydrolysis constant for the latter at 25° is $1\cdot0\times10^{-6}$ corresponding with the value $1\cdot0\times10^{-8}$ for the ionisation constant of the acid. L. J. H.

Conditions of Maximum Solubility: Gypsum. A. COLSON (*Compt. rend.*, 1924, **179**, 1041—1045).—Gypsum shows a maximal solubility at 35°, and, according to the thermochemical data of Berthelot, the heat of dissolution at this temperature is zero, a result which is said to be incompatible with theoretical conclusions. If the gypsum is previously dried at 140°, a supersaturated solution, when kept at 35°, deposits its excess of gypsum with the evolution of 8·8 cal. per g. of anhydrous salt. Nearly the same value is obtained by determining the heat of solution of the similarly dried powder and subtracting the heat of hydration. These values are in fair agreement with that calculated by means of the Clapeyron equation (7·7 cal. per g.). These results indicate that the heat of dissolution is positive at the point of maximum solubility.
W. H.-R.

Measurement of Vapour Pressures of Aqueous Salt Solutions by Depression of the Freezing Point of Nitrobenzene. N. V. SIDGWICK and E. K. EWBANK (*J. Chem. Soc.*, 1924, **125**, 2268—2273; cf. Roberts and Bury, T., 1923, **123**, 2037).—The freezing point of dry nitrobenzene is 5·689°. The lowering in contact with solutions of known vapour pressure was determined and the relation may be expressed by the equation $d=0{\cdot}672p+0{\cdot}00148p^2$. This is in harmony with the assumption that water exists in nitrobenzene as single and double molecules only, and that the relative proportions are determined by the mass-action law. From the data it may be calculated directly that $[H_4O_2]/[H_2O]=2{\cdot}26$. The vapour pressures of other solutions are then determined from the freezing points of nitrobenzene in equilibrium with them.

L. J. H.

Hydration of Salts and their Effect on the Vapour Pressure of Water. N. V. SIDGWICK and E. K. EWBANK (*J. Chem. Soc.*, 1924, **125**, 2273—2275; cf. preceding abstract).—The vapour pressure of some inorganic salt solutions is compared with the water of crystallisation of the solid salt. Those which are hydrated in the crystalline state give greater depressions, pointing to the hydration persisting correspondingly in solution. Nitrates are exceptional and association of the anion is inferred. No similar regularity is shown by aqueous solutions of the alkali salts of weak organic acids. L. J. H.

Equilibria at High Temperatures by the Pyrometric Method. N. A. PUSCHIN and J. V. GREBENSCHTSCHIKOW (*Z. physikal. Chem.*, 1924, **113**, 57—78).—An apparatus is described for determining the cooling curve of a substance at a constant high pressure. By means of this, cooling curves have been obtained, under pressures up to 4000 kg./sq. cm., for a number of compounds, namely, diphenylamine, urethane, *p*-toluidine, benzene, phenol, *p*-nitroanisole, and trimethylcarbinol dihydrate. In general, the experimental results are in good agreement with those of other investigators by the manometric method. From the time required for crystallisation, the latent heat of fusion of urethane has been determined. It diminishes from 40·7 cal./g. at a pressure of 25 kg./sq. cm. to 29·3 at 3050 kg./sq. cm., and the results agree well with those deduced by Bridgman (*Proc. Amer. Acad.*, 1915, **51**, 118) from theoretical considerations. The temperature of transition from one crystalline form of phenol to the other is 64·4° under a pressure of 2200 kg. per sq. cm. (cf. Tammann, A., 1910, ii, 1051; Bridgman, *loc. cit.*). The chief advantages of the pyrometric over the manometric method are: the greater rapidity in determination, the much smaller quantity of material necessary, the possibility of determining at the same time the change of heat of fusion with pressure, and also the possibility of employing the pyrometric method in the study of equilibrium in systems of more than one component (cf. A., 1912, ii, 331). M. S. B.

Heat of Solution of Alkali Halides. J. WÜST and E. LANGE (*Z. Elektrochem.*, 1924, **30**, 523—528).—Heats of solution at 25°

have been measured by adiabatic calorimetry, at the dilute end by dissolving solid salts, at the saturated end by measuring heats of dilution. The integral heats of solution for a series of concentrations up to saturation have been drawn up for chlorides, bromides, and iodides of potassium and sodium. For sodium salts, they lie throughout below those for the corresponding potassium salts, and in both series the integral heats are lowest for chlorides and highest for iodides. In the case of sodium halides, the curves show a maximum, which is especially well marked with sodium iodide, not far from the saturation point. W. A. C.

Calorimetric Researches. VI. Determination of Heat of Combustion of Salicylic Acid. Proposed Adoption of this Substance as Secondary Standard in Calorimetry. P. E. Verkade and J. Coops (*Rec. trav. chim.*, 1924, **43**, 561—581).—The desirability of introducing a secondary standard for determining the thermal capacity of the calorimetric system is advocated. As standard substance salicylic acid is proposed, because it fulfils the following necessary conditions: Its heat of combustion is accurately known, viz., 5242 cal.^{15}/g. (air) or 5232 cal.^{15}/g. (vac.). It is easily obtainable in the pure state, is quite stable and not hygroscopic. It is non-volatile and offers no difficulties in its combustion. W. E. E.

Dependence of the Heat of Vaporisation and the Surface Tension of a Liquid on the Molecular Forces. J. J. Plăcinteanu (*Z. physikal. Chem.*, 1924, **113**, 290—298).—The equation given by Hammick (A., 1919, ii, 389; 1920, ii, 85) showing the connexion between the molar latent heat of vaporisation and the surface tension of a liquid, viz., $Mr/6=\gamma V/d$, where M= molecular weight, r=heat of vaporisation per gram, γ=surface tension, V=molecular volume, and d=diameter of a molecule, has been derived by the author, who finds that the constant=3π instead of 6. Using this new constant, he shows that it gives a better agreement with experimental results. M. B. D.

Solubility, Heat of Solution, and Lattice Energy of Salts. J. A. V. Butler (*Z. physikal. Chem.*, 1924, **113**, 279—289).—A close parallelism exists between the heat of solution of salts and their solubility. The solubility can be estimated from the heat of solution, modified by the condition of the surface. Since the heat of solution of a salt is equal to the difference between the sum of the heats of solution of its gaseous ions and its lattice energy, these are the fundamental quantities from which to estimate the solubility. A comprehensive series of values of the heat of hydration of salts has been calculated from their lattice energies (cf. Grimm, A., 1923, ii, 16). These values confirm the addition rule of Fajans (A., 1920, ii, 12). M. B. D.

Conductivity of Aqueous Perchloric Acid. E. Linde (*Z. Elektrochem.*, 1924, **30**, 255—259).—The conductivity of perchloric acid has been measured at 25° over a range 1·05—13·50N and at 50° from 4·25—14·04N. The conductivity reaches a

maximum at 25° in 4·7*N*-solution. The viscosity of these solutions has been measured over the same range of concentration and the values for the degree of dissociation, after correction for viscosity, show a maximum at $HClO_4,3H_2O$ (approx.) and a minimum at $HClO_4,2H_2O$. The temperature coefficient of the specific conductivity of a 4·7*N*-solution is 0·0125. M. B. D.

Conductivity of Chlorides in Fused Antimony Trichloride and Ghosh's Theory. Z. KLEMENSIEWICZ (*Z. physikal. Chem.*, 1924, **113**, 28—34).—Determinations of the electrical conductivity of solutions of potassium, rubidium, ammonium, and thallium chlorides in fused antimony trichloride have been made at 98·5°. By plotting values of $\log_e \mu$ as ordinates against values of $100\sqrt[3]{\eta}$ as abscissæ, μ and η being the equivalent conductivity and concentration, respectively, straight-line graphs are obtained. The graphs for the first three chlorides are nearly parallel and the tangent of the inclination to the axis of abscissæ is in close agreement with that theoretically deduced by Ghosh for uni-univalent electrolytes. For thallium chloride, however, the tangent is much greater and approaches the value for bi-univalent salts, possibly on account of the subsidiary valencies due to tervalent thallium. With the help of Frycz and Tolloczko's determinations of the transport number of the chlorine ion in antimony trichloride ("Gedenkbuch der Lemberger Universität," 1912) an extraordinarily high value, 137·5, has been found for the average mobility of the chlorine ion. On the analogy of the behaviour of the hydroxyl ion in water, this might be due to the fact that the solvent and solute produce the same anion, but it is noteworthy that the correction applied by Ghosh in the case of the hydroxyl ion, in order to obtain the linear relation between $\log_e \mu$ and $100\sqrt[3]{\eta}$, is not necessary here. The mobilities of $K^{\cdot}$, $NH_4^{\cdot}$, $Rb^{\cdot}$, and $Tl^{\cdot}$ are 25·5, 16·5, 22·5, and 21·5, respectively, considerably less than in water, namely, 64·7, 64, 67·6, and 66. This is not accounted for by the difference in viscosity of the two solvents. The conductivity of mercuric chloride is so small that it can only be accounted for by incomplete ionisation, and this suggests that the variations in the behaviour of the uni-univalent chlorides may also be due to the same cause, contrary to Ghosh's complete ionisation theory. The effect of temperature on conductivity corresponds qualitatively with Ghosh's views, but a quantitative study is not possible owing to lack of data on the dielectric constant. M. S. B.

Electrical Conductivity of Solid Salts at High Temperatures. P. VAILLANT (*Compt. rend.*, 1924, **179**, 530—532; cf. A., 1922, ii, 418; 1924, ii, 456).—The conductivity of solid sodium chloride, measured over a wide temperature range, increases to a maximum at 28·6°, decreases up to 56·5°, and thence increases to a much greater value than that of the first maximum up to 420°, the highest temperature of experiment. On reheating immediately after the first experiment, the first maximum is practically absent whilst the conductivity values forming the second remain unchanged.

At the higher temperatures, the current passing is approximately proportional to the electrode surfaces, and the inference is drawn that the passage of electricity takes place over the whole cross-section of the solid. Potassium sulphate and chloride give similar results, but in the case of barium chloride maxima were observed at 28·4° and 107·9°. The second of these has a particularly high value, being much greater than the value at 456°, the highest temperature employed. On reheating, both these maxima are absent. H. J. E.

Migration of Ions in Solid Electrolytes. Le Blanc and M. Kröger (*Z. Elektrochem.*, 1924, **30**, 253—255).—Tubandt's experiments (A., 1921, ii, 426) are explained by assuming that the mobile ion is the one the displacement of which causes the least disturbance and suggest replacing the electrodes of the first cell by reversible iodine electrodes in order to test this theory. The experiments of Tubandt and Reinhold (*Z. Elektrochem.*, 1923, **29**, 313) do not clear up the work of Ketzer (A., 1920, ii, 217) on the change in conductivity of lead chloride powder produced by adding small amounts of sodium chloride. M. B. D.

Influence of Gelatin on Transport Numbers. G. Scatchard (*J. Amer. Chem. Soc.*, 1924, **46**, 2353—2357).—A criticism of recent work by France and his co-workers (A., 1922, ii, 114; 1924, ii, 148). The values obtained (*loc. cit.*) for the transport numbers are shown not to have the significance ascribed to them. The proof that the change in the liquid-junction potential cannot be due to a change in the concentration of the acids is independent of the experimental results; these afford no evidence either for or against the conclusions reached by the authors. S. K. T.

Introduction to a General Theory of Electromotive Force. E. Denina (*Gazzetta*, 1924, **54**, 750—765).—Theoretical. T. H. P.

Determination of the Decomposition Potential of Aluminium Bromide in Aqueous Solution. W. D. Treadwell and H. Stern (*Helv. Chim. Acta*, 1924, **7**, 627—637).—From observations on the cell $Al|AlBr_3$ KBr$|Br_2$ Pt, the decomposition potential of aluminium bromide has been derived for temperatures from 60° to 100°. The value for 100° is 1·76 volts. Since the heat capacities of the hydrated and anhydrous salts are nearly equal, there is practically no difference between the heat of hydration and the free energy of the process. Introducing this quantity a value of 1·76 + 1·23 = 2·99 volts is obtained for the decomposition potential of saturated aqueous aluminium bromide and 2·99 − 1·07 = 1·92 volts for the normal potential of aluminium. Corresponding numbers have been obtained for aluminium chloride and iodide. H. T.

Differences of Potential at the Boundaries of Solutions. R. Fricke and C. Rohmann (*Z. Elektrochem.*, 1924, **30**, 537—544).—Measurements of *P.D.* in concentration cells connected by

capillary siphons are not trustworthy when the capillary bore is 0·3 mm. or less, or when the concentration is lower than 0·1*N*. At comparatively low normalities, the *P.D.* of sodium and potassium hydroxide solutions is slightly below the calculated *P.D.*, owing to incomplete dissociation. From 2—3*N* onward, however, the *P.D.* found progressively exceeds that calculated. W. A. C.

Diffusion Potentials and Ionic Mobilities of Benzoates and Salicylates and their Modification by a Membrane of Parchment Paper. E. B. R. PRIDEAUX and W. E. CROOKS (*Trans. Faraday Soc.*, 1924, **20**, 37—44).—The transport numbers of the anion calculated from the limiting conductivity and from observations of diffusion potentials for solutions of potassium and sodium benzoate and potassium salicylate are in good agreement. The mean values at 18° are potassium benzoate, 0·396; sodium benzoate, 0·310; potassium salicylate, 0·325. When a parchment paper diaphragm is interposed between the two solutions, a higher diffusion potential is found which corresponds with transport numbers of 0·318, 0·248, and 0·242, respectively, for these three salts. This is ascribed to the retardation of the anion by the membrane, the retardation being approximately constant for the two benzoates and greater in the case of the salicylate. S. S.

Barium and Strontium Amalgam Electrodes. P. S. DANNER (*J. Amer. Chem. Soc.*, 1924, **46**, 2385—2390).—Three types of electrodes for use with two-phase alkali and alkaline-earth amalgams are described. The *E.M.F.* of barium and of strontium two-phase amalgams against calomel in 0·1*N*-solutions of the chlorides of the respective earth metals are 2·0240 and 2·2472 volts. These results are said to afford further evidence of the salt-like character of the mercurides. S. K. T.

Seat of the Electromotive Force in the Galvanic Cell. J. A. V. BUTLER (*Phil. Mag.*, 1924, [vi], **48**, 927—935).—An extension of a previous paper (cf. A., 1924, ii, 598). The existence of large metal contact *P.D.*'s is in no way inconsistent with the correspondence between the *E.M.F.* of a galvanic cell and the energy of the chemical reaction occurring therein. The cell $M|M^{\cdot}aq|H^{\cdot}aqH_2|Pt$ is taken as an example, and statistical expressions for the different junctions $M|Pt,M|M^{\cdot}aq$, $H^{\cdot}aqH_2|Pt$, are combined to give an expression for the total *E.M.F.* of the combination. Differentiation of this latter expression yields the Gibbs–Helmholtz equation. C. W. B.

Zinc–Carbon Battery. H. D. NYBERG (*Z. Elektrochem.*, 1924, **30**, 549—552).—With a view to facilitate depolarisation of the carbon anode by means of atmospheric oxygen, the anode is made of porous carbon and is impregnated with paraffin, but in such a way that its outer surfaces are not prevented from being wetted by the electrolyte, which consists of 10% sodium hydroxide solution. The zinc cathode is converted into insoluble zinc hydroxide when current is produced. An initial *E.M.F.* closely approximating to the calculated value of 1·2 volts is obtained. W. A. C.

Photovoltaic Phenomena. R. AUDUBERT (*Compt. rend.*, 1924, **179**, 682—684; cf. A., 1923, ii, 827).—The effect of illumination is to render cupric oxide electropositive and cupric bromide electronegative. With silver chloride or sulphide, the sign of the effect depends on the mode of formation and thickness of the film; for very thin films, the effects of red and blue rays are of opposite sign, but with thick deposits, the chloride becomes electropositive and the sulphide electronegative. Polarisation of opposite sign to that of the deposit always increases the effect slightly, whilst polarisation of the same sign diminishes or even annuls, but never reverses, the effect. If other conditions are equal, blue rays are more active in this respect than red rays. These results are not in accord with Athanasiu's conclusions (A., 1924, ii, 239). Thermal and photochemical effects may, indeed, be superposed on and may mask the photo-electric effect, but if precautions are taken to avoid the former and carefully cleaned electrodes are used, results attributable to a photo-electric mechanism are obtainable. T. H. P.

Electrolysis at the Mercury Dropping Cathode. J. HEYROVSKY (*Compt. rend.*, 1924, **179**, 1044—1046; cf. A., 1924, ii, 598, 599).—Theoretical. If π and π' are the potentials of the mercury dropping cathode in solutions of concentration c and c', and if the current intensities are identical in the two cases, $\pi - \pi' = RT/nF \log_e c/c'$, where n is the valency of the metal and R, T, and F are the usual energy symbols. The current–*E.M.F.* curves (cf. Heyrovsky, *loc. cit.*) in solutions of different concentrations are thus superposable, being simply moved a distance $RT/nF \log_e c/c'$ along the axis of potentials. But if there are only traces of a metal of the order 10^{-6} mol. per litre, the slight electrolysis changes the concentration of the ions that may be deposited, and the saturation current is soon attained, forming a wave in the current–*E.M.F.* curve, and the two curves are no longer superposable. W. H.-R.

Electrolytic Polarisation. I. Cathodic Overvoltage of Lead. S. GLASSTONE (*J. Chem. Soc.*, 1924, **125**, 2414—2423).—As long as bubble formation is taking place, the potential of an electrode at small current density measured by the direct method is almost identical with the instantaneous back *E.M.F.* The overvoltage may be calculated from a formula of the type $E = a + b \log (I - c)$, where c is a term which takes account of the loss of potentiometric material by diffusion and may become important at low current densities. At appreciable current densities, the cathodic potential of a lead electrode is influenced by the presence of alkali-metal ions, probably owing to alloy formation, but the minimum overvoltage is uninfluenced. Roughening the surface of the electrode affects the minimum overvoltage. L. J. H.

Hydrogen Overvoltage at Arsenic Cathodes. G. GRUBE (*Z. Elektrochem.*, 1924, **30**, 517—523).—The cathode potential at which hydrogen begins to be evolved from galvanically deposited crystalline arsenic is 0·358 volt in 2*N*- and 0·284 volt in *N*-sulphuric acid. In sodium hydroxide solutions, it approximates to 1·0 volt.

Further experiments show that the potential imparted by arsenic hydride when it decomposes at an arsenic electrode in presence of sodium hydroxide solution is also about 1·0 volt. Hence, whereas in acid solutions formation and decomposition of arsenic hydride play a minor part, in alkaline solutions electrolysis leads primarily to arsenic hydride, of which the hydrogen evolved is a decomposition product. W. A. C.

Hydrogen Overvoltage on Alloys. P. FISCHER (*Z. physikal. Chem.*, 1924, **113**, 326—328).—The hydrogen overvoltage for various alloys of cadmium, zinc, lead, tin, silver, and copper has been measured by experiments in 0·1*N*-sodium hydroxide solutions. The solution was stirred and the alloys were carefully polished. The author finds that the overvoltage is independent of the percentage composition of the alloy and is determined by the constituent having the smallest overvoltage. M. B. D.

Passivity Phenomena and Cathodic Overvoltage. E. LIEBREICH and W. WIEDERHOLT (*Z. Elektrochem.*, 1924, **30**, 263—279).—The anodic and cathodic behaviour of chromium, iron, and mercury in 1·02*N*-sulphuric acid is shown in a series of current–potential curves in which discontinuities divide them into several regions corresponding with different electrode processes. A chromium anode at high current densities dissolves as chromate, but at lower current densities and potentials below $e_h = +1{\cdot}3$ volts this process ceases, the metal being probably coated with a chromic chromate film and dissolving only slightly. At about $e_h = +0{\cdot}5$ volt and a very small current density, the potential shows slight abrupt rise with falling current density and the true passive condition, ascribed to the insolubility of a film of chromic hydroxide, is attained. At zero current density, the passive metal has a potential of about $e_h = +0{\cdot}45$ volt. This passive condition persists, when the metal is made a cathode, at small current densities. At $e_h = -0{\cdot}4$ volt, the curve rises steeply owing to the metal dissolving as Cr^{++} ions, which are partly oxidised near the electrode, giving secondary hydrogen evolution (*a*). At higher current densities, metal solution gives place entirely to direct hydrogen evolution at about $e_h = -0{\cdot}5$ volt (*b*). Reducing the current density at an electrode in the condition (*a*) results in the metal returning to the passive state, but from the condition (*b*), the metal remains active even when the current is reduced to zero ($e_h = -0{\cdot}48$ volt). This base potential is retained when the metal is made an anode, but at a certain current density the potential jumps to a positive value and the metal dissolves as chromate. The curves for iron show similar discontinuities, but they are less marked except in the case of the generally recognised passivation change. The passivity of iron differs from that of chromium chiefly in that it corresponds with the highest state of oxidation, and is explained by the existence of a transparent film of a higher oxide. The curves for mercury are also discontinuous and cathodic treatment is shown to cause the formation of visible oxide films before the potential for hydrogen evolution is reached. The authors conclude that on cathodic treatment of a

metal, the monatomic hydrogen, resulting from hydrogen-ion discharge, is at first used up in reducing any oxygen present and by being dissolved in or adsorbed on the metal. Hydroxyl ions thus accumulate at the metal surface and react to form hydroxides. After these processes have taken place, the evolution of hydrogen as gas is retarded by the performance of chemical work in reducing the hydroxide layer which has formed, as well as of surface work in detaching the gas bubbles from the electrode. Film formation may thus be an essential factor in cathodic overvoltage as well as in passivity phenomena. M. B. D.

Theory of Electrolytic Oxygen Evolution with Anodic Polarisation. I. Magnesium, Cadmium, Zinc, and Mercury Electrodes in Alkaline Solutions. F. JIRSA and K. LORIS (*Z. physikal. Chem.*, 1924, **113**, 235—240).—The polarisation of magnesium, mercury, zinc, and cadmium anodes has been measured at 25° in *N*-sodium hydroxide for varying current densities. At low densities, the metals dissolve in the bivalent form; Hg = − 0·15 volt, Cd = − 0·60 volt, and Zn = − 1·35 volts. On increasing the current density, oxygen is evolved and the metal becomes passive. The higher oxides formed are unstable, since when the current is stopped the potentials gradually sink to the above values. Magnesium, in contrast to the other metals, gives a more negative potential with increasing current density. M. B. D.

Theory of Electrolytic Oxygen Evolution with Anodic Polarisation. II. Palladium in Alkaline Solution. F. JIRSA (*Z. physikal. Chem.*, 1924, **113**, 241—247).—The relation between current density and the potential of a palladium anode (against the normal hydrogen electrode) has been studied in *N*-sodium hydroxide at 18°. The graphed results indicate that palladium may exist in at least two active states, in addition to the usual passive form. An electrode which has previously been heated in air is always passive. By comparing the potentials at which breaks occur in the current density–polarisation curves with those in the corresponding curves for the anodic and cathodic treatment of palladium coated with PdO and PdO_2, respectively, it is concluded that in alkaline solution a palladium anode is oxidised in the following steps; to Pd_2O (at + 0·15 volt); to PdO (at + 0·4 to 0·5 volt); to PdO_2 (at + 0·95 volt); and to unstable PdO_3 at 1·22 volts. Oxygen evolution occurs at more positive potentials through the medium of PdO_3, which breaks down into PdO_2 and oxygen. M. B. D.

Conditions of the Appearance of Anode Effect in the Electrolysis of Fused Chlorides. T. A. HEPPENSTALL and W. J. SHUTT (*Trans. Faraday Soc.*, 1924, **20**, 97—105).—Fused potassium, zinc, and lead chlorides were electrolysed with a conical anode arranged to vary the area of immersion in the fused mass. At a given temperature, the anode effect (a sudden large increase in resistance when the fused salt ceases to wet the anode) set in at a definite current density. This limiting current density increased

with rising temperature; at a given temperature, the superposition of alternating current on the direct current lowered the current density at which the anode effect appeared. Sodium chloride gave irregular results owing to corrosion of the cathode and crucible used.

S. S.

Electrochemical Behaviour of Chromium. N. Bouman (*Rec. trav. chim.*, 1924, **43**, 399—402).—From results previously obtained (A., 1924, ii, 150), the author calculates the ratio of chromic to chromous ions in the liquid boundary layer to be 10^{-2} : 1, so that whilst the solution in which the chromium electrode is immersed consists of pure chromic sulphate, the boundary layer contains mainly chromous ions. In order to maintain chromium in an active condition, the hydrogen-ion concentration must be at least 10^{-3}, and it would appear from previous reasoning that the boundary liquid is alkaline. This is attributed to an error in the value of the hydrogen solubility product, which is now shown to be abnormally large, 10^{2x-42} in place of 10^{2x-48}. The author now regards his measurements of the potential of a chromium electrode on which another metal has been deposited as values of the potential of the two metals, the chromium not being completely covered by the small quantity of separated metal.

H. J. E.

Influence of Light and *X*-Rays on Anodically Polarised Platinum Electrodes. G. Grube and L. Baumeister (*Z. Elektrochem.*, 1924, **30**, 322—332).—Platinised platinum electrodes which had been treated with gaseous oxygen or anodically polarised were dipped in 2*N*-sulphuric acid and exposed to the light of a quartz mercury vapour lamp. The nobler the initial potential, the greater was the fall in potential. This continued in the same direction for 15 minutes after the light had been turned off, after which it rose again. Smooth platinum, coated with a golden-yellow oxide by superposition of alternating current on direct current, also showed an initial reduction of potential on exposure to light. On continued illumination, the potential rose until it was higher than the initial value and after four successive illuminations the total rise in potential was 0·179 volt. An electrode which had been strongly oxidised and kept in the dark showed no decrease in potential on exposure to light, but only a positive effect. The sensitivity of the electrode to light is weak in potassium cyanide and still weaker in sodium hydroxide. The action of *X*-rays is similar to that of light. The results are explained on Baur's photolysis theory (A., 1919, ii, 264). The electrodes are assumed to be covered with a solid solution of PtO_3, PtO_2, and PtO. In light, PtO_2 is converted into PtO_3 and PtO. The PtO_3 can then either decompose into PtO_2 and oxygen or recombine with PtO to form PtO_2. As to which of these reactions predominates depends on the relative concentrations of the oxides, *i.e.*, on the potential of the electrode. The effect of increasing the (alternating) current density on an oxygen electrode is to make its potential pass through a minimum.

M. B. D.

Studies in Electro-endosmosis. I. F. FAIRBROTHER and H. MASTIN (*J. Chem. Soc.*, 1924, **125**, 2319—2330).—An experimental method of measuring electro-endosmosis through a diaphragm of powdered material, together with the potential gradient across the diaphragm (using reversible electrodes) is described. The effective cross-section of the diaphragm is measured electrically. With carborundum powder, the electro-kinetic potential varies with hydrogen-ion concentration reaching a maximum in dilute alkali, the carborundum being relatively negative. In distilled water, the value is −0·0698 volt. Contrary to other observers, no reversal is observed up to *N*/50-hydrochloric acid. L. J. H.

Magneto-chemical Phenomena. A. SCHÜKAREW (*Z. physikal. Chem.*, 1924, **113**, 441—463).—Numerous observations are recorded of currents observed between two electrodes immersed in a solution in which a chemical reaction is occurring or has just occurred, and of the effect on these currents of a strong magnetic field; of the increase caused by a magnetic field in a current maintained between two plates in a space in which certain gaseous reactions are occurring, and of the current which arises between two electrodes when placed in a strong magnetic field and in the vicinity of one plate in an electrolytic cell carrying a small current. The last effect is similar to, but not identical with, the Hall effect. No explanation of these phenomena is suggested. G. M. B.

Velocity of Bimolecular Reactions in Solutions. J. A. CHRISTIANSEN (*Z. physikal. Chem.*, 1924, **113**, 35—52).—Theoretical. Expressions for the velocity of non-ionic and ionic bimolecular reactions in solution are deduced on the basis of the expression for the velocity of a bimolecular gas reaction, $h = C_1 . C_2 . v_{12}\sqrt{T}e^{-Q_{12}/RT}$, where h is the velocity, C_1 and C_2 are the molar concentrations of the reacting gases 1 and 2, and v_{12} and Q_{12} two characteristic constants. These equations are compared with Brönsted's formula (A., 1922, ii, 699; see also Bjerrum, A., 1924, ii, 240). M. S. B.

Kinetics of Coupled Reactions. R. WEGSCHEIDER (*Z. physikal. Chem.*, 1924, **113**, 55—56).—Polemical with Thiersch (A., 1924, ii, 666). M. S. B.

Improvements in the Apparatus for Measuring the Velocity of Very Rapid Chemical Reactions. H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Camb. Phil. Soc.*, 1924, **22**, 426—431).—A continuation of previous work (A., 1923, ii, 746). More rapid reactions can now be investigated, four new modified types of the apparatus being described. One of them should be capable of dealing with reactions half completed in 1/1000 second, and has been tested with bimolecular reactions half completed in 1/700 second. A thermal method has been devised for determining the stages reached by a reaction at different intervals of time from its commencement. The principle of this method is to measure the temperature of the mixed fluid at different cross-sections of an observation tube. The apparatus employed allows the first observation of the temperature

to be taken 1/5000 second after the commencement of mixture, and for five subsequent measurements to be made at intervals of 1/7000 second; it has been used with 0·1*N*-hydrochloric acid and 0·1*N*-sodium hydroxide, to confirm the authors' conclusions as to the rate of mixture attained in their previous experiments.

L. F. G.

Temperature Coefficient and Mechanism of a Chemical Reaction. F. O. Rice, C. F. Fryling, and W. A. Wesolowski (*J. Amer. Chem. Soc.*, 1924, **46**, 2405—2418).—The temperature coefficient of a reaction is said to depend on certain "residual molecules" the concentration of which is very small and varies rapidly with the temperature. Thus acetone is probably largely hydrated in solution, and the non-hydrated molecules are "residual molecules." At least one reactant molecule must be a "residual molecule" if a reaction is to proceed with measurable speed; from this, the existence of slow unimolecular reactions is denied. Variation of the solvent has only a very slight influence on the temperature coefficient of a reaction. The name "protions" is suggested for unsolvated ions. The errors accompanying the determination of reaction velocities are discussed in detail. S. K. T.

Formation of Ammonia in the Oxyhydrogen Flame. H. Tominaga (*Z. Elektrochem.*, 1924, **30**, 528—534).—It is pointed out that Maxted's (T., 1918, **113**, 168, 386; 1919, **114**, 113) extrapolation of Haber's formula for the equilibrium $N_2 + 3H_2 \rightleftarrows 2NH_3$ to temperatures approaching 4000° is unsafe, since it leads to values for the specific heat of hydrogen and nitrogen which are somewhat too high. Moreover, the oxyhydrogen flame cannot be regarded merely as a source of heat, because at the temperatures concerned there is dissociation of water vapour, with consequent formation of nitric oxide. In the author's apparatus, mixtures of nitrogen (1 part) and hydrogen (1·8 to 6·0 parts) were passed under pressures up to 30 atm. on to an oxyhydrogen flame burning at a porcelain jet. Temperatures of about 3000° Abs. were observed. Approximately equal parts of ammonia and nitric oxide are formed. In agreement with calculation, the yield is increased as the temperature is lowered, *i.e.*, as the amount of water formed is diminished. Considerably larger yields were obtained than by Maxted's method. W. A. C.

Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures. I. Mixtures of Air and One Gas at Ordinary Temperature and Pressure. A. G. White (*J. Chem. Soc.*, 1924, **125**, 2387—2396).—A summary of previous data is given. Lower and upper limits of propagation upward, downward, and horizontally have been determined afresh for ten combustible gases. The relations previously found in the case of vapours (T., 1922, **121**, 1244) hold less well in these cases, but for carbon monoxide and all the hydrocarbons examined (except acetylene) the lower limits may be calculated with reasonable approximation from the calorific values. [Cf. *B.*, 1925, 2.] L. J. H.

Mechanism of the Oxidation of the Iodine Ion by the Ferricyanide and Ferric Ion. C. WAGNER (*Z. physikal. Chem.*, 1924, **113**, 261—274).—On the assumption of the formation of a di-iodide ion (an additive product of atomic iodine and an iodide ion) the author explains the oxidation of iodide ions by ferricyanide ions and the retarding effect of the ferrocyanide ion on the rate of the reaction (cf. Just, A., 1908, ii, 825). In accordance with Herzfeld's explanation (A., 1919, ii, 503) of the rate of formation of hydrogen bromide from its elements, it is assumed that there is a primary reaction resulting in the formation of a di-iodide ion, followed by two further concurrent reactions in which this ion is converted either into iodine or into two iodide ions. The same explanation applies in the case of oxidation of iodide ions by ferric ions. M. B. D.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. IX. Reduction of Permanganate Passing from Neutral to Alkaline Solution. J. HOLLUTA (*Z. physikal. Chem.*, 1924, **113**, 464—481; cf. A., 1924, ii, 115, 187).—A continuation of previous work. The influence of the hydroxyl ions on the velocity of the reduction of permanganate by sodium formate in slightly alkaline solutions has been studied. The results are fully in accord with the theories previously developed. The effect of the hydroxyl ions increases gradually with increasing concentration of alkali, manganate appearing more and more as an intermediate product in the process. The two stages in the reaction (A., 1922, ii, 771) characteristic of strongly alkaline solutions can be detected at relatively low hydroxyl-ion concentrations, although not so clearly. A side reaction occurs when the concentration of alkali is very low, according to the equations $MnO_4' + HCO_2' + H_2O = H_2MnO_4' + HCO_3'$ and $2MnO_4' + 2OH' + HCO_2' = 2MnO_4'' + HCO_3' + H_2O$. With slight alkalinity hydroxyl ions cause a diminution of the oxidising action of permanganate owing to a decomposition of the manganate first formed with regeneration of permanganate. G. M. B.

Velocity of Esterification of *n*-Butyric Acid in Glycerol. A. KAILAN and R. OBOGI (*Rec. trav. chim.*, 1924, **43**, 512—525).—The velocity of esterification of *n*-butyric acid at 25° in absolute glycerol, or in glycerol + $1\frac{1}{3}$ mol. of water per litre, is proportional to the concentration of the catalyst (hydrochloric acid). In glycerol, the retarding action of water is less than in alcohol. The velocity of esterification of butyric acid without a catalyst was measured in absolute and aqueous glycerol at 183° and the reaction was found to be "sesquimolecular" (so also for benzoic acid). The water had not a retarding, but a weakly accelerating action when its concentration was $1\frac{1}{3}$ to 2 mol. per litre. F. M. H.

Mutarotation. R. KUHN and P. JACOB (*Z. physikal. Chem.*, 1924, **113**, 389—431).—Measurements of the velocity of mutarotation of dextrose in aqueous solutions having p_H values from 0·77 to 8·64 show that the isomeric change occurs chiefly to un-ionised

molecules. Dextrose is found to have an acid dissociation constant of $10{\cdot}5\times10^{-13}$ at 25°, agreeing well with the value of Michaelis and Rona (A., 1913, ii, 379), whilst a basic dissociation constant is indirectly estimated to be $7{\cdot}8\times10^{-17}$ at 25°. The observations show that the velocities of change of undissociated molecules, cations, and anions are, respectively, 0·0104, 54·4, and 113·2, and the observed velocities of mutarotation are given by $k=0{\cdot}0104+0{\cdot}334[H^{\cdot}]+9345[OH']$ (cf. Hudson, A., 1907, ii, 942).

Observations of the influence of a number of alkali salts and also of acetate, phosphate, and citrate mixtures on the velocities of mutarotation are discussed in detail from the point of view of the activity theory, and the reaction velocity is shown to be proportional, not to the concentration (Brönsted, A., 1922, ii, 699), but to the activity of the reacting molecular species. The conclusion of Baker, Ingold, and Thorpe (T., 1923, **125**, 268) that water is not involved in the mutarotation of tetra-acetylglucose in methyl-alcoholic solution is confirmed for dextrose in aqueous solution by the fact that the velocity of the change does not vary, as the participation of the water in the reaction would require, when the activity of the water is varied in solutions of 2—50% concentration.

Measurements of the velocity of the Lobry de Bruyn change of dextrose in presence of alkalis show this to be an ionic phenomenon. The constitution of the ions is discussed and the conclusion is reached that the hydrogen ion separates from the terminal hydroxyl group, the spatial configuration of the groups attached to the second carbon atom being unaltered. The mechanism of the Lobry de Bruyn and the Fischer inversions is considered. The enolisation theory is supported by the behaviour of sugars in alkaline solution towards permanganate, but the conclusion of Armstrong and Hilditch (T., 1919, **115**, 1410), that there is no connexion between the alterations in structure revealed by their experiments and those involved in mutarotation, is disproved by a study of the permanganate reduction in phosphate buffer solutions of known p_H in which the minimum reducing effect coincides with the minimum of velocity of mutarotation (at p_H 3·0—4·5). Corresponding results are obtained with lactose and arabinose. In the case of lævulose, a maximum reaction velocity with permanganate was found between two minima, and this is held to indicate the existence of a particularly reactive form of lævulose in phosphate solutions between p_H 3 and 4. G. M. B.

Reaction of some Glycols with Acetone. P. H. Hermans (*Z. physikal. Chem.*, 1924, **113**, 337—384; cf. Böeseken and Hermans, A., 1924, i, 257).—The Böeseken boric acid method is trustworthy only where a comparison is made of molecules so closely related as to eliminate errors due to direct constitutive influences on conductivity. The degree of formation of cyclic acetals by reaction with acetone is now shown to give results qualitatively parallel with those obtained by the boric acid method in the cases of a number of glycols. Exact measurements are recorded for the equilibrium, and the velocity of the reaction at

two temperatures, between acetone and *cis*-hydrindene-1 : 2-diol, *cis*-tetrahydronaphthalene-1 : 2- and -2 : 3-diols, and the two stereoisomeric hydrobenzoins. The results in the case of the two hydrobenzoins are explained by the assumption that the two phenyl groups repel each other strongly and hinder free rotation. This conception and the suggested mechanism of the reaction are supported by a thermodynamic consideration of the data obtained. The critical increment in such a reaction may be of a complex nature, one portion being due to a " steric increment " involved in the preliminary passage of the molecule into the suitable orientation for reacting with acetone (" steric activation "). G. M. B.

Reducibility of certain Metallic Halides by means of Hydrogen. F. DE CARLI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 94—97).—Measurements have been made of the proportions of the halides undergoing reduction at various temperatures when a definite quantity of hydrogen is passed over stannic, stannous, cupric, cuprous, lead, and cobalt halides. The chlorides are reduced in smaller proportion than the bromides and these in smaller proportion than the iodides, and the halogens are given up the more readily by the metal with the higher than by the same metal with lower valency. [Cf. *B.*, 1924, 941.] T. H. P.

Oxidation of Hydrogen by Potassium Permanganate. E. WILKE and H. KUHN (*Z. physikal. Chem.*, 1924, **113**, 313—325).—Measurements of the amount of hydrogen oxidised when the gas is bubbled through a solution of potassium permanganate show that the reaction is not so simple as was assumed by Just and Kauko (A., 1911, ii, 494). The anomalies are probably due to the separation of manganese dioxide. The velocity of oxidation is decreased by the addition of acid and alkalis or by the action of *X*-rays. M. B. D.

Electromagnetic Nature of Colloidal, Enzyme, and Catalytic Action and its Significance. N. E. DITMAN (*Science*, 1924, **60**, 183—184).—If hydrogen peroxide solution and colloidal platinum suspension, in separate vessels, are connected by a platinum or other metallic wire, a well-marked evolution of gas occurs from the hydrogen peroxide. If the primary circuit of an induction coil forms part of the conductor, and one pole of the secondary circuit is connected with another quantity of hydrogen peroxide, evolution of oxygen occurs much more rapidly than from samples connected with the primary coil or directly with the colloidal suspension. It would appear that an interrupted or oscillating electrical effect must pass through the metallic conductor. A similar result is obtained with various colloidal substances and with small detached pieces of platinum, copper, or iron. Potassium permanganate appears to produce a similar effect, as also does pancreatin in sodium carbonate solution. The production was observed of peptone from albumin solutions connected in the above manner with a solution of pancreatin in sodium carbonate. A. A. E.

Landolt's Reaction. IV. J. EGGERT (*Z. Elektrochem.*, 1924, **30**, 501—503; cf. A., 1921, ii, 686).—Sodium thiosulphate catalyses the second stage of Landolt's reaction, viz., $IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O$. The experiments do not decide whether the true catalyst is thiosulphate ion or sulphur in colloidal suspension. When the reagents are present in 0·001*N*-solution, thiosulphate in $N/10^9$ concentration accelerates the reaction velocity by 7%. Similar effects are observed when a crystal of sulphur is momentarily dipped into the solution, and this provides a delicate test for traces of sulphur. The inference is drawn that iodine is acted on more rapidly by sulphite ion than by thiosulphate ion. W. A. C.

Behaviour of Active Hydrogen. K. F. BONHOEFFER (*Z. physikal. Chem.*, 1924, **113**, 199—219).—Active hydrogen produced in long vacuum tubes (cf. Wood, A., 1920, ii, 569; 1921, ii, 665) is found to reduce certain metallic oxides, halides, and sulphides. Sulphur, arsenic, and phosphorus are converted into their corresponding hydrides, and oleic acid is hydrogenated. Molecular hydrogen is formed under the catalytic influence of thin layers of metals or metallic oxides. The amount thus formed was determined by smearing the bulb of a thermometer with the metal or its oxide and noting the rise in temperature. The catalytic activity of a metal depends on its previous treatment and corresponds with its hydrogen overvoltage value, metals with high overvoltage being poor catalysts. The results are best explained on the assumption that active hydrogen is monatomic hydrogen. M. B. D.

Active Hydrogen. K. F. BONHOEFFER (*Z. physikal. Chem.*, 1924, **113**, 492; cf. preceding abstract).—Errata. G. M. B.

Activation of Oxygen in the Slow Oxidation of Sodium Sulphite. W. P. JORISSEN and C. VAN DEN POL (*Rec. trav. chim.*, 1924, **43**, 582—585).—A study of the simultaneous oxidation of sodium sulphite and sodium antimonite, when mixed in aqueous solution in the presence of sodium hydrogen carbonate (Jorissen, *Z. physikal. Chem.*, 1897, **22**, 34; A., 1900, ii, 720). (*a*) The mixture was titrated with iodine immediately after its preparation and then at intervals of some days until the value was constant. The difference between the initial and final titrations was double the titration corresponding with the sodium sulphite originally present. (*b*) A solution of sodium sulphite, sodium antimonite, and sodium hydrogen carbonate was allowed to oxidise at 30° in a closed vessel fitted with a manometer. At the same time, an equal quantity of sodium sulphite solution was diluted with water to the same total volume and allowed to oxidise at 30° in an identical apparatus. Although the sodium sulphite solution alone was completely oxidised after 2 days, the absorption of oxygen by the mixture continued for 6 days. At the end of that time, the fall of pressure caused by the mixture was double that caused by the sodium sulphite alone. Thus the quantity of oxygen activated by the sodium sulphite is equal to that which it absorbs itself. Potassium carbonate, potassium hydroxide, and to a small extent quinol, inhibit the activation of oxygen by sodium sulphite. W. E. E.

Autocatalysis. A. QUARTAROLI (*Gazzetta*, 1924, **54**, 713—750).—Results are given of a large number of experiments on the decomposition of hydrogen peroxide in presence of metallic oxides or hydroxides. In alkaline solution, the decomposition effected by hydroxides of the heavy metals is distinctly febrile, the velocity of the reaction sometimes increasing to one hundredfold its initial value, then remaining stationary for a time, and afterwards diminishing more or less rapidly. With certain oxides, such as mercuric oxide, the decomposition exhibits an ephemeral febrile period, owing to the formation of an active catalyst, which afterwards undergoes rapid decomposition. When cupric hydroxide is used, under certain conditions there are formed green oxides of enormous catalytic activity, which increases with dilution of the hydrogen peroxide and of the copper; thus the velocity increases continuously as the reaction proceeds and is approximately inversely proportional to the mass of the reagents. Of all the metals examined, silver, or better, its oxide catalyses the decomposition of hydrogen peroxide most actively; gold is slightly less effective.

The decomposition of hydrogen peroxide under the influence of colloidal metals is a unimolecular reaction, whilst in presence of powdered and presumably inert substances, such as amorphous carbon, the velocity diminishes continuously as the reaction proceeds. T. H. P.

Catalysis of Hydrogen Peroxide by Iron Salts. E. SPITALSKY and N. PETIN (*Z. physikal. Chem.*, 1924, **113**, 161—198).—The existence of ferrous iron in the presence of hydrogen peroxide (Manchot and Wilhelms, A., 1901, ii, 658) indicated by the formation of a blue precipitate when potassium ferricyanide is added, may be due to reduction of the ferricyanide by hydrogen peroxide. The catalysis of hydrogen peroxide on the addition of ferrous sulphate has been studied in both acid and alkaline solutions. In acid solutions, the reaction velocity is accurately reproducible. Previous results which show that the reaction velocity is directly proportional to the iron concentration and inversely proportional to the hydrogen-ion concentration are confirmed. In slightly acid and neutral solutions, the catalysis is complicated by the formation of a yellow basic precipitate which is catalytically inactive. This precipitate has an indirect retarding action for which alternative explanations are suggested. The catalytic activity of the clear solution is determined by its content of ferric and hydroxyl ions. In slightly alkaline solutions a reddish-brown precipitate is formed which at first has a strong catalytic activity, but this disappears as the precipitate ages. The clear solution is inactive. In strongly alkaline solutions, the reaction is again homogeneous until near the end, when the reddish-brown precipitate again separates. M. B. D.

Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Methane–Air Mixtures. W. P. JORISSEN and J. C. MEUWISSEN (*Rec. trav. chim.*, 1924, **43**, 591—597; cf. A., 1924, i, 253).—The observed

limits of inflammability depend on the nature of both explosion vessel and spark. The limits for pure methane–air mixtures are found to be: at 20°, 3·7 and 11·55% (by vol.) of methane; at 11·5°, 4·9 and 12·6%; in a round-bottomed flask of 1120 c.c. capacity, at 20°, 5·15 and 13·65%. For technical methane, the limits are: at 20°, 5·15 and 10·15%; at 11·5°, 4·5 and 12·6%.

At 7·9°, in the presence of 7·2% (by vol.) of pure carbon tetrachloride vapour, the limits for pure methane are 6·4 and 8·95%; at 10·1°, with 7·5% of vapour, 7·4 and 8·15%; at 11·0° with 7·8% of vapour, the limits coincide at 7·8%.

With technical methane commercial carbon tetrachloride completely inhibits explosion under the following conditions: with 9·6% of vapour at 15·0° between the limits 8·65 and 10·0%; with 9·0% of vapour at 14·0° between 8·65 and 10·2%; with 8·5—8·7% of vapour at 13·0° between 8·6 and 9·8%.

Explosion is also inhibited by 8·5 to 8·6% of pure carbon tetrachloride vapour at 13·0° between 8·0 and 9·0%. With 7·5% of pure vapour at 10·0°, the limits of inflammability coincide at 8·5%; with 7·2% of vapour at 8·0° the limits are 7·9—9·7%.

With technical methane, trichloroethylene completely inhibits explosion under the following conditions: with 3·5—3·6% of vapour at 5·0°, between 7·7 and 9·5%; with 2·7% of the vapour at 0·2°, between 8·0 and 9·6%.

Using one particular burette, the limits of inflammability of pure methane–air mixtures in the presence of 5·8% of trichloroethylene vapour are 2·6 and 9·8%.

In the case of pure methane–air mixtures trichloroethylene depresses the lower limit of inflammability very considerably. This anomaly is thought to be due to the presence in the trichloroethylene of some lower-boiling inflammable constituent. W. E. E.

Electrolytic Separation of Base Radioactive Elements. F. Tödt (*Z. physikal. Chem.*, 1924, **113**, 329—335).—Systematic study of the separation of radium and its isotopes (thorium-*X* and actinium-*X*), thorium and its isotope, and actinium or mesothorium-II (cf. A., 1912, ii, 10; 1913, ii, 821; 1914, ii, 607; 1915, ii, 126). Thorium-*X* is separated from calcium by depositing it electrolytically on a silver wire cathode covered with a layer of silver chromate. The chromate precipitate containing only 0·5 mg. of barium can now be redissolved in hydrochloric acid and electrolysed without difficulty. Thorium is deposited cathodically in 0·1*N*-hydrogen chloride, using a high current-density. Mesothorium-II is electrolysed in 0·1*N*-hydrogen chloride containing ferric chloride and barium chloride. The barium chloride increases the conductivity of the solution and mesothorium-II is deposited with the iron owing to the similarity of their hydroxides. M. B. D.

Anodic Oxidation of Gold. III. F. Jirsa and H. Jelinek (*Z. Elektrochem.*, 1924, **30**, 534—537; cf. A., 1924, ii, 692).—From electrolytically prepared solutions of auric nitrate, by hydrolysis, the solubility product $[Au^{\cdots}] \times [OH']^3 = 5{\cdot}5 \times 10^{-46}$ is deduced, in fair agreement with the result from auric sulphate. Hence the

solubility of auric hydroxide is $2{\cdot}4\times10^{-12}$ mol. per litre. The value of the potential Au—Au$^{\cdots}$ is found to be +1·37 volts, confirming previous results. The affinity constant of auric hydroxide, allowing for the formation of $HAu(SO_3)_2$ in sulphuric acid solutions, is calculated to be $1{\cdot}1\times10^{-6}$, so that the basicity of the former is similar to that of hydrazine. W. A. C.

Rectifying Action of Contact Detectors. I. Stranski (*Z. physikal. Chem.*, 1924, **113**, 131—144).—The possible mechanism of the process required by the electron theory (cf. Schottky, *Z. Physik*, 1923, **14**, 99) of the rectifying action of a contact detector, consisting of a conductor in the form of a point and a crystal of a metallic compound, is discussed. Every atom is subjected to stresses, due to the electric fields produced by neighbouring atoms, and these tend to bring about deformation. The extent of deformation increases with atomic volume, and is therefore much greater in the anion than in the cation. The deforming action of the cation on the anion increases with the charge on the former, and should be greatest in the heavy metals, especially as, in compounds containing heavy metals, the ions are nearer together than in compounds containing cations which have the atomic structure of the rare gases (Fajans and Herzfeld, A., 1921, ii, 174). The deformation taking place may result in a tendency for the anion to lose an electron, either by electron emission from the molecule, or by transference to the cation whereby the molecule changes from a heteropolar to a homopolar condition. Either process would tend to a rectifying action on the passage of an alternating current. At high temperatures, alkalis and alkaline-earth oxides show high electron emission, and at the same time they may exert a rectifying action. The heavy metal cations have not the large repulsive power due to the inert gas structure, and, instead of electron emission, there is probably a tendency to the production of a homopolar state. Any heteropolar compound should be capable of becoming a detector, but those must be the most sensitive in which the anion is already so much deformed that only a very small increase of energy is necessary to cause the transference or emission of an electron. Oxides, sulphides, selenides, and tellurides are chiefly employed as detectors. The halides do not give such deformable anions and the nitrides are already more or less homopolar compounds. If the point rests on more cations than anions on the crystal lattice, the current will flow from the point to the crystal and *vice versa*, poor response being obtained if the numbers of the two types of ion are nearly equal. The direction will probably depend also on the amount of pressure brought to bear by the point on the crystal surface. With too large a current strength there may be transference or emission of the whole anion and a regrouping of the atoms, accompanied by an inversion of the current. By continued action the crystal may be ruined. M. S. B.

Fluorescence and the General Laws of Reaction Velocity. J. Perrin and (Mlle.) Choucroun (*Compt. rend.*, 1924, **178**, 1401—1406).—An application of Arrhenius' conception of acti-

vated molecules and the quantum theory to certain photochemical reactions. The actinic destruction of methylene-blue and of eosin in glycerol has been studied. In this solvent, the concentration of molecules in the critical state is fixed by the temperature and is proportional to $e^{(-H\nu_2/RT)}$, where ν_2 is the frequency of the radiation effecting the conversion of the glycerol molecules into the critical state. This frequency corresponds with an infra-red absorption of $3{\cdot}3\mu$. The fluorescence of these substances decreases with concentration. It follows from the theory developed that if the concentration of the critical molecules is decreased, the destruction in glycerol is diminished. For the same light intensity, the destruction of methylene-blue (1 in 5000) in glycerol was one-tenth as great as at a concentration of 1 in 50,000. Similar results were obtained with eosin. Methylene-blue was studied in varying concentrations of glycerol and it was found that the "pseudo" velocity constant decreases as the glycerol concentration increases. In the case of eosin, which has previously been shown to react directly with ordinary (not critical) molecules of glycerol, the velocity constant was found to be directly proportional to the concentration of the latter. A hypothesis is advanced to explain these results.

L. L. B.

Oxidation of Hydrogen Iodide. II. C. WINTHER (*Z. physikal. Chem.*, 1924, **113**, 275—278).—Polemical, in reply to Plotnikov (A., 1924, ii, 668). M. B. D.

Photochemical Decomposition of Gaseous Sulphur Dioxide. R. A. HILL (*Trans. Faraday Soc.*, 1924, **20**, 107—112).—The decomposition of sulphur dioxide by light of a small range of frequencies has been studied using the radiation from a mercury lamp passed through suitable filters. The line $313\mu\mu$ was found to be responsible for 94% of the decomposition under the conditions of the experiment; it is concluded, however, that any wave-length within the absorption band is capable of bringing about decomposition if it is of sufficient intensity. The thermal decomposition of sulphur dioxide is discussed in terms of the radiation quantum hypothesis.

S. S.

Photo-electric Properties of Silver Halides and the Mechanism of the Formation of the Photographic Latent Image. R. AUDUBERT (*Compt. rend.*, 1924, **179**, 1046—1049).—An explanation is given of the formation of the photographic latent image in terms of the photo-electric properties of the silver halides (Audubert, *ibid.*, 1924, **179**, 682). The silver halide micellæ are surrounded by a gel in the water of which the silver halide molecules can dissolve and ionise; a potential difference probably exists between the grain and the electrolyte. Under the influence of light, an electron leaves the halide grain, enters the electrolyte, and attaches itself to a silver ion, which thereby becomes a free atom. At the same time, a chlorine ion leaves the electrolyte and discharges on the surface of the granule. These two ions are then immediately replaced by the dissolution of a further molecule of

the halide. In this way, exposure to light produces a number of free metallic atoms which act as nuclei for further reduction under the influence of the developer. The number of nuclei formed will depend on the length of the exposure, and will be greater with rays of short wave-lengths, since these are specially active in producing photo-electric effects. Calculation shows that the expulsion of an electron is favoured by increase in size of the particles.
W. H.-R.

Photochemical Decomposition of Silver Bromide. E. J. HARTUNG (*J. Chem. Soc.*, 1924, **125**, 2198—2207).—The decomposition of silver bromide was investigated by means of a Steele-Grant microbalance sensitive to 2×10^{-5} mg. A silver film was deposited on a flat silica support and freed from occluded matter by ignition at 400° in a silica flask. It was then brominated. The relative weights of silver and bromine were in all cases within 0·1% of the theoretical. A glass exposing vessel is described into which the film could be sealed. In a side tube through which the vessel was exhausted was placed a roll of copper gauze as bromine absorbent. After exposure, the film was weighed, exposed to bromine vapour, and weighed again. With the use of copper 95% of the bromine content of the film was removed by insolation; with less efficient absorbents, somewhat less. It is suggested that the 5% not removed is due to contamination of the reduced silver film by gases from the glass walls of the vessel or from the atmosphere. The rate of bromination of silver films was studied by exposing films for varying times to a definite concentration of bromine vapour in a large flask. No discontinuity which might indicate the formation of a sub-bromide could be detected. Insolated silver bromide films absorb bromine much more rapidly than freshly-prepared silver films, presumably on account of different surface conditions.
C. I.

Mercury and Helium. J. J. MANLEY (*Nature*, 1924, **114**, 861).—Under certain conditions, and in the presence of an electric glow discharge, mercury and helium combine to form mercury helide. This is a stable substance, decomposed at a bright red heat, and is but slightly absorbed by charcoal cooled in liquid air; it has not yet, however, been analysed quantitatively.
A. A. E.

Active Hydrogen. F. PANETH (*Z. Elektrochem.*, 1924, **30**, 504—507).—Active hydrogen, supposed to have the composition H_3, has been obtained by two methods. Hydrogen may be passed over an incandescent Nernst filament, but within a short time the filament is partly reduced and becomes useless. Alternatively, hydrogen is passed under reduced pressure through a palladium capillary heated to redness. All the active hydrogen formed was retained by a U-tube dipping in liquid air, and was given off again when the refrigerant was removed. The active hydrogen, which at best was formed in traces only, was detected by its reactions with sulphur and with tungstic acid.
W. A. C.

Polysulphides of the Alkali Metals. V. Lithium Monosulphide and Disulphide. J. S. THOMAS and J. H. JONES (*J. Chem. Soc.*, 1924, **125**, 2207—2214).—Lithium hydrosulphide alcoholate was heated very rapidly in a vacuum at 300°, yielding a faintly yellowish-brown mixture of lithium monosulphide and lithium ethoxide. This was treated with a current of hydrogen, containing 10% of hydrogen sulphide, at 120°, the ethoxide being reconverted into hydrosulphide. It was then heated to 300° in presence of phosphoric oxide and solid potassium hydroxide, when nearly pure lithium monosulphide was obtained. Lithium disulphide was prepared by boiling alcoholic lithium hydrosulphide with sulphur and concentrating the solution obtained, both operations being performed in a current of dry hydrogen. No higher polysulphide was produced. The solubility of sulphur in 0·5*N*-alcoholic lithium hydrosulphide was found to be, at 80°, 7·99 parts of sulphur to 2 parts of metal; at 25°, 6·94 parts of sulphur, and at 15°, 6·52 parts of sulphur. The excess of sulphur in these solutions over that present in the disulphide is to be accounted for by residual valency. The constitution of the disulphide was demonstrated by treatment with allyl iodide, diallyl disulphide being formed.

C. I.

Normal and Basic Copper Sulphate. A. KRUGER (*J. pr. Chem.*, 1924, [ii], **108**, 278—296; cf. Casselmann, *Z. anal. Chem.*, 1865, **4**, 24).—By warming a dilute solution of copper sulphate (5 g. per litre) in presence of sodium acetate, a green precipitate, approx. $8CuO,2SO_3,7H_2O$, was produced. By the slow hydrolysis of copper sulphate in dilute solution, a small quantity of precipitate of variable composition is produced; solutions containing 10—40 g. of copper sulphate per litre give a precipitate having the formula $6CuO,2SO_3,5H_2O$ (cf. Pickering, A., 1883, 853). The first compound is also produced by hydrolysis in the slightly alkaline solution obtained by the addition of potassium hydrogen carbonate. It corresponds very closely with the mineral langite, $4CuO,SO_3,4H_2O$, which may be produced by the hydrolysis of copper sulphate in dilute solution in presence of sodium acetate, potassium hydrogen carbonate, or magnesium oxide under very definite conditions of temperature and concentration, as a pale blue, crystalline precipitate, insoluble in water. On addition of a little copper sulphate or acetic acid to the aqueous suspension, the green salt, $8CuO,2SO_3,7H_2O$, is produced. With alkalis or alkali carbonates, a dark brown, amorphous hydroxide is produced. By hydrolysis of a very dilute solution of copper sulphate with potassium hydroxide, an amorphous precipitate, $4CuO,SO_3,5H_2O$, is produced. The following formulæ are proposed for the basic copper sulphates described:

$$[Cu(OH)_2]_3,CuSO_4,2H_2O;\quad [Cu(OH)_2]_3,CuSO_4,H_2O;$$
$$2\frac{1}{2}[Cu(OH)_2]_3,CuSO_4,H_2O.$$

Langite appears to be formed by digestion of the brown copper hydroxide in excess copper sulphate solution at 30—40°, the precipitate becoming green, and being, apparently, an adsorption compound. Details are given for the preparation of the dark amor-

phous copper hydroxide, $8CuO,H_2O$, and for the preparation of normal copper sulphate. A. E. C.

Action of Chlorine on Mercury. A. F. O. Getman (*J. Physical Chem.*, 1924, **28**, 1218—1220).—Polemical against Venkataramaiah (A., 1923, ii, 149). M. B. D.

Thallous Thallic Halides. A. J. Berry (*Proc. Camb. Phil. Soc.*, 1924, **22**, 363—368).—Solutions of thallous and thallic chlorides containing the two halides in varying proportions were prepared, and the composition of the crystals deposited from such solutions determined. Whilst the composition of the liquid phase could be varied over a wide range, the composition of the solid phase deposited was practically constant and corresponded with the formula $TlCl_3,3TlCl$. That this substance is therefore a definite compound and not the end member of a series of mixed crystals as is considered by Meyer (A., 1900, ii, 655) was confirmed by the fact that it recrystallised unaltered from 0·01*N*-hydrochloric acid. The compound, $TlBr_3,3TlCl$, orange-red crystals, can be prepared by the action of thallous chloride on solutions of thallic bromide (cf. Thomas, A., 1907, ii, 547; Cushman, A., 1900, ii, 725; Meyer, *loc. cit.*). The analysis of these bromide–chloride mixtures was facilitated by the fact that the thallic constituents are soluble in methyl alcohol, whereas the thallous constituents are insoluble or only slightly soluble in this substance. A method of readily preparing the compound $TlBr_3,TlBr$ is described; $TlBr_3,3TlBr$ is difficult to prepare in the pure state. The observations of previous investigators that these compounds are decomposed by water are confirmed. Thallous thallic halides in aqueous solution exhibit no evidence of the formation of any stable complex ions. In this connexion, the observations of Cushman (A., 1902, ii, 322) on the interaction of silver nitrate and thallium chloride in the presence of nitric acid are confirmed. In all cases, exposure to low temperatures causes a very marked temporary diminution in the intensity of the colour of thallous thallic halides. L. F. G.

Preparation of Tin Hydride by Cathodic Reduction. F. Paneth and E. Rabinovitsch (*Ber.*, 1924, **57**, [*B*], 1877—1890; cf. A., 1920, ii, 41; 1922, ii, 383).—Tin hydride is formed by the electrolysis of a solution of tin sulphate between tin or lead electrodes, but the yield is very small and subject to great fluctuation. The addition of a small proportion of colloids (dextrin, gelatin, gum arabic, or agar-agar) or of larger amounts of certain crystalloids (sugar) to the electrolyte, not only increases the yield very greatly, but also stabilises it. In general, dextrin to the amount of 0·5% is found to be suitable. The lead electrodes then require an induction period of about 15—30 minutes, after which the cathodes gradually become coated with a loose, black deposit of spongy lead. Uniformly high yields of tin hydride may be obtained from such cathodes for an indefinite period if the electrolyte is renewed every 6—8 hours. The yield appears to increase somewhat with increasing strength of current, but to be independent of current density

between the limits 0·5—7·5 amps./sq. cm. Under all conditions with respect to the material of the cathode and the nature of the organic addenda, it increases initially with increasing concentration of tin in the electrolyte, attains a maximum (below 0·02% Sn), and then decreases rapidly to zero. Temperature appears to have little influence on the yield. Lead, as cathode, may be replaced by tin, cadmium, or platinum, but not by zinc or mercury or by amalgamated zinc or lead. The theory of the reaction is discussed in detail, and the authors are led to the conclusion that the optimum conditions for the production of tin hydride are the greatest possible concentrations of "overvoltage hydrogen" and "overvoltage metal." The concentration of the hydride in the electrolytic hydrogen is 1 : 10,000 in the most favourable case; this ratio is approximately that of the tin and hydrogen ions in the solution.

Electrolysis is effected conveniently in a crystallising dish or beaker, in which the anode, made of lead rod, is placed in a small, porous cell. The cathode is formed by melting lead in a curved glass tube, through one end of which a copper wire is inserted into the metal while hot; the metal at the other end of the tube is affixed to a lead disc. The junction between metal and glass is rendered liquid-tight by gypsum or paraffin. The cathode is placed under a small bell, which is readily made from a Gooch adapter. This form of cathode has the advantage that it may be removed without disturbing the remainder of the apparatus. H. W.

Preparation and Properties of Pure Tin Hydride. F. PANETH, W. HAKEN, and E. RABINOVITSCH (*Ber.*, 1924, **57**, [*B*], 1891—1903).—Tin hydride, prepared by the electrolysis of tin sulphate between lead electrodes in a series of the cells described in the preceding abstract, is washed by water and alkaline lead acetate solution, dried by passage through tubes at −80° or −100°, and condensed by means of liquid air. It is purified by Stock's method of fractional distillation and fractional condensation, whereby considerable difficulties are found in the removal of propane, arsine, hydrogen sulphide, carbon dioxide, and ethane and other volatile hydrocarbons. A final, very slow fractional distillation yields tin hydride containing not more than 0·3% of impurities. The formula, SnH_4, is derived by the quantitative thermal decomposition of the gas into its elements. Indications of the formation of higher hydrides were not obtained, but their existence is not impossible. Tin hydride has m. p. −150°(±2°); the variation of vapour pressure with temperature is expressed by the formula $\log p = -1000/T + 7{\cdot}4$; the latent heat of evaporation is 4·55 Cal. The colour imparted by tin hydride (mixed with hydrogen) to the flame depends greatly on its concentration. Tin mirrors, obtained by thermal decomposition of the hydride, are generally pale grey, occasionally silvery. In Marsh's tube, the deposit is formed in front of or in the heated part; the brown mirrors obtained previously behind the heated part (A., 1922, ii, 383) are due to tin sulphide. Tin hydride is relatively stable; in glass vessels, it decomposes spontaneously after several days, but the change is not

accelerated by light. It decomposes immediately at 145—150°. It is very sensitive to the nature of the surface with which it is in contact, being decomposed at ground glass joints and, particularly, at tin mirrors, even when the latter are invisible to the unassisted eye. The instability of the gas in contact with solid desiccating agents (calcium chloride, phosphoric oxide) is probably a manifestation of this phenomenon. It is unaffected by dilute alkali hydroxide solutions (up to 15%), dilute sulphuric acid, dilute and concentrated nitric acid, and most metallic salts (sodium carbonate, copper sulphate, lead acetate, ferric chloride); it is absorbed to some extent by concentrated alkali hydroxide solutions or by concentrated sulphuric acid, completely by solid alkali hydroxides and soda-lime. It is quantitatively absorbed by silver nitrate (or sulphate) solution, giving a black precipitate which contains silver and tin in varying proportions, whilst tin is also present in the solution. It appears to reduce mercuric chloride to mercurous chloride. H. W.

Action of Normal Sodium Arsenite on Azido Compounds. A. GUTMANN.—(See i, 84.)

Bismuth. II. Tendency of Bismuth to Form Complex Salts. H. MÜLLER and L. KÜRTHY (*Biochem. Z.*, 1924, **147**, 385—389).—The relative amount of bismuth recoverable by precipitation with hydrogen sulphide, after the metal has been added in the form of the nitrate to normal urine, gradually diminishes with lapse of time. This is ascribed to the formation of complex salts—more especially in the presence of chlorides—in which the bismuth is present in a non-ionisable form. Such complexes are not formed in the presence of nitric acid, whilst in certain concentrations of glycine bismuth nitrate undergoes considerable hydrolysis, which is ascribed to the interaction of the amphoteric acid with both positively (simple) and negatively (complex) charged bismuth ions. J. P.

Compounds of Tervalent Molybdenum. II. Molybdenyl Monochloride. W. WARDLAW and R. L. WORMELL (*J. Chem. Soc.*, 1924, **125**, 2370—2372.—A solution of molybdenum trioxide in hydrochloric acid was electrolytically reduced in a diaphragm cell, concentrated with exclusion of air, and again electrolysed until a sample of the cathode liquid gave a buff-coloured precipitate when poured into acetone. This precipitate, which contains only tervalent molybdenum and has the composition $MoOCl,4H_2O$ was washed with acetone, alcohol, and ether, with exclusion of air, and stored in a desiccator under carbon dioxide, which was then evacuated. This compound oxidises gradually in air, but does not deliquesce. It is soluble in water or hydrochloric acid and is a strong reducing agent. Addition of lead acetate and acetic acid to its solution does not cause precipitation of lead chloride. C. I.

Cobaltammines of the Nitrogen Sulphonic Acids and Sulphato Cobaltammines. F. EPHRAIM and W. FLÜGEL (*Helv. Chim. Acta*, 1924, **7**, 724—740).—The solubilities of a number of

cobaltammines of the nitrogen sulphonic acids were determined in order to test Ephraim's theory (A., 1923, ii, 644). In the majority of cases, compact molecules, *i.e.*, those with equi-valent cation and anion, were less soluble than those in which the anion and cation possessed different values. The luteo salts of imidodisulphonic acids are exceptions, in that they are less soluble than the bivalent xantho salts. The preparation of the following new *cobalt* compounds is described: nitrilosulphonic acid, *hexammine* and *aquopentammine*; imidosulphonic acid, *hexammine, aquopentammine,* and *nitritopentammine*; amidosulphonic acid, *hexammine, aquopentammine,* diaquotetrammine, *nitritopentammine,* cis- and trans-*dinitritotetrammine* and *carbonato-tetrammine*; hydroxylaminetrisulphonic acid, *hexammine, aquopentammine,* cis- and trans-*dinitritotetrammine*; hydroxylaminedisulphonic acid, *nitritopentammine*; hydroxylamine*iso*disulphonic acid, *hexammine, nitritopentammine, chloropentammine,* cis- and trans-*dinitritotetrammine*; hydroxylaminemonosulphonic acid, *hexammine*; sulphatoaquotetramminecobalt *chloride, bromide, iodide, nitrate, perchlorate, picrate,* and *sulphate*; sulphatopentamminecobalt *chloride, iodide, picrate, chromate, dichromate, chlorate, perchlorate,* and *fluosilicate*; *hexamminecobalt iodide sulphate*; *aquopentamminecobalt nitrate sulphate, nitrate iodide,* and *iodide sulphate.* H. T.

Electrolytic Preparation of Ozone with an Alternating Superposed on a Continuous Current. G. Malquori (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 102—106).—Good yields of ozone are obtainable by the electrolysis of aqueous sulphuric acid of density 1·1—1·4 by means of superposed continuous and alternating currents, an internally cooled anode of either lead coated with lead peroxide or platinum being used. [Cf. *B.*, 1924, 942.] T. H. P.

Preparation of Very Pure Barium and Strontium. P. S. Danner (*J. Amer. Chem. Soc.*, 1924, **46**, 2382—2385).—Very pure metallic strontium or barium (99·9%) was prepared as follows. The pure oxide of the metal was partly (10%) converted into the peroxide and reduced by mixing with coarse aluminium metal (free from volatile impurities) and striking an arc in the mass. The cold fused mass was then ground, the fine particles sifted off, and the remainder sealed up in a distillation apparatus of special design, which was evacuated as rapidly as possible. When the absorbed gases had been removed and the pressure had reached 10^{-4} mm., the temperature was raised to 950°, and the alkaline-earth metal distilled off in the form of soft, silver-white, crystalline pellets. The barium was spontaneously inflammable in moist air and hydrogen and tarnished rapidly in pure, dry carbon dioxide. Strontium was slightly less reactive. S. K. T.

Separation of Zirconium and Hafnium. Naamlooze Vennootschap Philips' Gloeilampenfabriken (Fr. Pat. 568978; from *Chem. Zentr.*, 1924, ii, 541).—Solutions of the salts, *e.g.*, those obtained by fusing the raw materials with potassium hydrogen

fluoride or potassium hydrogen sulphate, after removal of other metals by known methods, are either treated with a base or a basic substance (such as ammonia, sodium acetate, or sodium thiosulphate) in quantity insufficient to precipitate both the metals, the resultant precipitate being richer in zirconium and poorer in hafnium than the original material, or both elements are precipitated as hydroxides by excess of base and the washed precipitate is then treated with a quantity of acid insufficient for complete dissolution, the residual precipitate being poorer in hafnium and the solution richer. By frequent repetition of the process and, if necessary, purification of the fractions, a hafnium-free precipitate of zirconium hydroxide is obtained, and a zirconium-free solution of a hafnium salt from which the metals may be obtained in the usual manner. F. A. M.

Separation of Zirconium and Hafnium. NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN (Fr. Pat. 569016; from *Chem. Zentr.*, 1924, ii, 541).—Ores containing zirconium and hafnium are fused with potassium hydrogen fluoride, then dissolved in water or hydrofluoric acid, and the solution mixed with potassium hydrogen fluoride; alternatively, the ores are fused with other substances and the mass is dissolved and treated with hydrofluoric acid or potassium hydrogen fluoride etc. The resultant solution is then fractionally crystallised, the crystals being richer in zirconium and poorer in hafnium than the original substance. The mother-liquor is then evaporated, again allowed to crystallise until the solution is practically free from zirconium, and is then worked up in the usual way for hafnium. Alternatively, the solution of the double fluoride is treated with a quantity of disodium hydrogen phosphate insufficient for complete precipitation, the washed precipitate is dissolved in hydrofluoric acid, and again fractionally precipitated etc., the precipitates becoming gradually richer in hafnium (cf. preceding abstract). F. A. M.

Mineralogical Chemistry.

Composition of the Earth's Crust. F. W. CLARKE and H. S. WASHINGTON (*U.S. Geol. Survey Prof. Paper*, 1924, **127**, 1—117).—The following new average composition for igneous rocks of the earth's crust is deduced from 5159 of the more trustworthy published analyses: SiO_2, 59·12; Al_2O_3, 15·34; Fe_2O_3, 3·08; FeO, 3·80; MgO, 3·49; CaO, 5·08; Na_2O, 3·84; K_2O, 3·13; H_2O (over 110°), 1·15; CO_2, 0·102; TiO_2, 1·050; ZrO_2, 0·039; P_2O_5, 0·299; Cl, 0·048; F, 0·030; S, 0·052; $(Ce,Y)_2O_3$, 0·020; Cr_2O_3, 0·055; V_2O_3, 0·026; MnO, 0·124; NiO, 0·025; BaO, 0·055; SrO, 0·022; Li_2O, 0·007; Cu, 0·010; Zn, 0·004; Pb, 0·002%, and other elements in still smaller amounts. Averages for different regions and continents are also deduced. Ninety-nine % is accounted for by ten

oxides, and by but few common minerals. Possible analytical errors are considered in detail for each element. Igneous rocks (including metamorphic rocks) form 95% of the solid crust (lithosphere), the remainder being the sedimentary rocks, shale (4%), sandstone (0·75%), and limestone (0·25%). An average composition is deduced for each of these rocks; and taking into account also the oceans and the atmosphere, an average composition is deduced for the whole of the earth's exterior (to a depth of 10 or 20 miles in the solid crust). For a 10-mile crust, hydrosphere, and atmosphere the average is: O, 49·52; Si, 25·75; Al, 7·51; Fe, 4·70; Ca, 3·39; Na, 2·64; K, 2·40; Mg, 1·94; H, 0·88; Ti, 0·58; Cl, 0·188; P, 0·12; C, 0·087; Mn, 0·08; S, 0·048; Ba, 0·047; Cr, 0·033; N, 0·030; F, 0·027; Zr, 0·023; Ni, 0·018; Sr, 0·017; V, 0·016; Ce, Y, 0·014; sum of remainder 0·042%. These elements are in vast preponderance and, with some others, are classed as "petrogenic" elements. "Metallogenic" elements are those falling below Cu, Zn, Ga, Ge, As, Se, Br in the periodic table. The compounds of these two "natural" groups of elements as represented in nature by minerals are compared in detail. Petrogenic elements form mostly oxides and oxygen salts, whilst metallogenic elements form mostly sulphides, arsenides, and sulpho-salts. General remarks are added on the evolution of the elements.

L. J. S.

Dumontite, a new Radioactive Mineral. A. SCHOEP (*Compt. rend.*, 1924, **179**, 693—695).—This mineral, which occurs in pockets of the compact torbernite of Chinkolobwe, in the Belgian Congo, forms translucent, ochre-yellow, biaxial, elongated prisms, $n>1·78$. The chemical reactions of the mineral are the same as those of dewindtite (A., 1922, ii, 305) and parsonsite. The composition is:

H_2O.	P_2O_5.	UO_3.	PbO.	TeO_3.	Total.
5·78	8·65	56·49	27·19	1·01	99·12

which, neglecting the tellurium, corresponds with the formula, $2PbO,3UO_3,P_2O_5,5H_2O$. The whole of the water is expelled at about 300°, and oxygen is lost at above 500°. T. H. P.

Alkali Granite and Nepheline Syenites, Canadite, and Foyaite, in the Vredefort Mountainland, South Africa. G. A. MOLENGRAAFF and A. L. HALL (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 465—486).—Descriptive. L. J. H.

Specific Gravities of Minerals and Crystallised Chemical Compounds. U. PANICHI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 182—188).—Theoretical considerations. T. H. P.

Analytical Chemistry.

Apparatus for the Determination of p_H. M. TRÉNEL (*Z. Elektrochem.*, 1924, **30**, 544—548).—A platinum electrode is fixed in a porous cell which is impregnated with a saturated solution of

potassium chloride and filled with the standard solution. Surrounding this diaphragm is a glass tube carrying the annular second electrode, also of platinum. The whole is immersed in the solution to be tested, and the potential difference is measured by potentiometer. Arrangements for temperature-compensation and for direct reading of p_H are described. W. A. C.

Determination of Carbon, Hydrogen, and Nitrogen in Organic Compounds. J. HESLINGA (*Rec. trav. chim.*, 1924, **43**, 551—560).—The method depends on the quantitative conversion of carbon and hydrogen in organic compounds into carbon dioxide and water, respectively, by passing the vapour over manganese dioxide at 400° or above. When halogens are present, lead dioxide is added to the manganese dioxide, whilst temperature modifications are made for substances containing sulphur or nitrogen. Similarly, manganese dioxide may be used in a Dumas nitrogen determination. In the combustion of benzil, it is shown that two-thirds of the oxygen comes from the manganese dioxide and one-third from the air. It is said that, with halogen compounds, the halogen is the true catalyst. [Cf. *B.*, 1924, 970.] F. M. H.

Critical Studies on Methods of Analysis. XIV. Chlorine. L. A. CONGDON, W. B. CRABTREE, H. W. COLES, L. L. SMITH, and M. L. VEHALGO (*Chem. News*, 1924, **129**, 302—304, 317—320, 334—336).—A record of comparative results obtained in the determination of chlorine by several different methods. The indirect method of adding an excess of silver nitrate and determining the excess by titration with thiosulphate gave more accurate results when the silver chloride was first removed by filtration, but direct titration with silver nitrate, using chromate as indicator, gave better results than either indirect method except in the presence of ammonium salts, when high results were obtained. A. R. P.

Potentiometric Determinations with Mercurous Salts. C. MÜLLER and H. AARFLOT (*Rec. trav. chim.*, 1924, **43**, 874—878).—A solution of mercurous perchlorate, prepared by boiling mercuric oxide (1 mol.) with concentrated perchloric acid (2 mols.) and excess of mercury, gives better results than mercurous nitrate solution (Behrend, A., 1893, i, 387) in the potentiometric titration of chlorides or bromides with a mercury electrode. The decomposition potentials for chlorides (+0·32 ε) and bromides (+0·29 ε) are too close together to allow of determinations of two halogens in the presence of each other. Iodide, cyanide, and thiocyanate can be determined when solutions containing these are run into the mercurous perchlorate solution. If the procedure is reversed, results are obtained for the iodide and thiocyanate which are 0·5—0·8% too low, and in the case of the thiocyanate the differences are even greater. This is attributed to the greater tendency of mercuric as compared with mercurous ions to form complex ions, such as HgI_4''. In the case of the iodide, this is shown by the initial production of a dark coloured solution containing free mercury according to the reaction $Hg_2'' \rightarrow Hg + Hg''$. Cyanides, thiocyanates,

and iodides can be determined more exactly by Kolthoff's method (A., 1923, ii, 873). Chlorides can also be determined by potentiometric titration with mercuric perchlorate solution, the decomposition potential being +0·41 ε, but the method cannot be used for the determination of mercurous and mercuric mercury in a mixture. R. B.

"Chloramine" as a Substitute for Iodine in Chemical Analysis. A. NOLL (*Chem.-Ztg.*, 1924, **48**, 845—846).—"Chloramine T" (the sodium salt of *p*-toluenesulphochloroamide), behaves like an inorganic hypochlorite except that it is much more stable and can be purified by recrystallisation from water. A 0·1*N*-solution is suitable for most analytical processes in which the much more expensive iodine solution is used; a small amount of potassium iodide and starch solution is used as indicator and the solution is preferably standardised against arsenic trioxide. A. R. P.

Determination of Nitrogen in Organic Compounds by Catalytic Hydrogenation. H. TER MEULEN (*Rec. trav. chim.*, 1924, **43**, 643—644).—The organic nitrogen compound is heated in a current of hydrogen and the mixture of gases passed over nickelised asbestos prepared by low-temperature reduction; all the nitrogen is reduced to ammonia, which is collected in acid and determined volumetrically.

If the substance contains sulphur or halogens, the hydrogen sulphide or halide formed is absorbed in soda-lime. W. E. E.

Determination of Nitrogen by Kjeldahl's Method and its Modifications. II. P. FLEURY and H. LEVALTIER (*J. Pharm. Chim.*, 1924, [vii], **30**, 265—272).—The authors' method (cf. A., 1924, ii, 273) gives good results in most cases, including pyridine derivatives, if the mixture is heated for 1½ hours. Nitrates, nitriles, oximes, and azo compounds, however, require the addition of benzoic acid, and aromatic nitro derivatives and hydrazines and their derivatives require the addition of zinc. The benzoic acid method gave the best results (96% of the theoretical) for antipyrine and pyramidone. Semicarbazide and its derivatives require for their reduction the addition of both zinc and benzoic acid to the standard mixture of sulphuric acid, phosphoric acid, and potassium sulphate. J. K.

Application of the "Formol Titration" to the Kjeldahl Method of Nitrogen Determination. W. S. SHAW (*Analyst*, 1924, **49**, 558—565).—The distillation of the colourless solution obtained after digestion with acid in the Kjeldahl method may be eliminated by titrating an aliquot portion of the neutralised, reacidified, boiled, and reneutralised solution to which a definite quantity of formaldehyde of known acidity has been added, with standard sodium hydroxide solution. [Cf. *B.*, 1925, 30.] D. G. H.

Pemberton-Neumann Method for the Determination of Phosphorus. M. B. RICHARDS and W. GODDEN (*Analyst*, 1924, **49**, 565—572).—The main sources of error were found to be

(1) variation in the volume of standard alkali used to dissolve the precipitate (1—2 c.c. excess gave the best results); (2) carbon dioxide absorbed by the alkali used to dissolve the ammonium phosphomolybdate precipitate may not all be expelled, and to effect this it is necessary to boil with excess of acid before the final titration; (3) the factor used. Assuming the formula of the precipitate to be $(NH_4)_3PO_4,2MoO_3$ the factor is 0·001365. [Cf. *B.*, 1925, 30.] D. G. H.

Detection of Ortho-, Pyro-, and Meta-phosphate Occurring Together, and in Presence of Sodium Fluoride. J. H. DE BOER (*Chem. Weekblad*, 1924, **21**, 561—566).—A 1% solution of luteocobalt chloride gives a distinct cloudiness with a 0·01% metaphosphate solution; with stronger solutions, an amorphous precipitate, which does not settle, and is not arrested by filter-paper, is obtained. Pyrophosphate gives no precipitate in dilute solutions, but a characteristic crystalline precipitate is obtained, after seeding, with a 0·05% solution; this, unlike the metaphosphate precipitate, dissolves in dilute acetic acid. Orthophosphate gives no precipitate, even in 5% solution. Small quantities of pyrophosphate may be detected by means of zinc or copper sulphate in presence of acetic acid; ortho- and meta-phosphates under these conditions give precipitates only when present in large quantities. Orthophosphate is detected by means of silver nitrate or ammonium molybdate; the latter test is extremely sensitive and specific.

In presence of fluorides, metaphosphate may be detected as before; the phosphates are then separated by means of silver nitrate, and zinc or copper sulphate is employed to test for pyrophosphate. Orthophosphate is detected as above, thorium nitrate being also added. S. I. L.

Physico-chemical Analysis, by Conductivity, of Vegetable Ash. I. Determination of Phosphoric Acid. L. DESHUSSES and J. DESHUSSES (*Helv. Chim. Acta*, 1924, **7**, 681—688).—Phosphoric acid in vegetable ash can be quickly determined with an accuracy of 1—2% by titrating the acid extract of the ash with uranyl nitrate solution in the presence of ammonium acetate, the end-point being determined by a conductivity method similar to that used by Dutoit et Duboux ("L'Analyse des Vins par Volumétrie phys. chim.," 1912). The amount of ammonium acetate added is regulated by the amount of acid present. H. T.

Preparation of the Magnesium Ammonium Phosphate Precipitate for the Determination of Phosphoric Acid or of Magnesia. B. SCHMITZ (*Z. anal. Chem.*, 1924, **65**, 46—53).—As a result of investigation into the best method of producing a precipitate of magnesium ammonium phosphate free from trimagnesium phosphate and from tetrammonium magnesium diphosphate, the following procedure is recommended for the determination of phosphoric acid. The slightly acid solution is treated with magnesia mixture, ammonium acetate, and a few drops of phenol-

phthalein. After heating to incipient boiling a 2·5% solution of ammonia is allowed to drop in slowly from a burette while the liquid is stirred until it becomes turbid; stirring is continued until the precipitate becomes crystalline, ammonia is added until the solution becomes pink, and the whole is allowed to cool. Concentrated ammonia solution equal to one-fifth the volume of the liquid is added and the mixture is stirred for a few minutes and filtered on a Neubauer crucible. The precipitate is washed with 2·5% ammonia, then with alcohol, ignited at 1000° for 30 minutes, cooled, and weighed. [Cf. *B.*, FEB.] A. R. P.

Removal of Phosphates in Systematic Qualitative Analysis. L. J. CURTMAN, C. MARGULIES, and W. PLECHNER (*Chem. News*, 1924, **129**, 299—301, 315—317).—Instead of the usual procedure of precipitating the phosphoric acid as ferric phosphate, precipitation as zirconium phosphate is recommended. The solution is treated in succession with ammonium chloride, zirconium oxychloride, and ammonia until alkaline, boiled for 2 minutes, acidified with hydrochloric acid, and again boiled and filtered. If only small amounts of phosphoric acid are present a little fine asbestos added to the solution aids in filtering the zirconium phosphate. Excess of zirconium is found with the aluminium in the subsequent separation and may be removed by digestion of the mixed precipitate with sodium hydroxide. A. R. P.

Separation of Arsenic and Antimony by Distillation. F. L. HAHN and H. WOLF (*Ber.*, 1924, **57**, [*B*], 1858—1860).—Complete separation of arsenic from antimony by distillation of solutions of the chlorides can be effected if the distilling flask is placed on an asbestos board pierced with a small hole and heated with a small flame which touches only that portion of the glass which is invariably covered by liquid. The operation is tedious and requires great care. A rapid and quantitative separation is obtained, however, if the flask is provided with a fractionating inset which is figured in the original. H. W.

Invert-sugar as a Reagent for Boric Acid Determinations. G. VAN B. GILMOUR (*Analyst*, 1924, **49**, 576—577).—The reagent is prepared by inverting commercial granulated sugar with sulphuric rather than hydrochloric acid, since the small quantities of chloride present in the latter case would interfere with sodium chloride determinations which, in the case of butter and margarine, are frequently made on the same solution. [Cf. *B.*, 1925, 54.] D. G. H.

Qualitative and Quantitative Analysis of Sodium Dithionate. F. M. LITTERSCHEID and H. LÖWENHEIM (*Chem.-Ztg.*, 1924, **48**, 881—883).—The ordinary crystallised sodium dithionate contains $2H_2O$; specimens with $5H_2O$ are sometimes found and an unstable form with $6H_2O$ undergoes efflorescence to the stable form with $2H_2O$ at the ordinary temperature. Water of crystallisation is determined by drying at 60° for 1½ hours and finally at 100°

for ½ hour. The pure salt should show no reaction for sulphate, sulphite, chloride, or carbonate. In testing for iron and other metallic bases care should be taken not to boil the salt with strong acids owing to liberation of sulphur dioxide. When heated at 250° or to low redness, the whole of the sulphur dioxide is expelled, leaving a residue of sodium sulphite. This residue should be examined for purity and freedom from sulphite and carbonate. If during heating a sublimate of sulphur is formed or if the salt turns brown or black, it is impure. A method is described whereby the sulphur dioxide is expelled in a current of carbon dioxide as when conducting a combustion analysis of organic materials. The sulphur dioxide is absorbed in standard iodine solution and determined by titration of the latter. J. F. B.

Precipitation of Calcium Oxalate in the Presence of Ammonium Citrate. W. F. Jakób (*Roczniki Chemji*, 1923, **3**, 308—324).—The precipitation of calcium in the form of oxalate has been examined with special reference to the inhibiting action of citrates. It is found that the latter appreciably increase the solubility of calcium oxalate, more especially in the presence of free ammonia, this effect being attributed to the formation of complex calcio-citrate ions; the tribasic citrate ion is mainly responsible for complex formation. The complete precipitation of calcium is nevertheless possible if a sufficient excess of ammonium oxalate is used. The shape of the precipitation curve indicates that the process takes place in two phases corresponding with two hydrates of calcium oxalate; the principal constituent obtained at 40° is one containing $2{\cdot}5H_2O$, whilst the remainder is the monohydrate which is precipitated towards the end of the reaction. The former of these is coarsely granular and easily filtered and is probably well adapted to the determination of calcium, as it will not tend to form isomorphous mixtures with magnesium oxalate. G. A. R. K.

Contradictions and Errors in Analytical Chemistry. V. Precipitation of Magnesium Ammonium Phosphate from Solutions containing Aluminium. F. L. Hahn and S. Scheiderer (*Ber.*, 1924, **57**, [*B*], 1854—1858).—The simultaneous presence of tartaric acid and aluminium can not only delay, but may also actually prevent the precipitation of magnesium as magnesium ammonium phosphate. Magnesium if present in small amount (about 1%) in aluminium alloys cannot therefore be determined in this manner. Separation of magnesium from aluminium and zinc is effected by the use of an excess of alkali hydroxide; the precipitate is contaminated with zinc and aluminium, but is so far enriched in magnesium that a quantitative separation is brought about by redissolution and subsequent precipitation by ammonium sulphide. H. W.

Volumetric Determination of Zinc. E. Beyne (*Bull. Soc. chim. Belg.*, 1924, **33**, 507—516).—Various modifications of Schaffner's method of titrating zinc in ammoniacal solution with sodium

sulphide are discussed. To obtain satisfactory results, a compensatory method is necessary. The amounts of ammoniacal salts are important, as is the density of the ammonia, which should be 0·92. Various passages in Olivier's pamphlet (1921) on the Vieille Montagne method are commented on. [Cf. *B.*, 1924, 1016.]

F. M. H.

Volumetric Determination of Zinc. K. KIEPER (*Chem.-Ztg.*, 1924, **48**, 893).—An excess of standard sodium sulphide solution is added to the ammoniacal zinc solution, the mixture is heated and the precipitate filtered off. The filtrate is cooled, acidified with acetic acid, and titrated with iodine. [Cf. *B.*, 1925, 29.]

A. R. P.

Co-ordination Studies on the Analytical Behaviour of Heavy Metal Sulphides. F. FEIGL [in part with F. PAVELKA and R. SCHACHERL] (*Z. anal. Chem.*, 1924, **65**, 25—46).—The chief characteristics of the heavy metal sulphides are their very pronounced colour, great insolubility, and ability under certain conditions to carry down with them sulphides of other metals which are normally soluble. The freshly-precipitated sulphides are much more soluble than those which have aged for some time and are capable of forming compounds with other metallic salts, such as $(HgS)_2,HgCl_2$, whilst some double sulphides of the types FeS,NiS and $Tl_2S,2CuS$ are known. These phenomena may be explained by assuming that the precipitates formed by addition of a soluble sulphide to a salt of a heavy metal are polymerides of the single sulphide and that on ageing the polymerides become more complex; in all cases, the formation of these complexes is due to the subsidiary valencies of sulphur. Further investigations on the nature of heteropolysulphides have led to the discovery of many new examples of which the following are the best defined: nickel sulphide co-precipitated with lead sulphide is appreciably soluble in 1 : 10-hydrochloric acid, but in the absence of lead sulphide absolutely insoluble; manganese sulphide is readily soluble in acetic acid, but digestion with acetic acid of a mixture of zinc and manganese sulphides that have been precipitated together leaves a residue of zinc sulphide that may contain up to 24% of manganese; cadmium and manganese sulphides precipitated together by ammonium sulphide yield the compound 2MnS,3CdS; mercuric sulphide, precipitated from acid solutions containing zinc, usually contains 2—3% of zinc, or precipitated from very strongly acid chloride solutions containing cadmium, may contain as much as 60% of the total cadmium present. Precipitated together with manganese sulphide by means of ammonium sulphide, it gives the compound 2HgS,MnS, which does not yield all its mercury to sodium sulphide or its manganese to acetic or 1 : 1-hydrochloric acid. A further type of co-ordination complex is exemplified by the polysulphides of the metals; molybdenum polysulphide is prepared by treating a boiling mixture of ammonium molybdate and yellow ammonium sulphide with sulphuric acid and extracting the free sulphur from the precipitate by means of bromocamphor which leaves a dark

brown residue of $MoS_3 \cdot\cdot\cdot\cdot S_2$. This sulphide is readily formed by passing hydrogen sulphide into a molybdenum solution containing free iodine, and this procedure obviates the necessity of heating the liquid under pressure to obtain complete precipitation.

The above facts show that under certain conditions the sodium sulphide procedure of qualitative analysis may fail to reveal the presence of some elements, whilst others may appear in the wrong place. Even the ordinary hydrogen sulphide method fails to effect a complete separation of, for example, mercury from zinc and cadmium and tin from cobalt. A. R. P.

Analytical Separation of Rare Earths from Uranium. Alkali Uranylsalicylates. G. CANNERI and L. FERNANDES (*Gazzetta*, 1924, **54**, 770—773).—Hauser's modification of the oxalate method for separating rare earths from uranium (A., 1908, ii, 987) yields inaccurate results, but a satisfactory separation may be effected by conversion of the uranium into uranylsalicylic acid.

The uranylsalicylates have the formula $UO_2(\cdot O \cdot C_6H_4 \cdot CO_2R)_2$, and are moderately stable, the uranium not being detectable by the ordinary reagents, including concentrated alkali hydroxide solution. The *sodium* ($+9H_2O$) and *potassium* ($+10H_2O$) salts form orange-red needles; the *ammonium* salt ($+13H_2O$) was also prepared. [Cf. *B.*, 1925, 54.] T. H. P.

Separation of Gallium. E. H. SWIFT (*J. Amer. Chem. Soc.*, 1924, **46**, 2375—2381).—Gallium may be separated from many metals with which it occurs (*e.g.*, lead or indium, but not iron) by extraction with ether of a solution in 5—6*N*-hydrochloric acid. The most efficient extraction occurs when 5·5*N*-acid is used. Gallium does not volatilise when solutions of the chloride are evaporated. It may be separated from iron as follows. Sodium hydroxide, not less concentrated than 0·3*N*, is added in slight excess to the solution in hydrochloric acid, the mixture is boiled for 2 minutes, cooled, and the precipitated iron hydroxide filtered off. The filtrate is just acidified with 6*N*-hydrochloric acid, diluted to 100 c.c., and the gallium precipitated by boiling for 2 minutes with 5 c.c. of 3*N*-ammonium acetate. In a neutral or slightly acid solution, the metal is completely precipitated with the iron. A detailed procedure is given for the detection of gallium based on the above method; it can also be used for obtaining pure gallium salts from natural materials. S. K. T.

Hahn's Iron Titration Method and Rosenmund's Modification Thereof. E. RUPP (*Apoth. Ztg.*, 1924, **39**, 422—423; from *Chem. Zentr.*, 1924, ii, 512).—The success of Hahn and Windisch's iron titration method (A., 1923, ii, 262) depends on the purity of the thiosulphate solution; an increase in the amount of potassium iodide is frequently but not invariably of value. At present the usefulness of the method is limited. F. A. M.

Prussian-blue Reaction. E. SCHULEK (*Pharm. Zentralh.*, 1924, **65**, 693—694).—The presence of even small amounts of ammonium chloride hinders or entirely prevents the formation of

Prussian-blue in the usual test for small amounts of cyanide. In such cases the solution should be distilled with boric acid and the distillate tested as usual. [Cf. *B.*, 1925, 40.] A. R. P.

Determination of Nickel by means of Dimethylglyoxime in Presence of Iron and Cobalt. J. G. WEELDENBURG (*Rec. trav. chim.*, 1924, **43**, 465—473).—Tartaric and citric acids interfere with the determination of nickel by means of dimethylglyoxime in presence of iron and cobalt, the results obtained being too high. This is due to the simultaneous precipitation of an iron–cobalt–dimethylglyoxime compound of the formula $FeCoC_{12}H_{19}O_6N_6$. The properties of this substance are described and compared with those of the nickel compound. A method of determining nickel under the stated conditions is based on the reduction of the solution by warming with sodium hydrogen sulphite or sulphurous acid until the yellow colour of ferric iron has disappeared. Sodium hydroxide is then added until a permanent precipitate is formed; this is dissolved in a few drops of hydrochloric acid. To avoid atmospheric oxidation, the solution is treated with a reducing agent and diluted until not more than 0·1 g. of metal per 100 c.c. is present. Excess of dimethylglyoxime and a few g. of sodium acetate are added. The precipitate is allowed to settle, filtered, washed with dilute sulphurous acid, then with water, dried at 110—120°, and weighed. If the amount of iron and cobalt present is equal to or less than that of nickel, the quantity of dimethylglyoxime corresponding with the latter is sufficient, otherwise excess must be added. H. J. E.

Ignition of Precipitates. II. Conversion of Molybdenum Sulphide into Oxide and the Volatility of Molybdenum Trioxide. P. H. M.-P. BRINTON and A. E. STOPPEL (*J. Amer. Chem. Soc.*, 1924, **46**, 2454—2457).—Molybdenum trioxide is non-volatile below 500° and volatilises only very slightly between 500° and 600°. Hence the conversion of molybdenum trisulphide into the oxide in analysis may be carried out by heating the sulphide precipitate with the filter-paper at 600° in a crucible suspended in an improvised air-muffle, consisting of a large crucible with a disc of asbestos in the bottom. S. K. T.

Determination of Uranium in Carnotite. P. H. M.-P. BRINTON and R. B. ELLESTAD (*Ind. Eng. Chem.*, 1924, **16**, 1191—1192).—A rapid method of moderate accuracy for the determination of uranium in its ores depends on the fact that iron, vanadium, and the excess of lead used for precipitating the latter can be removed in one operation with lead nitrate and ammonium carbonate by precipitation under slight pressure. Any lead still in solution is removed as sulphide, the uranium precipitated as ammonium diuranate, and the precipitate freed from aluminium in the usual way. C. I.

Potentiometric Determination of Vanadium, Chromium, and Iron in Presence of each other and its Application to Steel Analysis. I. M. KOLTHOFF and O. TOMÍČEK (*Rec. trav. chim.*, 1924, **43**, 447—456).—Whereas vanadic acid is reduced to

vanadyl salt and chromic acid to chromic salt by a ferrous salt in acid solution, only the vanadyl ion is oxidised to vanadic acid on titration with permanganate. The determination is most advantageously carried out at 70—80°. The method may be applied to the potentiometric determination of chromium and vanadium in presence of one another and details are given of the experimental method of determining vanadium and chromium in steel. [Cf. *B.*, 1924, 969.] H. J. E.

Iodometric Determination of Vanadium. A. E. Stoppel, C. F. Sidener, and P. H. M.-P. Brinton (*J. Amer. Chem. Soc.*, 1924, **46**, 2448—2453).—The vanadium in a concentrated neutral solution of a vanadate may be accurately determined by adding to 10 c.c. an equal volume of 6*N*-mineral acid (*e.g.*, hydrochloric or sulphuric, but not acetic acid) and a few grams of potassium iodide and then, after considerable dilution, titrating with standard thiosulphate solution. The liberated iodine is exactly equivalent to the reduction of the vanadium to the quadrivalent vanadyl stage. The operations must be conducted without undue delay. To ensure all the vanadium being in the quinquevalent condition, it should be previously oxidised with alkaline hydrogen peroxide solution, the excess of the latter being destroyed by boiling. Small quantities of molybdenum do not interfere if phosphoric acid is used for the mineral acid, but the presence of tungsten causes low results. Uranium must be absent. S. K. T.

Bismuth. I. Determination of Bismuth. L. Kürthy and H. Müller (*Biochem. Z.*, 1924, **147**, 377—384).—A method for the determination of bismuth suited to biological application is described. The bismuth is precipitated from neutral solution as the phosphate by addition of a known excess of diammonium hydrogen phosphate, and, after 1 hour, is separated by centrifuging. The excess of phosphate is then determined by colorimetric comparison with a standard solution, utilising the blue colour which develops on adding molybdic acid, quinol, and sodium carbonate. The excess of phosphate may also be determined by titration with 0·1*M*-bismuth nitrate solution, using potassium iodide, which gives a yellow colour with bismuth nitrate, as an internal indicator. J. P.

Boiling-point Correction Chart for Normal Liquids with Special Application to Petroleum Products. W. H. Bahlke and R. E. Wilson (*Ind. Eng. Chem.*, 1924, **16**, 1131—1132).—Where distillations of unassociated paraffin hydrocarbons are made at temperatures which vary from those at which the b. p. are required, the necessary corrections may be made from the given chart prepared from accurate vapour pressure observations. D. G. H.

Analysis of Naphthalenesulphonic Acids and Naphthalene. W. S. Calcott, F. L. English, and F. B. Downing (*Ind. Eng. Chem.*, 1924, **16**, 1190; cf. A., 1924, ii, 208).—Manipulative details, omitted in the previous paper, are given for the determination of

the naphthalene carbon by oxidation of the naphthalene residue to phthalic anhydride, and of the sulphonic acid sulphur by isolation of the soluble barium sulphonates and gravimetric determination of barium. [Cf. *B.*, 1924, 1007.] W. A. S.

Determination of Anthracene in Anthraquinone. H. F. LEWIS (*Ind. Eng. Chem.*, 1924, **16**, 1184).—When a solution of anthracene in "oleum" is heated, charring takes place, but a similar solution of anthraquinone remains yellow. The anthraquinone containing anthracene is dissolved in "10% oleum" heated at 150°, then poured into water and filtered. The colour of the filtrate is compared with those of solutions of potassium dichromate and cobalt chloride, standardised against prepared mixtures of anthracene and anthraquinone. An accuracy of 0·1%, up to 7% of anthracene, is claimed. W. A. S.

Determination of Invert-sugar by the Reduction Titration Method in Liquids containing Sucrose. M. A. H. VAN DEN HOUT, P. A. NEETESON, and A. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1924, **21**, 578—582).—The possible errors in Schoorl's method have been investigated. Sucrose reduces Fehling's solution, but the extent of the reduction is at first constant and finally diminishes with increasing concentration of sucrose. The concentration of the Fehling's solution markedly affects the results. The previous history of the flasks employed is also a factor, constant results being obtained only after boiling out with sodium hydroxide and washing; the hydrogen-ion concentration of the distilled water used for dissolving is of influence, so that this should be made alkaline before use. The time of boiling has little effect, but cooling should be as rapid as possible. The amount of potassium iodide added and the time elapsing after acidification before titration both affect the results. The quantity of starch used should be constant. Salts, and especially those of the alkaline earths, have some influence; the latter should be removed as oxalates.

S. I. L.

Determination of Starch using Malt. T. CHRZASZCZ (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 306—311).—The starch containing grist is heated with water at 106°; the hydrogen-ion concentration is then adjusted to about p_H 5, and the mash cooked in an autoclave. It is then cooled to 70°, malt extract is added, and a temperature of 65° to 70° is maintained until the liquid and grist cease to give a colour reaction with iodine. After cooling and diluting, a portion of the filtrate is hydrolysed with hydrochloric acid, neutralised with sodium hydroxide, and the reducing power determined by the usual methods. The determination is made on duplicate samples, the first being used for the iodine test during diastatic action. Correction is made for the malt extract added.

G. S. W.

Determination of Copper Value of Celluloses. E. BENESCH (*Chem.-Ztg.*, 1924, **48**, 861).—Following the method described by Adanti (A., 1916, ii, 155), 3—4 g. of cellulose are placed in a 1 litre

Erlenmeyer flask with 50 c.c. of Fehling's solution, washed down with 50 c.c. of water. Boiling is continued for 15 minutes, the mouth of the flask being covered with a glass dish; the mass is then collected under suction in a small Büchner funnel on a double layer of "quantitative" filter-paper. It is washed until free from Fehling's solution, then transferred together with the filter-paper to a large beaker, using 100 c.c. of water. Oxidation is effected by the addition of 25 c.c. of a solution of 10 g. of ferric ammonium sulphate in 10% sulphuric acid until the previously red filter-paper is completely colourless. The liquid is filtered off through the same funnel and the mass washed six or seven times with 50 c.c. of water by decantation until free from iron. The amount of ferrous salt in the filtrate is titrated with permanganate at a temperature above 50° and the result corrected by a control titration of 25 c.c. of the same iron alum solution diluted with 200 c.c. of water. J. F. B.

Determination of Tartaric Acid by Precipitation as Calcium Tartrate. M. François and C. Lormand (*J. Pharm. Chim.*, 1924, [vii], **30**, 276—283).—Gravimetric determination of tartaric acid as the calcium salt (cf. A., 1923, ii, 129) is directly applicable to cream of tartar, potassium sodium tartrate, complex lithium mixtures containing tartaric acid, and potassium borotartrate. With tartar emetic, the antimony must first be eliminated, preferably with hydrogen sulphide. With potassium ferric tartrate, the iron should be removed, either as sulphide by the addition of ammonium sulphide and acetic acid, or as basic ferric acetate. J. K.

Determination of Citronellal in Citronella Oil. J. Dupont and L. Labaune (*Amer. Perf. Essent. Oil Rev.*, 1924, **19**, 257—258).—By acetylation with acetic anhydride and sodium acetate, the total quantity of compounds capable of acetylation is obtained. Acetylation is then effected on the oil remaining after treatment with hydroxylamine hydrochloride and sodium carbonate. The difference between the acetylation values is an indication of the citronellal content. Chemical Abstracts.

Determination of Cineole in Essential Oils by Cocking's Process. L. S. Cash and C. E. Fawsitt (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 157—159).—Cocking's method (A., 1920, ii, 645) gives more accurate results than other methods provided the oil contains at least 65% of cineole. Cineole was added to various eucalyptus oils to give a content of 65—95% of cineole, and f.p.–specific gravity curves were drawn. It is concluded that the cineole content of an oil should be capable of determination with a maximum error of 2%. W. T. K. B.

Phenolphthalin as a Reagent for Hydrocyanic Acid. J. Stamm (*Arch. Pharm. Chem.*, **4**, 18; from *Chem. Zentr.*, 1924, ii, 515).—Alkaline phenolphthalin solution (2 drops in 5 c.c. of water) is a sensitive reagent for hydrocyanic acid or hydrogen peroxide

and can be utilised, in the absence of oxidising agents, for detecting hydrocyanic acid. F. A. M.

Fluorescin as a Reagent for Hydrocyanic Acid. J. STAMM (*Arch. Pharm. Chem.*, 4, 25; from *Chem. Zentr.*, 1924, ii, 515—516).—Fluorescin is oxidised to fluorescein by hydrocyanic acid in alkaline solution and in presence of very dilute copper sulphate. On adding to 4 c.c. of very dilute potassium cyanide solution, the same volume of the reagent (0·00025% of fluorescin) and 2 drops of 1 : 2000 cupric sulphate, a brilliant green fluorescence is shown at once. The reagent is prepared by dissolving fluorescein in alcoholic aqueous sodium hydroxide solution and heating with zinc dust on the water-bath until decolorised, followed by dilution with aqueous alcohol. After keeping in the dark for 12 hours, the solution is filtered and suitably diluted. Other oxidising agents besides hydrocyanic acid also give the reaction. F. A. M.

Micro Determination of Carbamide and Ammonium Salts by Titration with Hypobromite. B. POHORECKA-LELESZ (*Bull. Soc. Chim. biol.*, 1924, 6, 773—787).—Carbamide and ammonium salts may be determined by micro methods in which the sodium hypobromite used in decomposing these compounds is measured by iodometric titration in cold, or by alkalimetry in hot solutions. The former process is recommended for determining ammonia in the micro Kjeldahl method, the method being applied direct to the neutralised product from the acid digestion, thus eliminating the necessity of distillation. J. P.

Analysis of Cyanamide in its Calcium Compound. R. FOSSE, P. HAGENE, and R. DUBOIS (*Compt. rend.*, 1924, 179, 408—410).—The cyanamide is hydrolysed by means of dilute nitric or hydrochloric acid and a portion of the resulting solution, made slightly alkaline with ammonia and diluted to known volume, is treated with methylxanthydrol in presence of acetic acid. The xanthylcarbamide thus formed is dried and weighed. H. J. E.

Influence of Colloids in the Reductase Test. A. I. VIRTANEN (*Z. Unters. Nahr. Genussm.*, 1924, 48, 141—151).—The influence of colloidal adsorption of the methylene-blue on the rate of reduction in milk was examined by means of a series of tests under different colloidal conditions. Decrease of the adsorption surface by coagulation by electrolytes caused no decrease in the time of reduction, nor was the time increased by the addition of normal milk colloids in the form of condensed milk and cream. A considerable decrease in the rate of reduction was obtained in the presence of foreign colloids, especially in the case of gelatin. Increase of the continuous phase by addition of water up to 20% had no influence. [Cf. *B.*, 1924, 960.] G. S. W.

General, Physical, and Inorganic Chemistry.

The Displacement Law of Arc and Spark Spectra. W. F. MEGGERS, C. C. KIESS, and F. M. WALTERS, jun. (*J. Opt. Soc. Amer.*, 1924, **9**, 355—374).—A review of the laws which have been found to govern the structures of practically all spectra is given, and illustrated by six tables, including the multiplets of Sc^+, Ti^+, V^+, Cr^+, Mn^+, and Fe^+. The work of the Bureau of Standards on spark spectra is shown to prove the displacement law of Kossel and Sommerfeld. C. W. B.

Spectrum Regularities for Scandium and Yttrium. W. F. MEGGERS (*J. Washington Acad. Sci.*, 1924, **14**, 419—430).—Examples of multiplets in the arc and spark spectra of scandium and yttrium are given. The doublets in the spectrum of Sc I, triplets in the spectrum of Sc II, doublets in the spectrum of Y I, triplets in the spectrum of Y II, Zeeman effect for Y I and Y II are classified in tables. C. W. B.

Intensity Measurements in Flame Spectra. C. E. BLEEKER and I. A. BONGERS (*Z. Physik*, 1924, **27**, 195—202).—A comparison has been made of the relative intensities of the lines of the diffuse and sharp series of rubidium and cæsium when excited in flames of different temperatures and with various concentrations of metallic chlorides in the flames. The intensity relations are unaffected by such changes, and the intensities of each pair of lines composing a doublet are also uniformly in the ratio 1 : 2. S. B.

Doublets of the Alkali Metals. F. J. DE WISNIEWSKI (*Compt. rend.*, 1924, **179**, 1316—1317).—A formula, $\Delta\gamma=\alpha_z/n^3 . (1-0{\cdot}5/n)$, is given for the width of the successive doublets in the principal series. This is simpler than that previously given (*Physikal. Z.*, 1923, **24**, 294). $\Delta\gamma$ is the difference in frequency of the two lines of the doublet, n the numerical order of the doublet (Thitz's notation), and α_z a constant for each element. Calculated and observed values are given, showing good agreement. L. L. B.

Line Spectrum of Nitrogen. F. CROZE (*Compt. rend.*, 1924, **179**, 1603—1605; cf. A., 1914, ii, 600).—The lines emitted by N^+ as distinct from neutral N and N^{++} have been resolved by the aid of the Zeeman effect. Although the complete N^+ spectrum cannot yet be laid down, there is evidence of series of simple lines and of three series of terms with triple multiplicity disclosed by the presence of multiplets of the types *ps*, *pd*, *df*, *pp'*, *dd'*, *p'd'*, *p'p''*, *p''s*. W. A. C.

Low-voltage Arc Spectra of Copper. A. G. SHENSTONE (*Nature*, 1924, **114**, 934).—The absorbed lines of copper vapour are: 3247·55, 3273·97, 2492·14, 2441·63, 2244·24, 2225·67, 2165·06, and, with slight uncertainty, 2181·68, 2024·33 Å. A. A. E.

Spark Spectrum of Iron in the Schumann Region. L. and E. BLOCH (*Compt. rend.*, 1924, **179**, 1396—1399).—The spark spectrum of iron in the region 1855—1505 Å. was re-examined: 253 lines are recorded, more than half of which are new. The lines of carbon and nitrogen given by Simeon and by Hopfield and Leefson were used as primary and the lines of aluminium as secondary standards. The absolute precision is not greater than that of the standards, *i.e.*, 0·2 Å., but the differences between successive lines are accurate to a few hundredths of this unit. H. T.

Ultra-violet Spectrophotometry. T. R. MERTON (*Proc. Roy. Soc.*, 1924, **A**, **106**, 378—384).—A method is described for the preparation of optical "wedges" of platinum, by the cathodic sputtering of the metal on to a quartz plate in a vacuum. These may be used for spectrophotometry throughout the range of the quartz spectrograph, in the same manner as wedges of neutral-tinted glass are used in the visible. S. B.

Absorption Measurement in the Ultra-violet by Photographic Photometry. H. LEY and F. VOLBERT (*Z. wiss. Phot.*, 1924, **23**, 41—51).—The photometric method of Henri gives satisfactory results agreeing with those of an independent method (A., 1923, ii, 519). The plate factor is practically independent of the wave-length of the light within the region studied (3900—2300 Å.) and the extinction coefficient, ϵ, is independent of the intensity of the light. L. J. H.

Irregularity of the $L\alpha$-Doublet in the X-Ray Spectra. B. B. RAY (*Phil. Mag.*, 1924, [vi], **48**, 707—711).—Measurements were made of the change in the wave-length of the L-doublet of the elements of atomic numbers between 41 and 92. When these differences were plotted against the atomic numbers, changes of slope were obtained in the regions Pd (46), Ce (58), and La (71), results which in a general way support the Bohr theory. Calculations made on the $L\alpha$-doublet show that both lines undergo similar changes, pointing to a similarity between the two orbits (cf. Landé, A., 1924, ii, 511). H. T.

Döppler Effect of Arc and Spark Lines. H. KREFFT (*Physikal. Z.*, 1924, **25**, 352—366).—A summary of the work done in this field up to date. L. J. H.

Döppler Effect in Canal Rays of Hydrogen. H. KREFFT (*Ann. Physik*, 1924, [iv], **75**, 513—520).—Supplementary to previous work (this vol., ii, 3). Additional observations have been made on the Döppler effect of H_β. The intensity distribution of the Döppler effect is not the same immediately in front of the cathode as at some distance behind it. Probably the canal rays are not yet in equilibrium at the cathode. Addition of oxygen to the discharge space reduces the range of velocities to which the Döppler effect is limited, but the addition of nitrogen produces no effect. With increasing current strength, the maximum velocity decreases. Variations also take place in the intensity maxima.

If a spark gap be introduced in circuit with the discharge tube a strengthening of the intensity maximum at higher velocity, due to accelerated atoms, takes place. M. S. B.

Paschen-Back Effect in Hydrogen. H. FALKENHAGEN (*Z. Physik*, 1924, 28, 1—10).—A theoretical discussion of the changes in the Zeeman pattern of the Balmer lines with the application of very intense magnetic fields. S. B.

Inverse Stark Effect in Sodium Vapour. R. LADENBURG (*Z. Physik*, 1924, 28, 51—68).—The effect of an intense electrical field on the *D*-line absorption of sodium vapour has been studied, under the dispersion of a Lummer-Gehrcke plate. The construction of a sodium vapour lamp, designed to emit the *D*-lines without self-reversal, is described. The light from this lamp passed between two plane electrodes maintained at potential differences of up to 160,000 volts/cm., and the space between the electrodes contained sodium vapour at pressures of the order of 10^{-5} mm. Observations in directions perpendicular to the lines of force showed that the electrical field shifted both absorption lines equally to the red. The shift of the parallel component of D_2 is greater than that of the perpendicular component and is 0·025 Å. for 160,000 volts/cm. It is proportional to the square of the field strength. The Stark effects here recorded are in agreement with those predicted by the Bohr theory for non-hydrogenic orbits when the applied external field is small in comparison with the atomic fields. S. B.

Absorption of Cathode Rays in Aluminium Foil. H. M. TERRILL (*Physical Rev.*, 1924, 24, 616—621).—Between 18 and 52 kv., Lenard's equation, $I/I_0=e^{-ax}$, where x is the thickness of the aluminium, holds. Within the range of velocities, 8·09—12·23$\times10^9$ cm./sec., the values of a are given by Thomson's approximate expression, $av^4=0{\cdot}268\times10^{44}$, where v is the mean of the velocities before and after penetrating the foil. A. A. E.

[Intensity and Distribution of] Light Emission from the Striated Discharge. R. SEELIGER and J. ÔKUBO (*Physikal. Z.*, 1924, 25, 337—342). L. J. H.

[Theory of the Diffusion of Positive and Negative Ions to the Walls of a Discharge Tube.] W. SCHOTTKY (*Physikal. Z.*, 1924, 25, 342—348). L. J. H.

Energy Consumption in Ionisation by *X*-Rays of Different Wave-lengths. L. GREBE and L. KRIEGESMANN (*Z. Physik*, 1924, 28, 91—94).—Measurements have been made of the energy in the form of *X*-rays of different wave-lengths required to produce a given degree of ionisation in air. It is found that the ratio energy/ionisation decreases exponentially with increasing wave-length of the *X*-rays. S. B.

Mobility of Actinium Active Deposit Ions. H. A. ERIKSON (*Physical Rev.*, 1924, 24, 622—626; cf. this vol., ii, 6).—When actinium active deposit ions are drawn through a stream of air between

two metal plates maintaining an electric field of more than 100 volts/cm., two depositions are observed corresponding with ionic mobilities of 4·35 and 1·55 cm./sec./volt/cm. The results indicate that the ions are, respectively, (*a*) atomic actinium-*A* and -*B*, and (*b*) actinium-*B*, and possibly -*A*, after union with a neutral molecule, presumably air. The mobility of an ion is determined chiefly by the charge, the structure of the ion, and the nature of the medium, but is practically independent of the mass. A. A. E.

Mobility in Air of Ions Produced in Another Gas. G. C. GRINDLEY and A. M. TYNDALL (*Phil. Mag.*, 1924, **48**, [vi], 711—719).—Accurate measurements were made of the mobility of ions produced directly in air and of ions produced in another gas and measured in air. No sensible differences could be detected (cf. Wellisch, A., 1909, ii, 299). H. T.

Visible Radiation from Solid Targets. P. D. FOOTE, W. F. MEGGERS, and R. L. CHINAULT (*J. Opt. Soc. Amer.*, 1924, **9**, 541—543).—An attempt to show if it were possible to excite a visible or ultra-violet line spectrum by bombarding targets of copper, carbon, platinum, and iron with 1000-volt electrons. The results are negative; in every case the first negative carbon group appeared despite every precaution with vacuum technique. These bands are enhanced by the presence of nitrogen. If the electron current is such that the target becomes heated, an almost imperceptible volatilisation is sufficient to excite the resonance lines of the element. C. W. B.

Proof of the Invariance under the Lorentz Transformation of the Equation of Motion of the Electron. L. PAGE (*Physical Rev.*, 1924, **24**, 627—630).—Mathematical. A. A. E.

Photo-electric Effect for Submicroscopic Mercury Drops. E. WASSER (*Z. Physik*, 1924, **27**, 203—225).—The photo-electric effect for small mercury drops varies in character with their radius. The normal effect (expulsion of negative charges) is observed with particles of radius larger than $1{\cdot}9\times10^{-5}$ cm., whilst for particles smaller than $1{\cdot}2\times10^{-5}$ cm. radius the inverse effect (expulsion of positive charges) takes its place. Measurements of the charges acquired have been made, and it is stated that these may be considerably less than the charge corresponding with the loss or gain of an electron (the minimum charge found was about $e/8$ in the inverse, and $e/2$ in the normal effect). Such results support Ehrenfest's belief in the existence of a "sub-electron." S. B.

Effect of Adsorption of Gases on the Density of Mercury Droplets. E. WASSER (*Z. Physik*, 1924, **27**, 226—236).—No explanation of the results recorded in the previous abstract can be based on the supposition of density variations in the droplets, due to adsorbed gas films on their surface. The phenomena are the same in carbon dioxide and in nitrogen, although both gases would not be expected to give films of the same thickness. Also, to

achieve an explanation, films of several hundred molecules in thickness must be assumed, a supposition not consonant with modern views on adsorption. S. B.

Photo-electric Emission of Selenium. W. Del Regno (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 163—167).—The author's experiments fail to reveal any differences between the emission of selenium in the dark and under the influence of light and hence justify the assumption that free electrons play no part in the phenomenon. Confirmation is also furnished of the previous conclusion that the electrical conductivity exhibited by selenium under the influence of light is an effect of purely electronic character and is not due to any chemical transformation, such as the conversion of one allotropic form into another. T. H. P.

Photo-electric Response of Potassium at Low Temperatures. J. W. Hornbeck (*Physical Rev.*, 1924, **24**, 631—638; cf. Ives, A., 1924, ii, 444).—The current–wave-length curve at −180° is shifted by 80—500 Å. towards the shorter wave-lengths with respect to the 20° curve. Monochromatic heating and cooling curves run approximately parallel to the temperature axis except between −80° and −100°, where a change of crystal structure is known to take place. A. A. E.

Thermionic Work Function of Oxide-coated Platinum. C. Davisson and L. H. Germer (*Physical Rev.*, 1924, **24**, 666—682).—Measurements of the thermionic work function of platinum coated with the oxides of barium and strontium by a calorimetric and a temperature variation method give results in agreement, but insufficiently accurate to determine whether or not an electron within the metal possesses the thermal energy $3kT/2$. A. A. E.

***X*-Ray Emission of Electrons from Metal Films, with special Reference to the Region of the Absorption Limit.** L. Simons (*Proc. Physical Soc.*, 1924, **37**, 58—70; cf. A., 1924, ii, 140).—Particulars are given of an experimental quantitative investigation of absorption and ionisation phenomena exhibited by electrons emitted from gold and silver films exposed to *X*-rays, and the correlation of these phenomena with the photo-electric equation $(mv^2/2)_{\text{K,L,M, etc.}}=h\nu-h\nu_{\text{K,L,M, etc.}}$ is discussed. The author has determined directly the aggregate number of β-rays of all types emitted by the films when exposed to *X*-rays of wave-lengths between 388×10^{-11} cm. and 871×10^{-11} cm., and has shown that no selective change in the average energy of the rays occurs when the *K*-fluorescence spectrum is excited. It is suggested that is thus due to a re-grouping of the numbers and energies of the β-ray constituents, together with the additional emission of the *K*-group of minimum individual energy. The origin of δ-rays is discussed from the respective points of view of thermionics, recoil electrons, and impact electrons, and it is concluded that these rays are impact electrons the most frequent energy of which is little greater than 3·5 volts and independent of the exciting wave-length and of the

nature of the emitting substance. They appear to be influenced, at the time of their emission, by the scattered X-rays. J. S. G. T.

Magnetic Spectra of Iron and Nickel Wires at Wave-lengths of a Centimetre. W. ARKADIEV (*Z. Physik*, 1924, 28, 11—28).—Previous measurements of magnetic absorption spectra of metallic wires for Hertzian waves of about 1 cm. wave-length have been used to test theories developed in other papers (*Ann. Physik*, 1919, 58, 105). The inconstancy of the form of the magnetic spectrum of iron and nickel is attributed to variations in the magnetic properties of ferromagnetic materials. S. B.

Magnetic Properties of Thin Films of Ferromagnetic Metals Produced by the Evaporation Method. A. J. SORENSEN (*Physical Rev.*, 1924, 24, 658—665).—The maximum value of the intensity of magnetisation of films of iron, nickel, and cobalt of thickness 20—300 $m\mu$ is of the same order of magnitude as for bulk metal. The remanence is high for iron and cobalt, but low for nickel. There is an abrupt change in the high values of the coercive force at a thickness of 55, 70, and 200$m\mu$ for iron, cobalt, and nickel, respectively. A. A. E.

New Phenomenon in the Diamagnetism of Gases. A. GLASER (*Ann. Physik*, 1924, [iv], 75, 459—488).—A very sensitive method is described by which the magnetic susceptibilities of hydrogen, nitrogen, and carbon dioxide have been determined at different pressures. Down to a certain pressure, which differs for each gas, the decrease in magnetic susceptibility is directly proportional to the decrease in pressure. Below this pressure, however, there is a deviation in such a direction that the susceptibility is higher than is to be expected from the proportionality law. Ultimately, as the pressure and susceptibility both approach zero, they again become directly proportional to each other. The phenomenon is explained by supposing that, when the pressure becomes sufficiently reduced, it is possible for orientation of the molecule to take place under the influence of the magnetic field. This results in a relative increase of the susceptibility. The pressure at which this effect will begin to make itself felt depends on the relation between the time taken for orientation of the molecule and the interval between successive molecular collisions producing disorientation. It will therefore depend on the inertia of the molecule, that is, on the molecular weight, and on the strength of the magnetic field. M. S. B.

Origin of the Satellites of Mercury Lines. E. P. METCALFE and B. VENKATESACHAR (*Nature*, 1925, 115, 15—16).—Lines arising from isotopes must satisfy two conditions: (*a*) the intensities of the several isotope lines in the radiation from a thin layer must be in the ratio of the concentrations of the respective isotopes, (*b*) the radiation from the end of a long column should be distinguished by the equalisation of the brightness of corresponding lines when the column is sufficiently long for the lines to be "saturated." The second consideration, when applied to the line 5461 Å., indicates

that the line −0·024 Å. must be excluded from the isotopic group of satellites. Also, the components of 5769 Å., but not of 5971 Å., appear to satisfy the second condition. A. A. E.

Mass Ratio of Isotopes in Chemical Elements. F. M. JAEGER and D. W. DIJKSTRA (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 393—406).—Pure tetraethylsilicane was made from silica from various sources, terrestrial and meteoric. The specific gravity of all the samples was the same within a few units in the third decimal place per cent. Even this discrepancy was apparently due to traces of impurities as indicated by comparison of refractive indices. The ratio of the isotopes must therefore be the same whatever the origin of the silicon. L. J. H.

Separation of Isotopes by the Ionic Migration Method. J. KENDALL and J. F. WHITE (*Proc. Nat. Acad. Sci.*, 1924, **10**, 458—461).—Using the apparatus already described (A., 1923, ii, 282), the method has been tested with non-isotopic mixtures of salts with ions of slightly different mobilities. Complete separation is easily effected with mixtures of iodide and thiocyanate, and barium and calcium, the differences in ionic mobilities being 16% and 8%, respectively. Considerable partial separation is attained with mixtures of barium and strontium, and iodide and chloride, the differences in ionic mobilities being, respectively, 5% and 1%. Assuming the two isotopic chlorine ions to possess different mobilities, the method should give at least a partial separation, but experiments with sodium chloride were indecisive. It is suggested that a mass-spectrograph may be used to detect such a separation. In the case of lead, which possesses radioactive isotopes, the distribution of the radioactive component in an activated sample of lead salt could be determined at intervals during the course of the experiment. J. S. C.

Rare Gases of the Atmosphere. H. JEFFREYS (*Nature*, 1924, **114**, 934).—The tendency of a gravitating planet to collect heavier molecules and in certain circumstances to lose lighter ones cannot solely account for the rarity of the inert gases; possibly the ability of the other elements to form stable and liquid compounds has co-operated (cf. Aston, this vol., ii, 18). A. A. E.

Artificial Disintegration of Elements. E. RUTHERFORD and J. CHADWICK (*Proc. Physical Soc.*, 1924, **36**, 417—422).—The method previously employed (cf. A., 1921, ii, 293) was improved by observing the particles ejected at right angles to the direction of bombardment. This enables particles with a range of only 7 cm. (or less for light atoms) to be observed. Hydrogen nuclei from the presence of hydrogen, and scattered α-particles have not this penetration at this angle, whilst the particles from disintegration are ejected in all directions (cf. A., 1922, ii, 682). In addition to the cases previously reported, disintegration was found in the light elements neon, magnesium, silicon, sulphur, chlorine, argon, and potassium, but not in the case of hydrogen, helium, lithium, carbon, or oxygen. Of the heavier elements, nickel, copper, zinc,

selenium, krypton, molybdenum, palladium, silver, tin, xenon, gold, and uranium failed to give the effect. Elements from calcium to iron have not at present given conclusive results. The comparative ranges of the ejected particles suggest that the nuclei of the even-numbered light elements are stable, whilst those of the odd-numbered light elements are comparatively unstable. An estimate of the field of force within the atom (about three million volts for aluminium) is deduced from these ranges. L. J. H.

Absorption and Scattering of γ-Rays. E. A. Owen, N. Fleming, and W. E. Fage (*Proc. Physical Soc.*, 1924, **36**, 355—366).—The absorption and scattering of γ-rays from radium filtered through 23 mm. of lead have been measured in magnesium, aluminium, zinc, tin, and lead. On the assumption that the mean effective wave-length of the radiation employed is 0·021 Å., the experimental results are consistent with the following statements: (1) When γ-rays traverse matter, the characteristic radiations of the absorbing medium are excited. (2) The atomic fluorescent absorption coefficient of γ-rays depends on the wave-length of the incident radiation and the atomic number according to the law $\omega\pi/\rho=K\lambda^3N^4$ which holds for *X*-rays. (3) The absorption in light elements is due almost entirely to scattering. (4) The pure atomic scattering absorption coefficient is proportional to the atomic number of the absorber. (5) In addition, a true absorption exists, the atomic coefficient of which is proportional to the atomic number.

Compton's formula would account for the experimental results if the wave-length of the incident radiation were 0·020 Å., but Jauncy's formula would require the value 0·029 Å. L. J. H.

Effective Wave-lengths of γ-Rays. J. A. Gray (*Nature*, 1925, **115**, 13).—The author's conclusions are summarised as follows: (i) If the secondary β-rays produced in light elements by the hard γ-rays of radium-*C* are recoil electrons, with an energy given by the quantum theory of scattering, the effective wave-length of the γ-rays must be much smaller than that usually accepted. Thus no theory, as at present developed, can account for the properties of scattered γ-radiation. (ii) The internal atomic absorption coefficient of the hard γ-rays of radium-*D* is 0·67, as compared with an external coefficient of about 3×10^{-21}. On disintegrating, one atom of radium-*D* in five emits a γ-ray. (iii) The number of atoms of an element emitting one or more types of monochromatic γ-rays may be only a small fraction of the total number disintegrating and a large part of the γ-ray energy emitted may be due to white radiation. (iv) A knowledge of the wave-lengths and relative intensities of the lines in the spectrum of the γ-rays is not, in itself, sufficient for the determination of effective wave-lengths which can be used to interpret the results of experiments on γ-rays. A. A. E.

Scattering and Absorption of γ-Rays. J. A. Gray (*Nature*, 1925, **115**, 86; cf. preceding abstract).—Four assumptions, for

which there is some evidence, are specified which lead to a reasonable explanation of experimental results on the scattering and absorption of hard γ-rays. It is believed that γ-rays possess a "range"; this would indicate that the scattering of γ-rays is a scattering of "corpuscles." As a correction, it is stated that only one in every seven radium-*D* atoms emits a γ-ray on disintegration.

A. A. E.

Magnetic Spectrum of β-Rays of High Velocity from Mesothorium II. D. YOVANOVITCH and J. D'ESPINE (*Compt. rend.*, 1924, **179**, 1162—1163).—The existence of high-velocity rays (β=0·998 and β=0·985, velocity of light taken as unity) from mesothorium II has been completely proved (cf. A., 1924, ii, 447).

H. T.

γ-Radiation of Mesothorium II. J. THIBAUD (*Compt. rend.*, 1924, **179**, 1322—1324).—In a previous study (cf. this vol., ii, 10) of the secondary β-ray spectra from uranium, lead, and tungsten, excited by the γ-radiation from mesothorium, three lines were found in the latter with energies corresponding with 580,700, 908,200, and 962,700 volts, respectively. The first of these was due to thorium-*B*, and it was suggested that the other two were due to mesothorium II.

A study of the primary β-ray spectrum of mesothorium II confirms this view, on the supposition that this spectrum is due to the photo-electric effect of the γ-radiation during disintegration. According to this hypothesis, the primary β-ray spectrum should be similar to the secondary β-ray spectrum from the element 89. This is found to be the case.

A further study of the secondary β-ray spectrum from lead gave two lines in the γ-radiation of 333 and 459 kv., respectively, confirming the results of Broglie and Cabrera (A., 1923, ii, 109).

The energy, frequency, and wave-length of four lines in the characteristic γ-ray spectrum of mesothorium II are given.

L. L. B.

Distribution of Electrons among Atomic Levels. E. C. STONER (*Phil. Mag.*, 1924, [vi], **48**, 719—736).—A distribution of electrons in the atom is suggested in which the number of electrons associated with a sub-level is connected with the characterising inner quantum number. This leads to a greater concentration of electrons in the outer sub-groups and to an earlier completion of the inner sub-groups than given by the older Bohr distribution. The number of electrons in each completed level is equal to double the sum of the inner assigned quantum numbers, there being in the *K*, *L*, *M*, *N*, levels when complete 2, 8 (2+2+4), 18 (2+2+4+4+6), 32 . . . electrons. In the building up of elements, changes are made by the simple addition of electrons to the outer sub-levels without reorganisation of the group as a whole. Available evidence from intensities of *X*-ray lines, absorption of *X*-rays, magnetic properties, optical spectra, and chemical properties is given in support of the new distribution.

H. T.

Striated Glow Discharge in Mercury Vapour. K. T. COMPTON, L. A. TURNER, and W. H. MCCURDY (*Physical Rev.*, 1924, **24**, 597—615).—The theory of the glow discharge in a monatomic gas is considered, and certain predictions are verified in the case of mercury vapour. Striations are observed only when the current is small or a substance (*e.g.*, hydrogen) is present to remove excited atoms, which exist in the striations, but not in the intervening regions. Molecules of the compound HgH are apparently formed in the presence of excited atoms, since its band spectrum is strongly shown by the striations; it cannot, however, be excited by illuminating a mixture of mercury vapour and hydrogen with 2536 Å. resonance radiation. A. A. E.

Fine Structure of Band Spectra of Sodium, Potassium, and Sodium–Potassium Vapours. H. G. SMITH (*Proc. Roy. Soc.*, 1924, **A**, **106**, 400—415).—Several of the absorption bands of sodium and potassium vapours and two of the bands peculiar to mixtures of these vapours have been examined under high dispersion. They have been separated into their *P*, *Q*, and *R* components. The corresponding moments of inertia have been calculated, and are in agreement with the supposition that the "sodium–potassium" bands are emitted by an NaK molecule. S. B.

Regularities in Band Spectra. S. DATTA (*Phil. Mag.*, 1924, [vi], **48**, 673—692).—The general equation $\nu=A+mD+m^2C'+n(B'+2b'm)+b'n^2$ (cf. Heurlinger, *Physikal. Z.*, 1919, **20**, 188; Deslandres, A., 1902, ii, 373), in which n and m are simple integers having a definite physical meaning (n defining quantum changes and m the orbit of the atom), is theoretically deduced. Simplified forms are given in which (i) the rotational energy of the molecule is neglected, when $\nu=A+Bm+Cm^2$, and (ii) where the molecules are all in the same dissociated state, when $\nu=A+Bn+Cn^2$. The general equation has been applied with good agreement to the first positive nitrogen bands. An attempt has been made to explain the afterglow bands and to link up the photo-electric currents observed by Brandt (*Diss.*, Berlin) with the ionisation of mercury by ultra-violet radiation of the first positive bands corresponding to the limiting orbits. H. T.

New Variety of Spectra. W. H. MCVICKER, J. K. MARSH, and A. STEWART (*Phil. Mag.*, 1924, [vi], **48**, 628—636; cf. T., 1923, **123**, 642, 817, 2147; A., 1924, ii, 712).—The Tesla luminescence spectrum of benzene consists of more than 70 fine bands falling into eight groups each reproducing exactly the same system of bands differing in position by approximately 100 Å. External conditions, *e.g.*, pressure, temperature, and timing of the transformer, have little effect. By comparison with Hartley's absorption data (A., 1908, ii, 243) it is shown that the Tesla luminescence spectrum represents a reversal of the former, *i.e.*, the Fraunhofer effect is shown with a complex organic compound. H. T.

Infra-red Absorption of Ice. E. K. PLYLER (*J. Opt. Soc. Amer.*, 1924, **9**, 545—555).—The spectral transmission of a crystal of ice 0·5 cm. thick has been determined for the ordinary and extraordinary rays, and also for sections cut so that the incident energy was about equally divided into the ordinary and extraordinary rays. The extraordinary ray does not exhibit any general absorption in the region from 0·75 μ to 1·15 μ, but the ordinary ray shows general absorption for this region which probably extends into the visible. One mm. of ice at 1 μ absorbs 5% of the energy for the extraordinary ray and about 47% for the ordinary ray. Each ray has the corresponding absorption bands as found in liquid water, but the bands for ice are shifted toward the long wave-lengths.

C. W. B.

Absorption Spectrum of Sulphur Vapour and Molecular Constitution. V. HENRI and M. C. TEVES (*Compt. rend.*, 1924, **179**, 1156—1159).—Using a continuous spark under water as a background, the absorption spectrum of sulphur at different pressures and at temperatures between 100° and 1000° was examined. Below 250°, where only S_8 and S_6 molecules are present, between 2700 and 2300 Å. continuous absorption results. Above 250°, where S_2 molecules appear and under a pressure of 0·05 mm., a band spectrum between 2927 and 2713 Å. was observed. Increase of pressure increases rapidly the number of these bands, which extend through the region 2475—3700 Å. These bands can be separated into three distinct regions: (A) between 3700 and 2794 Å., where is produced a fine structure corresponding with a quantisation of the molecular rotation, (B) between 2794 and 2592 Å., where the spectrum consists of narrow bands without fine structure, and (C) between 2592 and 2475 Å., where broad continuous bands are obtained. From the lines in the A region, the moment of inertia of the normal molecule, S_2, and the active molecule were calculated. The former is $12{\cdot}6\times10^{-40}$ and the latter $13{\cdot}8\times10^{-40}$.

The limit 2592 Å. corresponds with an internal transformation of the sulphur molecule requiring 102,100 cal./g.-mol., and that at 2475 Å., 110,000 cal./g.-mol.

H. T.

Ultra-violet Absorption Spectra of Ketens and of their Dimerides. G. C. LARDY (*J. Chim. Phys.*, 1924, **21**, 281—307).—The absorption spectra of ketens consist of two bands, one very intense, in the ultra-violet, and the other at the limit of the visible spectrum and analogous to that of acetone. The positions of the bands depend on the substituent group, the displacement being towards the visible spectrum and increasing with the molecular weight. The exaltation of the specific displacement above the normal indicates that the non-saturation and hence the velocity of polymerisation increases in the order keten (CH_2:C:O), diphenyl-, dipropyl-, and diethyl-keten, respectively. The intensity of the absorption of the first band indicates that the lability (or velocity of reaction with other compounds) of keten and its aliphatic

derivatives is approximately equal to that of acetone, whilst that of the diphenyl derivatives is much greater.

The absorption spectra of a number of α- and β-diketones, and derivatives of diketo*cyclo*butane have been determined. α-Diketones such as diacetyl have an absorption band similar to that of acetone but displaced towards the red. Non-enolic derivatives of diketo*cyclo*butane show two absorption bands, one in the ultra-violet, and a second generally resembling that of the group :C:O, of which the intensity is roughly equal to that of acetone for the lower homologues, but is much more intense for the dimethyl diphenyl derivative. The first band has been resolved into three or four bands. Diketodiphenyl*cyclo*butane shows two absorption bands, one very intense due to the enolic form, and corresponding to the band given by the enolic form of acetylacetone, and a second comparatively faint, indicating that in solution in hexane about 12% of the compound is present in the ketonic form. The absorption spectra indicate that diketodimethyl*cyclo*butane in solution in ether is present entirely in the enolic form, and possibly in the dienolic form. It gives two bands, one corresponding with that of acetone and the other with that of acetylacetone. A comparison of these spectra with those given by the dimeric forms of ketens indicates that the latter in solution do not exist as $(CH_2{:}CO)_2$, but entirely in the form $\begin{matrix}CH_2\cdot CO\\ |\quad\quad |\\ CO-CH_2\end{matrix}$ in equilibrium with a very small amount of the corresponding enolic form. The relations existing between the diazo compounds, the ketens, the azides, and the carbimides are discussed theoretically. W. H.-R.

Influence of Magnetic and Electrical Fields on Ultra-violet Fluorescence of Iodine. O. Oldenberg (*Z. Physik*, 1924, **27**, 189—194).—The intensity maximum in the ultra-violet fluorescence spectrum of iodine is slightly shifted towards the red by a strong magnetic field, but the spectrum at 3460 Å. which appears only in presence of foreign gases is unaffected. An electrical field has no influence on these spectra. S. B.

Fluorescence of Metallic Compounds of Hæmatoporphyrin. C. Dhéré, A. Schneider, and T. van der Bom (*Compt. rend.*, 1924, **179**, 1356—1358).—The zinc compound of hæmatoporphyrin is obtained by addition of zinc hydroxide to the ammoniacal liquid and is precipitated by acetic acid, whilst the tin compound is prepared by the action of stannous chloride. Their alcoholic solutions exhibit fluorescence in the red-yellow, showing two bands, and this spectrum of each is characteristic and differs from that of hæmatoporphyrin. The lead and cadmium compounds (cf. Milroy, A., 1919, i, 178) possess fluorescence in the same region, not so the copper, iron, and cobalt compounds. F. M. H.

Luminescence of Solid Nitrogen and Argon. J. C. McLennan (*Nature*, 1925, **115**, 46—47).—Polemical and explanatory, partly on a question of priority (cf. Vegard, A., 1924, ii, 805). A. A. E.

Spectroscopic Study of the Luminescent Oxidation of Phosphorus. H. J. EMELÉUS and W. E. DOWNEY (*J. Chem. Soc.*, 1924, **125**, 2491—2495).—Phosphorus burning under various conditions always emits light with fundamentally the same spectrum; the higher the temperature of the oxidation the broader are the spectrum bands and the greater is the intensity of the light in the visible region.

The following bands were observed when phosphorus burned in a gas containing 80% of oxygen: 2390, 2475, 2530, 2630, 3275 Å.; the flame temperature was 800°. The same bands were emitted, but resolved into narrow bands, when the burning took place in air under reduced pressure, the flame temperature being 125°. The glow emits the same bands as the low-temperature flame, but they are less intense. These results support those of Centnerszwer and Petrikaln (A., 1912, ii, 709) but not the more recent results of Petrikaln (A., 1924, ii, 289). S. K. T.

Spectra of Luminescence of Grignard Compounds. R. T. DUFFORD, D. NIGHTINGALE, and S. CALVERT (*J. Opt. Soc. Amer.*, 1924, **9**, 405—409; cf. A., 1923, ii, 714).—By the use of a spectroscope of high aperture ratio it is possible to photograph the chemiluminescence spectra of Grignard compounds. In all cases, they prove to be continuous. In certain cases, unstable oxidation products of the type ROMgX are obtained which are strongly fluorescent in ultra-violet light; but in these cases the spectra are either banded, or in any case not identical with the chemiluminescence spectra. Hence it is argued that the mechanisms of their formation are dissimilar. C. W. B.

Luminescence in the Ingleside Calcites Affected by Acids. W. P. HEADDEN (*Amer. J. Sci.*, 1924, [v], **8**, 509—517).—Certain specimens of colourless, transparent calcite phosphoresce in sunlight after exposure to radium emanation; lack of responsiveness in sunshine is attributed to variability in the efficiency of the latter (*Proc. Colo. Sci. Soc.*, **11**, 399). Specimens of calcite containing a yellow core of organic material are now found to be responsive only after washing with commercial hydrochloric acid and then exposing to radium emanation; unresponsive colourless calcite becomes responsive after the same treatment. When the coloured variety becomes ineffective, it is renewed by washing with acid, although less permanently and less strongly. Eventually a period of unresponsiveness is reached which is succeeded by one of responsiveness. The material then becomes permanently unresponsive. Other peculiar phenomena are recorded. The history of the sample has a large influence on its behaviour. Change in atomic structure is offered as the only explanation. S. K. T.

Theory of the Decay of α-Ray Luminescence. E. E. WITMER (*Physical Rev.*, 1924, **24**, 639—643).—Approximate and exact expressions are developed for the decay of luminosity in substances which exhibit luminescence under α-ray bombardment. A. A. E.

Relation between the Depolarisation of the Scattered Light and the Kerr Effect in Liquids. W. H. MARTIN (*J. Physical Chem.*, 1924, **28**, 1284—1290).—Gauss' theory (*Z. Physik*, 1923, **17**, 353) of the relation between the depolarisation factor of the scattered light and the Kerr constant of electric double-refraction has been tested for fifteen liquids. The values of the depolarisation factors calculated from theory agree with experimental measurements except in the case of chloroform, water, and methyl alcohol. Measurements of the depolarisation factor for nitrobenzene made in a magnetic field of 5000 gauss failed to discover any change in the degree of polarisation of the scattered light. M. B. D.

Activation of Chlorine by Electric Discharge. K. SCHAUM and A. FELLER (*Z. wiss. Phot.*, 1924, **23**, 66—71).—Chlorine may be activated by electric discharge of all kinds as discovered independently by Venkataramaiah (A., 1923, ii, 149). The activated chlorine reacts more rapidly with toluene, especially as regards the attack of the side chain. L. J. H.

Presentation of the Periodic System. W. PALMAER (*Z. physikal. Chem.*, 1924, **110**, 685—704).—Priority is claimed for the arrangement of elements in periods determined by $2n^2$ where $n=1$, 2, 3, or 4. A property of the elements showing marked periodicity is the normal electrode potential. In cases where the element has more than one valency, the potential corresponding to the lowest valency is considered. Any system of classification must be based on the valencies of the elements, especially towards oxygen. The author's periodic table consists of eight groups, the first seven of which are subdivided into a primary and a secondary group. The eighth group has one principal sub-group and three subsidiary sub-groups. Hydrogen and the alkali metals occupy the principal sub-group of Group I. The rare earths are arranged in the principal sub-groups of Groups III (boron, aluminium) and IV (carbon etc.). There is no zero group, the inert gases occupying the principal sub-groups of Group VIII. The subsidiary sub-groups of Group VIII are occupied by iron and related elements. Various arguments in support of the arrangement are put forward. J. S. C.

Fine Structure of the Free Benzene Molecule. J. BECKENKAMP (*Z. anorg. Chem.*, 1924, **139**, 220—232).—The structure of the benzene molecule previously described (cf. A., 1924, ii, 754) is based on two assumptions, *viz.*, the principle of closest packing and the arrangement of the hydrogen atoms in the spaces between the carbon atoms of a graphite structure. Neither of these assumptions is fully justified when the low atomic weights of carbon and hydrogen are considered. It is now assumed that the carbon atoms in the surface of a benzene crystal are arranged in an individual lattice very similar to that of graphite; with the help of Bragg's space lattice for the benzene crystal and certain principles previously described (cf. A., 1924, ii, 32, and *loc. cit.*), two possible arrangements of the hydrogen atoms in the crystal arise. The

most probable one is that in which the centres of gravity of the carbon atoms form a spacial six-membered ring of the ρ_2 type, whilst the hydrogen atoms, which lie with their axes perpendicular to the main axis of the molecule, form a plane ring. The thirty valency electrons are distributed as follows. One comes between each pair of carbon atoms. One is attached to each carbon atom on the side towards the interior of the molecule; three of these are above and three below the normal plane of the molecule. The attraction of these electrons by the atomic kernels and their repulsion by the binding electrons mentioned above control the elastic equilibrium of the molecule. The remaining electrons are distributed three on the outer surface of each carbon atom; one of these lies in the normal plane through the molecule and holds the hydrogen atom, whilst the other pair lie above or below this plane in alternate atoms. The latter are enantiomorphs, and according as the upper set or lower set is substituted, should give rise to optically active molecules.

This structure is correlated with the formerly proposed structure of graphite. In the benzene crystal, electrodynamic forces appear to have a large influence, whereas in graphite and diamond electrostatic forces are mainly concerned. The cleavage of diamond is now explained electrodynamically and three possible methods of twin formation are deduced. S. K. T.

Compressibility, Internal Pressure, and Chemical Affinity. E. Saerens (*J. Chim. Phys.*, 1924, **21**, 265—280).—If the affinity of chemical combination produces an internal pressure on the atoms concerned, the contraction of volume will be greater if the elements are easily compressible. Thus cæsium is more compressible than lithium, and the contraction in the formation of cæsium chloride is much greater than with lithium chloride. In a compound, the internal pressure is equally divided among the atoms, and the specific compressibility of the elements in a given binary halogen compound is constant and equal to that of the compound. In the halides of the alkali and alkaline-earth metals, the metal on combination undergoes a contraction of volume with increase of internal pressure, and the compressibility of the compound is less than that of the free metal. In the case of silver, thallium, lead, copper, etc., combination results in expansion with decrease of internal pressure, and the compressibility of the compound is greater than that of the metal. There is no essential difference between chemical affinity and the affinity of cohesion.

W. H.-R.

Determination of Molecular Fields. I. Viscosity. J. E. Jones (*Proc. Roy. Soc.*, 1924, **A, 106**, 441—462).—The temperature variation of the viscosity of gases can be explained on the assumption that the repulsion and attractive forces between molecules each vary with an inverse power of the distance. The attractive forces are supposed to follow an inverse cube law, whilst the repulsive force may be assumed to vary with any power between

15 and 25, viscosity measurements alone being insufficient to provide a unique solution. S. B.

Determination of Molecular Fields. II. Gaseous Equations of State. J. E. JONES (*Proc. Roy. Soc*, 1924, **A, 106**, 463—477; see preceding abstract).—The molecular model employed in the previous paper has also been used in the investigation of the equation of state for argon. To explain existing data in this way, even larger indices in the inverse power law governing the repulsive force have to be assumed than were necessary for the explanation of viscosity values. It is suggested that the molecular fields determined by the two methods are not strictly comparable. S. B.

Heat of Combustion of Glycogen. R. MEIER and O. MEYERHOF (*Biochem. Z.*, 1924, **150**, 233—242).—The following heats of combustion are given: *Mytilus* glycogen, water-free, 3820·5 (0·9 g.); hydrate, 3800; dissolved, 3789 cals. (0·9 g.). Frog glycogen, water-free, 3807 (0·9 g.); hydrate, 3786; dissolved, 3775·5 cals. (0·9 g.). J. P.

Anomalous Dispersion in the Field of *X*-Rays. E. HJALMAR and M. SIEGBAHN (*Nature*, 1925, **115**, 85—86).—The lattice constants of calcite and gypsum have been compared, a series of spectral lines with wave-lengths from 0·7 up to 5·2 Å. being used. When values of $d_1/d_2=\sin\phi_2/\sin\phi_1$ are plotted against wave-length, the graph shows two marked discontinuities coincident with the wave-lengths of the absorption edges of calcium and sulphur. A. A. E.

Compton Effect. D. L. WEBSTER and P. A. ROSS (*Nature*, 1925, **115**, 51).—Experiments designed to test the reality of the Compton effect gave spectra which showed the Compton-theory lines as strongly as in earlier investigations. A. A. E.

Influence of Atomic Arrangement on Refractive Index. W. L. BRAGG (*Proc. Roy. Soc.*, 1924, **A, 106**, 346—368).—The refractive indices of certain birefringent crystals have been calculated, on the assumption that the atoms composing the crystal are ionised, and that each type of atom, when polarised by the electrical force associated with radiation, acts as an electrical doublet with a characteristic moment, determined by a constant λ.

The indices of calcite, aragonite, and alumina have been successfully calculated on this theory, with the help of *X*-ray data concerning the relative positions of the atomic centres. It is shown that it may later be possible, conversely, to obtain information about crystal structure from refractivity data, although examination of the values for alkali halides shows that the simple theory here developed is limited in its application, and that the "constant" λ may vary with the nature of the surrounding atoms. S. B.

Theoretical Calculation of Rhombohedral Angle of Calcite etc. W. L. BRAGG and S. CHAPMAN (*Proc. Roy. Soc.*, 1924, **A, 106**, 369—377).—The rhombohedral angle (α) of calcite, 101° 55′,

is not determined by the symmetry of the crystal. The authors assume that calcite is an assemblage of ions, held in their equilibrium positions by the interplay of the attractive electrostatic forces, and of repulsive forces of some kind, which are effective over a small range only. The electrostatic energy of the system may then be calculated for various values of α, and it is found that the angle giving a minimum energy is within 3° or 4° of the observed angle. The alteration of α with substitution of other metals for calcium is quantitatively explained. S. B.

Effect of Cold Rolling on Structure of Cubic Crystals. F. Weber (*Z. Physik*, 1924, **28**, 69—90).—Plates of iron and aluminium have been subjected to cold rolling and the resulting crystal deformations analysed by the *X*-ray method. The chief effect of the rolling is to cause a translatory motion along the glide planes of the crystals. When the deforming forces applied are great, a rotation of the component crystals also takes place about some important crystallographic direction. S. B.

Atomic Structure of Two Intermetallic Compounds. E. A. Owen and G. D. Preston (*Proc. Physical Soc.*, 1924, **36**, 341—348).—Magnesium silicide has a face-centred cubic lattice of silicon atoms of side 6·391 Å. symmetrically intermeshed with a simple cubic lattice of magnesium atoms of side 3·19 Å. The density from *X*-ray data is $1{\cdot}95\pm0{\cdot}05$ g./c.c. Aluminium antimonide has a face-centred cubic lattice of antimony atoms of side 6·126 Å. intermeshed with an identical lattice of aluminium atoms. The density from *X*-ray data is $4{\cdot}23\pm0{\cdot}04$ g./c.c. L. J. H.

Crystal Structure of Mercuric Sulphide. I. N. H. Kolkmeijer, J. M. Bijvoet, and A. Karssen (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 390—392).—Black precipitated mercuric sulphide is of face-centred cubic structure like zinc sulphide. The lattice parameter is $5{\cdot}85\times10^{-8}$ cm., the density is 7·69, and the radius of the atomic domain of mercury is $1{\cdot}51\times10^{-8}$ cm. There are four molecular groups per unit cell. L. J. H.

X-Ray Analysis of Mother-of-Pearl. J. H. Shaxby (*Compt. rend.*, 1924, **179**, 1602—1603; cf. A. Dauvillier (*ibid.*, 819); W. L. Bragg, A., 1924, ii, 373).—Laue diagrams, taken with a silver anticathode, show pseudo-hexagonal symmetry in the plane of stratification, whilst at right angles to the latter a rectangular arrangement of atoms is indicated. The structure is identical with that found by Bragg for aragonite. W. A. C.

Crystal Structure of Cuprite and Rutile. G. Greenwood (*Phil. Mag.*, 1924, [vi], **48**, 654—663).

Crystalline Form of Organic Derivatives of Arsenic. II. G. Gilta (*Bull. Soc. chim. Belg.*, 1924, **33**, 532—538).—A detailed crystallographic examination has been made of the potassium, ammonium, and lithium salts of *p*-aminophenylarsinic acid (cf. A., 1923, i, 407). Potassium salt, anhydrous: orthorhombic, [$a:b:c=0{\cdot}778011:1:0{\cdot}758124$], conchoidal fracture. The causes

of the occurrence of abnormal faces are discussed. Lithium salt, anhydrous: monoclinic, [$a:b:c=0{\cdot}944731:1:0{\cdot}830419$, $\beta=91°\ 16'$]. Ammonium salt, dihydrate: orthorhombic, [$a:b:c=1{\cdot}037944:1:0{\cdot}657969$], conchoidal fracture. W. E. E.

Crystal Form and the Crystal Lattice. M. YAMADA (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **13**, 53—74).—A mathematical paper in which the crystal forms of substances are derived from the structure of the lattice by means of the surface energy relationships of Born and Stern (A., 1919, ii, 418). Assuming a homopolar lattice and that the potential energy of the mutual action of a pair of atoms in the lattice is negligible except in the case of the two nearest atoms, Wulff's polyhedron (*i.e.*, the crystal form) is a cube for the simple cubic lattice, a cubo-octahedron for the face-centred cubic lattice, a rhombic dodecahedron for the space-centred cubic lattice, and an octahedron for the diamond lattice. If the assumption is made that the range of atomic action reaches the second nearest atoms, the shapes of the polyhedra are modified slightly, the cube having its corners cut off by octahedral planes, the cubo-octahedron having its cubic planes enlarged or diminished, the rhombic dodecahedron having its corners replaced by planes of the cube, and the octahedron undergoing slight changes of shape. The calculated shapes agree well with those found for some of the elements under ideal conditions. A. R. P.

Crystal Structure of Dolomite. R. W. G. WYCKOFF and H. E. MERWIN (*Amer. J. Sci.*, 1924, [v], **8**, 447—461).—The Laue diagram for dolomite is of a lower symmetry than that for calcite, indicating that dolomite is not a solid solution of calcite and magnesite, but is a definite crystalline species. The symmetry is either C_4^3 or Ci_2^3; the positions of the carbon and the oxygen atoms were not determined. Pure magnesium and iron-rich dolomites have units of practically identical shapes and sizes. S. K. T.

Electrical Conductivity of Metals. F. SIMON (*Z. Physik*, 1924, **27**, 157—163).—A theory is developed for the electrical conductivities of metals and their variations with temperature and physical conditions. These properties are regarded as being determined solely by the character of the outermost shell of electrons in the constituent atoms. S. B.

Optical Properties of Amino-acids. G. L. KEENAN (*J. Biol. Chem.*, 1924, **62**, 163—172).—Photomicrographs and crystallographic details are given of glycine, alanine, valine, leucine, serine, cystine, phenylalanine, tyrosine, tryptophan, and aspartic and glutamic acids. C. R. H.

Thermal Expansion of Bismuth Crystals. J. K. ROBERTS (*Proc. Roy. Soc.*, 1924, **A**, **106**, 385—399).—The coefficients of thermal expansion of bismuth crystals are constant between the ordinary temperature and 240°. The values given are: perpendicular to the crystal axis, $12{\cdot}0\times10^{-6}$; parallel to the axis,

$16{\cdot}2\times10^{-6}$; mean $13{\cdot}4\times10^{-6}$. Over the range of 30° lying between 240° and the melting point, the expansion falls off very markedly. An explanation of this fact is considered, based on the idea that a certain number of the atoms may here possess sufficient energy to dissociate themselves from their neighbours in the lattice. The linear law connecting the specific heat of pure solids with temperature, even up to their melting point, makes the explanation untenable, and the phenomenon is probably to be traced to the presence of impurities. S. B.

Changes in State of Aggregation and Polymorphism. II. Microscopical Study of Transition Processes. K. SCHAUM and W. RÖRIG (*Z. anorg. Chem.*, 1923, **132**, 77—89; cf. A., 1922, ii, 264).—An attempt has been made to determine the rate of transition from one crystalline form of a substance to another, by studying the behaviour of a thin layer of the substance when observed under the microscope with the aid of polarised light. The method has been tested by determinations of the linear velocity of crystallisation, both along a thin-walled tube inoculated at one end, and also radially from a point on a plate on which the molten material was spread. Suitable compounds for studying the rate of transition are difficult to find. Benzil-*o*-carboxylic acid, forming a yellow modification, which is a true benzil compound, at higher temperatures, and a white isomeride, resembling a lactone, at lower temperatures, has been examined. Tautomeric transformation was found to take place in the completely dry, crystalline state. In the gaseous condition, transition only occurs slowly. From the molten acid the yellow form alone separates. Determinations of the velocity of crystallisation when the melt is seeded, in one case with the white variety, and in the other with the yellow, show that it is much slower in the first than in the second case. No difference of solubility in chloroform has been found between the two varieties, possibly owing to an immediate transformation to the less soluble form on contact with the liquid. Benzil-*o*-carboxylic acid forms a unary-pseudobinary system. 3-Phenylindazole appears to behave similarly.

A microscopical study has also been made of the separation of the constituents in the crystalline aggregates obtained by freezing fused mixtures of organic compounds. Such observations are rendered difficult by polymorphic changes. M. S. B.

Heat of Transformation of Martensite. W. SCHNEIDER (*Werkstoffausschusses Ver. deut. Eisenhüttenleute, Bericht*, 1923, No. 32).—The heat of transformation of γ-iron into α-iron is computed to be 13·2 cal. per g., decreasing linearly with increasing carbon content, and vanishing at 6·68% C. If martensite is assumed to be a solid solution of Fe_3C in α-iron, the heat of solution of Fe_3C is 33·2 cal. per g. CHEMICAL ABSTRACTS.

Atomic Heat of Silver at High Temperatures. A. MAGNUS and A. HODLER (*Z. physikal. Chem.*, 1924, **110**, 188—191).—The specific heat of silver has been determined at temperatures between the ordinary temperature and 900°. The variation of the atomic

heat with temperature is given by $C_p=6{\cdot}047+7{\cdot}49\times10^{-4}t+7{\cdot}12\times10^{-7}t^2$. The value of C_v calculated from C_p, after first passing through a maximum, diminishes linearly with increasing temperature, in good agreement with the equation of Born and Brody (*Z. Physik*, 1922, 8, 205), $C_v=3R(1-3\sigma RT)$, where σ has the value $5{\cdot}53\times10^{-5}$. J. S. C.

Investigations of Specific Heat at Low Temperatures. F. Lange (*Z. physikal. Chem.*, 1924, **110**, 343—362).—A convenient apparatus for the determination of specific heats at low temperatures is described. The specific heats of quinol, quinone, quinhydrone, tungsten, iodine, and the two forms of tin were determined over a range of temperature 20—300° Abs. The specific heats of iodine and white and grey tin were also investigated over the range 9—14° Abs., employing the apparatus of Simon and Lange (A., 1923, ii, 458), the measurements verifying the reported transition of iodine at the temperature of liquid hydrogen. Calculations of the chemical constants of tungsten and diatomic iodine give the values $3{\cdot}68\pm0{\cdot}72$ and $3{\cdot}37\pm0{\cdot}20$, respectively. The data for tin are in agreement with the Nernst heat theorem. J. S. C.

Flow of Single Crystals. W. Geiss (*Z. Physik*, 1924, **29**, 78—80; cf. Schönborn, *ibid.*, 1922, **8**, 377).—The rate of movement of a tungsten crystal under different loads has been studied as a function of the time, the load being applied for 1 or 2 hours. With relatively small loads, the flow velocity decreases with time, and a consolidation of the material takes place which results in an increase in the elasticity limit. By increasing the load, the initial velocity is increased, but the retardation decreases until it becomes zero, that is, the flow velocity is constant. This is the extension limit. With still higher loads, the flow velocity increases with time, and plastic deformation begins above the elasticity limit. The exponential relation between the velocity of flow v, the load P, and the time of application t is given by the following equation, $v=A\,.\,e^{B(P-P_s)t}\,.\,[e^{C(P-P_E)}-1]$, where A, B, and C are constants, and P_s and P_E represent the loads at the extension limit and the elasticity limit, respectively. M. S. B.

Molecular Weight of Selenium Dioxide in Ethyl Alcohol. E. B. R. Prideaux and G. Green (*J. Physical Chem.*, 1924, **28**, 1273—1278).—The molecular weight of selenium dioxide by the elevation of the boiling point of ethyl alcohol, using the figure for constant molar elevation of 11·9, was found to be 122·6 (mean of 44 determinations), instead of the theoretical value 111·2. There is no trend in the molecular weights up to a concentration of 55 g. in 100 g. of alcohol. After a correction for the volatility of selenium dioxide has been applied, the mean molecular weight is found to be 117·5. M. B. D.

Specific Heat of Bromine at Low Temperatures and its Chemical Constant. R. Suhrmann and K. von Lüde (*Z. Physik*, 1924, **29**, 71—77).—The molecular heat of bromine at

constant pressure, between the temperatures 20·45° and 154·9° Abs., as determined in a vacuum calorimeter, increases from 3·52 to 12·64 cal./mol. over this range. With the help of these values and the vapour-pressure curve deduced from the observations of other investigators, the value of i has been found equal to 2·546± 0·10 (referred to atmospheres), and the heat of vaporisation at absolute zero 10980 cal./mol. (cf. Eucken, Karwat, and Fried, this vol., ii, 98). M. S. B.

Determination of the Molecular Thermal Conductivity and the Molecular Heat of Diatomic Gases at Low Temperatures. E. SCHREINER (*Z. physikal. Chem.*, 1924, **112**, 1—67).—The molecular heats of nitrogen, oxygen, and carbon monoxide were determined and no deviation from the normal value was observed on lowering the temperature to 64° Abs. This result is not in agreement with those of Scheel and Heuse (A., 1913, ii, 183) and of Eucken (A., 1913, ii, 474), who, working with these gases at temperatures not lower than 80° Abs., found that some loss of molecular heat had already occurred. The method employed of determining molecular heats depends essentially on a knowledge of molecular heat conductivity. The experimental determination of this value is based on that of Knudsen (A., 1911, ii, 368) and is described and discussed in detail. L. F. G.

Theory of Degraded Gases and Null Point Energy. K. BENNEWITZ (*Z. physikal. Chem.*, 1924, **110**, 725—767).—Mathematical. The laws of thermodynamics and the extended correspondence principle are not sufficient to determine whether an ideal supercooled gas will possess energy at absolute zero. Equations are deduced for the entropies and chemical constants of degraded gases. A complete thermodynamical survey of the equation of state is made and the limiting forms are compared at $T=0$ and $T=\infty$ on the assumptions of the existence and absence of energy at absolute zero. The existence of null point energy is further considered in reference to the integrated Clausius–Clapeyron equation. J. S. C.

Revised Trouton Rule for the Heat of Vaporisation and the Quantum Theory. A. BYK (*Z. physikal. Chem.*, 1924, **110**, 291—317).—The "constant" of the Trouton rule diminishes rapidly at low temperatures. A mathematical theory is developed, the problem being treated from the point of view of the author's quantum theory of corresponding states (*Ann. Physik*, 1921, [iv], **66**, 157; 1922, [iv], **69**, 161) and Bakker's theory of the heat of vaporisation. An equation is derived expressing the Trouton ratio as a universal function of the reduced temperature and volume. The values calculated for more than forty liquids ranging from hydrogen to stannic chloride are in fairly close agreement with those actually determined. J. S. C.

Entropy of Condensed Gases at the Absolute Zero. A. EUCKEN and F. FRIED (*Z. Physik*, 1924, **29**, 36—70; cf. this vol., ii, 98).—The integration constant i_k of the thermodynamic

formula for chemical equilibrium has been determined for a number of homogeneous and heterogeneous reactions. The values thus obtained are more exact than by any previous determinations, and they show that the relationship $i_k=\Sigma i$, required by Nernst's heat theorem, is not in general fulfilled. This necessitates a finite value for the entropy of a substance in the solid state at the absolute zero, and it has been shown that, for hydrogen, and probably for a number of other substances, this entropy is probably of the order of $R \log_n 2$. M. S. B.

Constant i of the Thermodynamic Vapour-pressure Equation for Polyatomic Molecules. A. EUCKEN, E. KARWAT, and F. FRIED (*Z. Physik*, 1924, **29**, 1—35).—A theoretical paper in which the value of the integration constant of the thermodynamic vapour-pressure equation, i, which is a function of the entropy constant of the gas, the entropy at absolute zero of the condensed liquid, and also of the specific heat at absolute zero, has been determined for a large number of gases, partly on the basis of recent determinations of the specific heat and vapour pressure at low temperatures. The mean error has also been calculated. The value of the moment of inertia of the molecule deduced from this value of i by statistical methods has been compared with that determined optically from the band-spectra of the gases, hydrogen, nitrogen, oxygen, nitric oxide, carbon monoxide, hydrogen chloride, hydrogen bromide, hydrogen iodide, carbon dioxide, and water. In all cases, the difference between the two is greater than the experimental error. M. S. B.

Chemical Constants of Chlorine, Bromine, and Iodine in the Monatomic and Diatomic States. K. WOHL (*Z. physikal. Chem.*, 1924, **110**, 166—187; cf. Simon, following abstract).—The differences between the observed and theoretical values of the chemical constants of iodine, bromine, and chlorine in the monatomic state increase with their heats of dissociation. The experimental values for the various constants are as follows, theoretical values being in parentheses: Cl, +1·66 (+0·73); Br, +2·07 (+1·27); I, +2·08 (+1·56); Cl_2, +1·96; Br_2, +2·86; I_2, +3·44; HCl, −0·40. J. S. C.

Chemical Constants of Monatomic Gases. F. SIMON (*Z. physikal. Chem.*, 1924, **110**, 572—586).—A comparison of the recently determined values of the chemical constants of fourteen elements with the theoretical values shows that the deviations increase with increasing heats of vaporisation. J. S. C.

Physico-chemical Investigations on Compounds of the *cyclo*Hexane Series. W. HERZ and W. BLOCH (*Z. physikal. Chem.*, 1924, **110**, 23—39).—A number of physico-chemical constants of carefully purified compounds of the *cyclo*hexane series have been determined. *cyclo*Hexanone: b. p. 155·9°/760·2 mm., d^0 0·9625, $n_D^{19·3}$ 1·45066, sp. ht. 0·433, surface tension in dynes/cm. at 45° (γ) 32·33, $\eta^{39·1}$ 0·01549. *o*-Methyl*cyclo*hexanone: b. p. 164·9°/756·3 mm., d^0 0·9423, $n_D^{16·7}$ 1·44916, sp. ht. 0·436, γ^{45} 29·61,

$\eta^{39\cdot1}$ 0·01217. *m*-Methyl*cyclo*hexanone: b. p. 64·5°/18·3 mm., d^0 0·9309, $n_D^{17\cdot3}$ 1·44635, sp. ht. 0·441, γ^{45} 28·36, $\eta^{39\cdot1}$ 0·01226. *p*-Methyl*cyclo*hexanone: b. p. 60·5°/16·8 mm., d^0 0·9312, $n_D^{15\cdot7}$ 1·44585, sp. ht. 0·441, γ^{45} 28·91, $\eta^{39\cdot1}$ 0·01234. *cyclo*Hexanol: m. p. 22°, b. p. 161·1°/751·3 mm., d^0 0·9627, $n_D^{20\cdot7}$ 1·46542, sp. ht. 0·417, γ^{45} 31·37, $\eta^{39\cdot1}$ 0·2032. *o*-Methyl*cyclo*hexanol: b. p. 167·2°/756·5 mm., d^0 0·9458, $n_D^{16\cdot4}$ 1·46215, sp. ht. 0·418, γ^{45} 29·43, $\eta^{39\cdot1}$ 0·06977. *m*-Methyl*cyclo*hexanol: b. p. 76·0°/16 mm., d^0 0·9353, $n_D^{16\cdot2}$ 1·46065, sp. ht. 0·422, γ^{45} 27·13, $\eta^{39\cdot1}$ 0·09676. *p*-Methyl*cyclo*hexanol: b. p. 76·7°/15·0 mm., d^0 0·9328, $n_D^{15\cdot4}$ 1·45916, sp. ht. 0·423, γ^{45} 27·94, $\eta^{39\cdot1}$ 0·1436. Methods for the calculation of other quantities from the above data are given. The influence of admixture with methyl alcohol, ethyl alcohol, and propyl alcohol on the density and viscosity of *cyclo*hexanone and *cyclo*hexanol has been investigated.

J. S. C.

Melting Point of Platinum. F. HOFMANN (*Z. Physik*, 1924, **27**, 285—304).—The melting point of platinum has been redetermined, for use as a thermometric fixed point, by means of comparisons at three wave-lengths of the intensities of the black body radiation from an iridium resistance furnace, maintained successively at the melting points of gold and of platinum. The value adopted for the melting point of platinum is 1771±2°. S. B.

The Three-temperature Rule. M. PRUD'HOMME (*J. Chim. Phys.*, 1924, **21**, 242—246).—The rule connecting the m. p., b. p., and critical temperature (A., 1921, ii, 376) has been found to give fairly good results for a number of chemically different substances.

W. H.-R.

Temperature Gradient in Gases at Various Pressures. W. MANDELL and J. WEST (*Proc. Physical Soc.*, 1924, **37**, 20—40).—Determinations have been made of the temperature gradients in air and hydrogen contained at various pressures ranging from atmospheric down to about 0·001 mm. in a cylindrical brass vessel 3·9 cm. long and 12 cm. in diameter, the end faces of which were maintained respectively at about 180° and 50°. The results definitely indicate the existence at low pressures of very large "temperature jumps" in the neighbourhood of the walls of the vessel. The general character of the results obtained is explained on the assumption of the presence on the walls of a gas film possessing properties arising from the attraction between molecules of the material of the wall and of the gas. J. S. G. T.

Superheating of Liquids. F. B. KENRICK, C. S. GILBERT, and K. L. WISMER (*J. Physical Chem.*, 1924, **28**, 1297—1307).—Various liquids, having boiling points ranging from −10° to 183°, have been superheated 50—170° by heating them in open capillary tubes at atmospheric pressure or by reducing the pressure on the liquids in closed capillary tubes at constant temperature. Various methods of treating both the tubes and the liquids are given and the conclusion is drawn that the initiation of bubbles from freshly-prepared capillary tubes is connected with nuclei loosely attached to the

walls of the vessel and to a property of the liquid in which there is an element of chance. Preparation of "mote-free" liquid and removal of adsorbed gases on the glass or dissolved gases in the liquid had no appreciable effect. The radius of the bubbles (calculated from the surface tension and the vapour pressure at the maximum temperature) which can exist in equilibrium with the liquids at the highest temperature varies from 2·5 to 16 $\mu\mu$. A simple relation is given between the external pressure and the maximum temperature attainable at this pressure, which holds in the case of ether over a wide range of pressure. M. B. D.

Experiments on the Carbon Arc. Vapour Pressures of Carbon. H. KOHN and M. GUCKEL (*Z. Physik*, 1924, **27**, 305—357).—Measurements have been made of the surface brightness of the anode of the carbon arc burning in various gases at pressures between 0·05 and 5·0 atm. The maximum temperature of the anode is thus found to be independent of the nature of the surrounding gas, and presumably depends solely on the vapour pressure of carbon. The heat of sublimation of carbon can be calculated from the change in temperature of the anode with gas pressure, from the Clausius–Clapeyron equation, and is given as 139·2 kg.-cal.$\pm$7% (at the ordinary temperature), in agreement with the value of 141·4 for a monatomic vapour, obtained from the chemical constant (cf. Fajans, A., 1922, ii, 818). The temperature of the negative carbon has also been measured. Its limiting maximum value appears to be the same as that of the positive crater. S. B.

Critical Pressure-ratio for Gases as affected by Variable Specific Heat. W. J. WALKER (*Phil. Mag.*, 1924, [vi], **48**, 703—707; cf. *ibid.*, 1922, [vi], **43**, 589).—The critical pressure-ratio during maximum discharge conditions of gases through orifices under variable specific heat conditions has been deduced and takes the form $p_2/p_1=(2/m+1)^{m/(m-1)}\{1+[3\lambda T_2(m-1)]/4(m+1)\}$. At normal temperatures, $[3\lambda T_2(m-1)]/4(m+1)$ is practically negligible. H. T.

Viscosities of Gases [Hydrogen and Helium] at Low Temperatures. P. GÜNTHER (*Z. physikal. Chem.*, 1924, **110**, 626—636).—The viscosities of hydrogen and helium have been determined at low temperatures (15—80° Abs.). The viscosity of hydrogen in the vicinity of 20° Abs. varies as $T^{3/2}$, in accordance with the Nernst theory. The behaviour of helium does not, however, conform to the theoretical requirements. J. S. C.

Origin of Free Oxygen in the Air. G. TAMMANN (*Z. physikal. Chem.*, 1924, **110**, 17—22).—An attempt is made to estimate the epoch in which free oxygen first appeared in the atmosphere. Oxygen, as such, is not found in lava or occluded in erupted rock. The possibility of molecules leaving the gravitational field of the earth is discussed and it is shown that the necessary velocity is 11 km./sec. From the mathematical treatment it appears that only the hydrogen molecule at very high temperatures is likely

to attain a velocity of this order. Free atmospheric oxygen probably made its appearance after the commencement of the solidification of the earth's upper crust. J. S. C.

Volume in Liquid Mixtures. R. Lorenz and W. Herz (*Z. anorg. Chem.*, 1924, **140**, 399—404).—The values of $\psi=(n^2-1)/(n^2+2)$ have been calculated for different concentrations of twelve binary liquid mixtures from the value of n for the mixture and from the values of ψ for each of the constituents according to the rule of mixtures. The two values thus obtained for each mixture agree fairly closely, but there is sufficient difference to indicate that the volume of mixtures is not strictly additive. Using the value of n for the solid salt, the volume of solutions of varying concentrations of potassium or sodium chloride in water agrees quite closely with that obtained by the rule of mixtures. A. R. P.

Contraction of Ethyl Alcohol on Dilution. H. P. Foran (*J. Soc. Chem. Ind.*, 1924, **43**, 338—340T).—The percentage contraction, C, when ethyl alcohol is diluted with water is given by the relation $C=3(V/P-1{\cdot}02)$, where V is the percentage increase in volume when the water is added and P the percentage decrease in strength. P, V, and V/P must not exceed 45%, 90%, and 1·90, respectively. S. K. T.

Vaporisation of Liquid Mixtures. J. F. King and S. P. Smedley (*J. Physical Chem.*, 1924, **28**, 1265—1272).—Three methods are described for determining the exact composition of the constant-evaporating mixtures of two miscible liquids. The constant-evaporating mixture for carbon tetrachloride and ethyl alcohol at 20° was found to contain 17·4% of ethyl alcohol by volume. The densities at 20°/4° for various mixtures have been tabulated. The methods are: determination of the maximum vapour pressure by Smith and Menzies' "submerged bubblet" method, change in the refractive index after evaporation, and density change after a given amount of air has been bubbled through the liquid. M. B. D.

Determination of the Vapour Pressures and of the Composition of the Vapour Phases in Equilibrium with Aqueous Solutions of Hydrogen Chloride and Hydrogen Bromide at Different Temperatures. M. Wrewsky, N. Sawaritzky, and L. Scharloff (*Z. physikal. Chem.*, 1924, **112**, 97—108).—The compositions of the vapour phases have been determined at about 20°, 55°, and 80°. A wide range of concentrations of the solutions was employed. The partial pressures of acid and water, respectively, are calculated. For both series of solutions, the total vapour pressure falls with increasing concentration to a minimum and then rises sharply. This sudden rise is due to the partial pressure of the halogen compound, which is negligible until the region of the minimum is reached, but then increases extremely rapidly. The compositions of the constant-boiling hydrogen chloride solutions agree very closely with those recorded by Roscoe and Ditmar (*Annalen*, 1860, **116**, 214). L. F. G.

Equilibrium between Liquid and Gaseous Phases of Aqueous Solutions of Hydrogen Chloride and of Hydrogen Bromide. M. WREWSKY (*Z. physikal. Chem.*, 1924, **112**, 109—116).—Theoretical. The change of vapour pressure of binary solutions with temperature and heat of formation is examined, and an expression derived with which the data available for hydrogen chloride, bromide, and iodide solutions are shown to be in agreement (cf. preceding abstract). L. F. G.

Determination of the Boiling and Condensation Curves of Mixtures of Hydrochloric Acid and Water under a Pressure of 760 mm. E. CARRIÈRE and ARNAUD (*Compt. rend.*, 1924, **179**, 1265—1267).—The results given correlate (1) boiling point with percentage of hydrogen chloride in the boiling liquid for the range 19—110—100°, and 41·9—20·15—0·03% HCl, and (2) temperature of distillation with percentage of hydrogen chloride in the distillate, for the range 20°—110°—100° and 100—20·15—0%. The results agree with those of Roscoe and Dittmar (T., 1859, **12**, 128) and conform to the Gibbs–Konovalov law (cf. A., 1923, ii, 555). T. H. P.

Equilibrium between Vapour and Liquid of Aqueous Solutions of Ammonia. M. WREWSKY (*Z. physikal. Chem.*, 1924, **112**, 117—127).—Theoretical. Data now available (cf. this vol., ii, 101, and above) are shown to be in agreement with values calculated from thermodynamic considerations. L. F. G.

Influence of Thin Surface Films on the Evaporation of Water. G. HEDESTRAND (*J. Physical Chem.*, 1924, **28**, 1245—1252).—The rate of evaporation of water into dry air from a surface of 18·2 sq. cm. at 20° has been measured. The amount of water evaporated for a given rate of flow was found to vary with the height of the edge of the vessel above the water surface. The evaporation increases with increased rate of flow of the dry air up to a limiting value. Films 1 mol. thick of palmitic and oleic acids were formed on the water surface by dissolving them in benzene and allowing it to evaporate. No change was observed in the rate of evaporation. Saponin solutions, which have a very low surface tension, due to adsorbed molecules at the interfacial surface, also had no effect. Salt solutions lowered the rate of evaporation in the ratio of the partial pressure of the solution to that of pure water. The surface films formed by adsorbed substances at the interfacial surfaces or by unimolecular layers must therefore follow the thermal agitation of the water molecules and do not exist as an impermeable layer on the surface. M. B. D.

Behaviour of the Simple Halides with Water. N. V. SIDGWICK (*J. Chem. Soc.*, 1924, **125**, 2672—2674).—The suggestion that the maximum covalency of an element depends on its position in the periodic table (A., 1924, i, 506) is shown to explain the various reactions of simple halides in aqueous solution, viz., ionisation, hydrolysis, either of the type $XCl \rightarrow XOH + HCl$ or $XCl \rightarrow XH + HOCl$, and no reaction. It is shown that hydration should facilitate

ionisation and that elements with a maximum covalency of four should form uni- and bi-valent cations, whereas those with a co-valency of six should also form tervalent ions. When ionisation is no longer possible, the water tends to attach itself to the molecule and to react with the halogen (*e.g.*, silicon tetrachloride). Carbon tetrachloride does not react because it cannot ionise and has a complete octet in which the carbon, unlike the silicon in silicon tetrachloride, is exerting its maximum covalency so that the molecule cannot take up water. Nitrogen trichloride reacts with water with formation of hypochlorous acid by offering its unshared pair of electrons to the hydrogen of the water, producing $Cl—N(Cl_2) \rightarrow H—O—H$, which then decomposes. S. K. T.

Critical Solution Temperature of Ternary Mixtures. A. Boutaric and G. Corbet (*Compt. rend.*, 1924, **179**, 1319—1322).—The miscibility of water with binary mixtures of phenol, aniline, salicylic acid, and benzoic acid has been examined. Where the two substances are chemically similar (*e.g.*, benzoic and salicylic acids), the critical solution temperature is a linear function of the composition. Experiments have also been made on the miscibility of phenol with mixtures of various alcohols and water. L. L. B.

Diffusion in Mixed Crystals. H. Braune [with H. Hellweg] (*Z. physikal. Chem.*, 1924, **110**, 147—165).—The lattice structure of crystals necessitates the vibration of atoms about equilibrium positions, their mean centres of gravity being fixed. The electrical conductivity of solid salts and the phenomenon of diffusion demonstrate the possibility of the atoms changing position. The probability of this is, however, small, and diffusion takes place in solid bodies only with measurable velocity in the neighbourhood of the melting point. Mixed crystals of the metals of the copper group are particularly suitable for diffusion experiments, since they form no intermetallic compounds and are apparently completely miscible. On the assumption that the rate of diffusion is dependent on the amplitude of atomic vibration, the expression is derived $D_T = Ce^{-3b^2T_s/T}$, where D_T is the diffusion coefficient at temperature T, T_s the m. p., b a constant, and C a constant characteristic of the substance. A description of the experimental technique for the determination of the diffusion of gold into silver is given, the values of D_T at various temperatures being in close agreement with the above expression. Copper diffuses more readily into those silver–gold alloys which are rich in the former metal. The alteration in the electrical conductivity of solid electrolytes with temperature may be represented by the formula $\kappa = Ce^{-\beta/T}$. J. S. C.

Cast Alloys of Aluminium containing Small Amounts of Magnesium. S. Daniels (*Ind. Eng. Chem.*, 1924, **16**, 1243—1249).—The effect of the addition of small proportions of magnesium to aluminium which contains silicon and iron as impurities appears to be the formation of magnesium silicide, Mg_2Si. The equilibrium between silicon, iron, and aluminium is materially

altered, the iron existing chiefly or entirely as $FeAl_3$. [Cf. *B.*, 1925, 73.] C. I.

Hardness of Copper–Tin Alloys. O. BAUER and O. VOLLENBRUCK (*Z. Metallk.*, 1924, **16**, 426—429).—The curve showing the hardness of copper–tin alloys rises slowly with increase of tin to 13·9%, the limit of the solid solution, then rapidly to a maximum at the point corresponding with Cu_4Sn; it then falls rapidly to a point corresponding with Cu_6Sn_5, after which the slope is gradual to pure tin. A slight kink occurs in the downward portion of the curve at Cu_3Sn. [Cf. *B.*, 1925, 73.] A. R. P.

Gold–Copper Alloys. E. SEDSTRÖM (*Ann. Physik*, 1924, [iv], **75**, 549—555).—The thermoelectric power against copper, heat conductivity, and electrical resistance of gold–copper alloys, prepared by fusion in a vacuum, have been determined. The heat conductivity was calculated from the thermoelectric effect by Borelius' method (*ibid.*, 1917, **52**, 398; 1918, **56**, 338). The results confirm the existence of a compound AuCu (cf. Kurnakov, Shemtschushni, and Zasedatelev, *J. Inst. Metals*, 1916, **15**, 305). The alloys which approximate to this composition are extremely brittle. A similar study has been made of a number of other alloys, but the results are recorded elsewhere (*Dissertation*, Stockholm, 1924). M. S. B.

Coefficients of Thermal Expansion for Aluminium Alloys and Alloys of Nickel–Iron and Cobalt–Iron. K. HONDA and Y. OKUBO (*Sci. Rep. Tôkohu Imp. Univ.*, 1924, **13**, 101—107).—A table showing the mean coefficients of linear expansion of aluminium, magnesium, and eleven light aluminium alloys for several temperature ranges from 20° to 500° is given, together with curves showing the variation of this coefficient in the iron–nickel and iron–cobalt alloys with the nickel and cobalt content, respectively. A very pronounced minimum in the first-named series occurs with 35% Ni, corresponding with the so-called "Invar" alloys; the cobalt curve, on the other hand, is fairly flat and more or less regular. [Cf. *B.*, 1925, 73.] A. R. P.

Influence of Indifferent Gases on the Saturated Vapour Concentrations of Liquids. F. POLLITZER and E. STREBEL (*Z. physikal. Chem.*, 1924, **110**, 768—785).—The alteration in the saturated vapour concentration of a liquid in presence of a compressed, chemically indifferent gas is due to two factors, the pressure exerted on the liquid and the solvent action of the gas on the vapour. The former causes an increase in the partial pressure over the liquid, independent of the nature of the gas and depending only on the pressure exerted. The second factor causes an increase characteristic of the gas concerned. The influence of hydrogen, air, and carbon dioxide on the vapour pressure of water and of hydrogen and nitrogen on the vapour pressure of liquid carbon dioxide has been investigated over a pressure range up to 200 kg./cm.^{2}. An equation is derived representing the increase in vapour pressure as a function of the total pressure. Deviations

are ascribed to the solvent action of the compressed gas. In the case of water this is negligible for hydrogen, small for air, and considerable for carbon dioxide. J. S. C.

Supersaturation of Gases in Liquids. F. B. KENRICK, K. L. WISMER, and K. S. WYATT (*J. Physical Chem.*, 1924, **28**, 1308—1315).—When water is saturated with oxygen and carbon dioxide, at concentrations corresponding with about 16 atm., bubbles do not form in an appreciable time when the pressure is reduced to 1 atm. at the ordinary temperature, but only after heating at about 60°. Colloidal platinum favours the formation of bubbles in water supersaturated with oxygen, but rapidly loses its effectiveness. Although carbon dioxide is thirty times as soluble as oxygen, the average time before bubble formation is about the same for the two gases when they are at the same temperature and when the supersaturation corresponds with the same equilibrium pressure. Nitrogen produced in solution by the reaction between hydrazine sulphate, ferric alum, and sulphuric acid at an equilibrium pressure of about 100 atm. can be brought to atmospheric pressure for an appreciable time without bubbles forming in the body of the liquid. M. B. D.

Temperature of Steam Evolved from a [Boiling Aqueous] Solution. E. REISSMANN (*Z. angew. Chem.*, 1924, **37**, 899—903).—An aqueous solution of calcium chloride was boiled in a vessel, the vapour space being jacketed by an electrically heated oil-bath. The temperatures of the boiling solution, vapour, and oil-bath were read over a period and the results plotted graphically. If the temperature of the bath is above or below that of the solution, that of the vapour is intermediate between the two, and if the temperature of the bath is varied the three curves intersect at a point. In this way, and from a comparison of the behaviour of pure water under similar conditions, it is proved that the steam leaves the boiling solution at the temperature of the solution, and not at 100°. The author concludes with a reply to Schreber's assertion to the contrary. (Cf. *Z. techn. Physik*, 1923, 19.) W. T. K. B.

Rate of Absorption and Equilibrium of Carbon Dioxide in Alkaline Solutions. R. V. WILLIAMSON and J. H. MATHEWS (*Ind. Eng. Chem.*, 1924, **16**, 1157—1161).—The absorption of carbon dioxide increases with the rate of flow of the alkaline liquid and is very sensitive to any disturbance of the surface, whilst doubling the rate of flow of gas results in a very marked decrease in the effectiveness of the liquid. The rate of absorption of carbon dioxide is greatly increased by increasing the concentration of the potassium hydroxide, but is almost independent of the potassium carbonate concentration. It corresponds with the absorption in distilled water plus an amount proportional to that of hydroxide and inversely proportional to that of hydrogen carbonate present. The rate of absorption with potassium carbonate solution increases to a maximum at 70—75° and then decreases, and is directly proportional to the partial pressure of the carbon dioxide. D. G. H.

Principles of Gas Absorption. W. K. Lewis and W. G. Whitman (*Ind. Eng. Chem.*, 1924, **16**, 1215—1220).—The "two-film" theory of the absorption of gas by a liquid assumes that the rate of absorption depends only on the rate of diffusion through the stationary films at the intersurface in which convection is absent. This rate is given by the general equation $dW/Ad\theta = k_g(P_g - P_i) = k_L(C_i - C_L)$, in which P, C are the concentrations of the solute in the gas and liquid and g, i, L refer to the gas, interface, and liquid, respectively. This equation is capable of simplification in cases of very high solubility (gas-film diffusion only significant) and very low solubility (liquid-film diffusion significant), and also for conditions in the case of intermediate gases where Henry's law holds good. [Cf. *B.*, 1925, 55.] C. I.

Absorption of Carbon Dioxide and Ammonia from Gas Bubbles. P. G. Ledig (*Ind. Eng. Chem.*, 1924, **16**, 1231—1233).—The rate of absorption of carbon dioxide in potassium hydroxide solution increases slowly with increasing concentration of the latter up to $9N$. Beyond this point, the increase becomes very rapid and no theory can be put forward to explain the discontinuity. With sodium hydroxide, the rate of absorption diminishes when the concentration exceeds $4N$. [Cf. *B.*, 1925, 69.] C. I.

Effect of Gas Velocity and Temperature on Rate of Absorption. R. T. Haslam, R. L. Hershey, and R. H. Keen (*Ind. Eng. Chem.*, 1924, **16**, 1224—1230).—The values for the "overall" absorption coefficients of sulphur dioxide and of ammonia in water in a particular absorption tower with varying gas velocities and temperatures were determined. From these on the "two-film" theory the individual film coefficients were calculated and experimental support was obtained to many of Lewis and Whitman's deductions (cf. above), in particular that the film conductivity is a function of the ratio of density to viscosity and that the molecular diffusivities of all solutes, under similar conditions, are the same. [Cf. *B.*, 1925, 55.] C. I.

Comparative Absorption Rates for Various Gases. W. G. Whitman and D. S. Davis (*Ind. Eng. Chem.*, 1924, **16**, 1233—1236).—The "overall" rates of absorption under similar conditions for oxygen, sulphur dioxide, ammonia, and hydrogen chloride in water and for ammonia in $2{\cdot}3N$-hydrochloric acid were determined. It is shown that on Lewis and Whitman's theory the results obtained in the first and last cases can be applied to the calculation of the other three and that these calculated results agree closely with those experimentally obtained. The "two-film" theory of absorption is thus strongly supported. The same constant is obtained by determining the rate of escape of a gas from solution as by measurement of the rate of absorption, the two processes being practically the same. [Cf. *B.*, 1925, 55.] C. I.

Mechanism of Absorption of Moderately Soluble Gases in Water. H. G. Becker (*Ind. Eng. Chem.*, 1924, **16**, 1220—1224).—The absorption constants for oxygen and nitrogen in air-free

water were determined by measuring the reduction of pressure within a gas bubble passing through a vigorously agitated column of water. The rate of solution can be expressed in the form $dw/dt=a-bw$. The rate of absorption at the surface of a volume of water stirred by means of an agitator was found to vary directly with the speed of stirring, but conditions of perfect mixing were unattainable. Experiments on the absorption of various gases at a stationary surface showed that carbon dioxide, hydrogen, and hydrogen sulphide form a saturated surface layer. Chlorine and some other gases do not, the difference being probably due to the varying effects on the density, viscosity, and surface tension of the liquid produced by the solution of the gas. [Cf. *B.*, 1925, 55.] C. I.

Mists from Chemical Reactions. II. Absorption of Chemical Mists. H. REMY and K. RUHLAND (*Z. anorg. Chem.*, 1924, **139**, 51—68).—The absorption of moist chemical mists by aqueous salt solutions depends on many factors; that of dry mists ("colloidal dust") is dependent only on the vapour pressure of the salt solution. The curve representing the absorption of dry sulphuric anhydride mists by sulphuric acid solutions of varying concentration runs parallel with the b. p.–concentration curve of the acid. A maximum is observed in each case with approximately 98% acid solutions. Sulphuric acid solutions below 5% absorb moist sulphuric anhydride mists better than water; the absorption decreases as the acid concentration rises above this strength. Viscosity effects cause a very variable absorption as the acid becomes highly concentrated; heat of solution also exerts some influence. Exactly similar results were obtained for the absorption of wet and of dry ammonium chloride mists in ammonium chloride and in calcium chloride solutions. S. K. T.

Mists from Chemical Reactions. III. Examination for Electric Charge. H. REMY and C. KOCH (*Z. anorg. Chem.*, 1924, **139**, 69—80).—Ammonium chloride and sulphuric anhydride mists do not carry electric charges. The temporary small negative charges which these fogs acquire after bubbling through water are due to the charging of the fog-bearing gas ("bubble effect"; cf. Coehn, *Z. Elektrochem.*, 1923, **29**, 1). The size of this charge depends on the amount of fog absorbed by the water. Pure air assumes a relatively large negative charge when bubbled through 0·0001*N*-ammonium chloride or sulphuric acid which changes to a small positive value as the concentration increases to *N*. S. K. T.

Adsorption of Arsenious Acid by Hydrated Aluminium Oxide. J. H. YOE (*J. Amer. Chem. Soc.*, 1924, **46**, 2390—2397).—Aluminium hydroxide adsorbs arsenious acid very rapidly for the first few minutes, after which the rate drops; after 24 hours an equilibrium is apparently reached, although further slight adsorption takes place after 232 hours. The adsorbed quantities agree with the usual adsorption formula in the case of adsorption periods of 24 and 72 hours, but not in the case of 232 hours; the latter,

however, is probably not a simple case of adsorption. The lower the temperature of precipitation of the hydroxide the greater is its adsorptive capacity, this effect being greater over the range 0—50° than over 50—100°. Boiling the precipitate also reduces its adsorptive power. The effect of high temperature may be to cause the formation of a more compact precipitate. S. K. T.

Adsorption by Precipitates. H. B. WEISER (*J. Physical Chem.*, 1924, **28**, 1253—1264).—The amounts of potassium, barium, and aluminium chlorides, and potassium alum required to precipitate negative arsenious sulphide sol at various concentrations have been determined in the presence of phenol and *iso*amyl alcohol. These non-electrolytes increase the amount of barium chloride required, decrease the amount of potassium chloride, and have no effect in the case of the other two salts, contrary to the results of Kruyt and van Duin (A., 1914, ii, 182). Although the amount of barium chloride required for precipitation is greater, the actual quantity of barium carried down by the sol is less, and, with concentrations of barium chloride less than the precipitation value, this amount follows the usual adsorption isotherm. Positive hydrous ferric and chromic oxide sols in the presence of these non-electrolytes show a slight diminution in the amounts of potassium chloride, oxalate, and sulphate required for precipitation. The adsorption of a non-electrolyte by the particles of a sol lowers its stability and at the same time it reduces the adsorption of the precipitating ion of the electrolyte added to it to produce coagulation. These two factors act in opposite directions and the amount of electrolyte required for precipitation is determined by the preponderance of either one or the other. M. B. D.

Effects of Gas on the Resistance and Resistance-Temperature Coefficient of Sputtered Platinum Films. F. W. REYNOLDS (*Physical Rev.*, 1924, **24**, 523—531).—Sputtered platinum films are assumed to contain adsorbed hydrogen; decrease of the resistance of a film on contact with oxygen is due partly to removal of hydrogen and partly to adsorption of oxygen, but the effects obtained depend on the conditions under which the film was produced. A. A. E.

Temper Colours. C. W. MASON (*J. Physical Chem.*, 1924, **28**, 1233—1244).—The author criticises the views of Mallock (*Proc. Roy. Soc.*, 1918, **A**, **94**, 561), Hinshelwood (A., 1923, ii, 29), and Raman (*Nature*, 1922, **109**, 105). Temper colours are due to interference of light reflected in a similar manner to Newton's rings from the two surfaces of a film of a compound of the metal which is formed on its surface. Explanations using diffraction or selective reflection are inadequate and also inconsistent with the behaviour of the colours. The colour is increased by a reticulated or granular structure and a moderate degree of opacity of the film. If the film is itself coloured, it obscures the interference colours in the case of thicker films. (Cf. this vol., ii, 138.) M. B. D.

"Temper" Colours [of Steel]. R. C. GALE (*J. Soc. Chem. Ind.*, 1924, **43**, 349—352T).—The thickness of the temper colours on steel as determined by direct weighing, assuming that the density of the film is 5·25 g. per c.c., varies from $4·2\times10^{-7}$ cm. for a pale straw colour to $21·3\times10^{-7}$ cm. for a dark purple. The figures do not agree with those calculated by Tammann from the thickness of an air layer of similar colour, and if the colours were due to interference then the refractive index of the film would vary from 2·53 to 0·63. Again, a blue film becomes purple or yellow when gently polished, and other evidence is adduced which seems to show that the films are granular. (Cf. Mason, preceding abstract; Hinshelwood, this vol., ii, 138.) A. R. P.

Interfacial Tension of some Aqueous Solutions against Oils, as Corrected for Specific Gravity. R. L. HOWARD and T. SOLLMAN (*J. Physical Chem.*, 1924, **28**, 1291—1296).—When surface tensions are measured by the Donnan pipette (A., 1900, ii, 201), a correction should be applied for the difference in density between the solutions and the oil. Surface tensions are given for solutions of sodium halides, sulphate, citrate, and carbonate, sucrose, glycerol, chloral hydrate, ethyl alcohol, carbamide, soap, bile salts, saponin, and tannin in water. M. B. D.

[Uni-molecular Films of Sodium Oleate on Water.] Determination of the Constant *N* of Avogadro. P. L. DU NOÜY (*Phil. Mag.*, 1924, [vi], **48**, 664—672).—Determinations of the surface tension of dilute aqueous solutions of sodium oleate after keeping for two hours show that three decided minima always occur at the concentrations 1/750,000, 1/1,220,000, and 1/1,390,000, respectively. It is suggested that these three minima correspond with the three possible modes of orientation of the molecules on the surface, unimolecular layers being in each case realised. Hence from these three minima it is possible to calculate the three dimensions of the sodium oleate molecule, from which N can be determined, a value $6·008\times10^{23}$ being obtained. H. T.

Phase Boundary Forces at the Gas-Liquid Surface of Separation. II. Adsorption and Orientation of Molecules of Aliphatic Compounds. A. FRUMKIN (*Z. physikal. Chem.*, 1924, **111**, 190—210).—By the arrangement previously described (A., 1924, ii, 462) the potential difference set up at the surface of separation between air and solutions of a large number of aliphatic compounds has been determined. The solutions were made conducting by the addition of potassium chloride, which, except at high concentrations, does not affect the values found. The typical curve obtained by plotting the potential difference ϵ against the concentration c for organic non-electrolytes or weak electrolytes conforms closely to the equation $\epsilon=Ac/(1+Bc)$, A and B being constants, which is of the form of the Langmuir adsorption isotherm. For neutral salts, however, the curve is represented by an expression which recalls the Freundlich adsorption isotherm. In homologous series of organic compounds, for example, aliphatic acids, alcohols,

ketones, and esters, increase in the number of carbon atoms brings about a diminution in the concentration at which a given charge may be reached, and the relative charge is the same for each carbon atom. The value of ϵ_∞, however, is practically identical for each member of the series. Acids, alcohols, ketones, esters, and amines give positive charges to the surface of the solution. Halogen substitution compounds and neutral salts give, for the most part, a negative charge. The general behaviour runs parallel with the effect on the surface tension and is therefore related to the adsorption of the substance at the air–water surface of separation.

Accepting the views of Langmuir and Harkins on the orientation of adsorbed molecules by surface forces, the results may be explained by supposing that in pure water the oxygen molecule is oriented towards the surface giving a negative charge. In solutions of aliphatic compounds which give a positive charge, the hydrocarbon radicals, having no tendency to hydrate, take up a position at the surface, but in the halogen derivatives the halogen is adsorbed at the surface giving a negative charge. Since increase in the number of carbon atoms does not increase the maximum charge, the linking C—C must be completely non-polar in character. To the linkings C—O, C—Cl, and C—N a definite polarity must be ascribed, the carbon atom in each case being positive. M. S. B.

Orientation of Ammonium Iodide Crystals on the Surface of Muscovite. M. Royer (*Compt. rend.*, 1924, **179**, 1610—1612; cf. Gaubert, A., 1924, ii, 549).—A drop of warm saturated solution of ammonium iodide is spread on a freshly-prepared cleavage surface of the mica, the lower temperature of which causes rapid crystallisation without formation of unoriented crystals. The crystals are invariably cubic, never octahedral. Unlike other alkali halides, ammonium iodide on a given fresh cleavage orients itself in one position only. A side of the triangular contour (normal to a triad axis of the cube) lies parallel to the mica plane (010), whilst all the apices point either in one direction or the opposite. When crystals are deposited on successive cleavages, the orientation is sometimes all in one direction and sometimes all in the other. It is inferred that muscovite is of triclinic symmetry, but is built up of laminations twinned at 180° to one another, the resulting crystal being pseudo-monoclinic. W. A. C.

Permeability of Membranes. W. D. Bancroft and C. Gurchot (*J. Physical Chem.*, 1924, **28**, 1278—1283).—A preliminary paper showing that the permeability of membranes is closely connected with their coagulability when prepared in the colloidal state. Copper ferrocyanide membranes are coagulated by low concentrations of methyl alcohol and of acetic acid, thereby becoming permeable to sugar. Alcohols and acids coagulate a copper ferrocyanide sol whilst alkalis peptise a copper ferrocyanide gel. The results of Barlow (A., 1905, ii, 507; 1906, ii, 273), Walden (A., 1893, ii, 203), and Czapek (*Ber. deuts. bot. Ges.*, 1910, 28, 159) are shown to be due to coagulation of the membrane by the alcohols or acids employed. M. B. D.

Theory of Osmotic Pressure, Membrane Potential, and Coagulation of Colloids. Colloidal Chromium Hydroxide. N. BJERRUM (*Z. physikal. Chem.*, 1924, **110**, 656—684).—Equations have been deduced for the osmotic pressures of colloidal ions; observations on colloidal solutions of chromium hydroxide are in approximate agreement with these. Determinations of membrane potential show that the relationships existing between this quantity and the activities of the ions (H^+ and Cl^-) on different sides of the membrane are in agreement with Donnan's theory. The membrane potentials calculated from the observed osmotic pressures are approximately half the measured values. From the osmotic pressure measurements it is calculated that the colloidal chromium particle consists on the average of 1000 chromium atoms and carries about 30 free charges. The amount of adsorbed anion (chloride) shows that the total charge carried by the colloid is about 240. For complete coagulation, the necessary amount of ferrocyanide corresponds exactly with the total charge on the colloid, whilst about 15% excess of ammonium or potassium sulphate is required. The change in the conductivity on addition of ammonium sulphate has been measured. Commencement of coagulation is indicated by a sudden break in the curve obtained on plotting conductivity against c.c. of ammonium sulphate. An apparatus is described for the determination of osmotic pressures, membrane potentials, and the activities of the ions on both sides of the collodion membrane. J. S. C.

Effects of Dilution on Colloids. W. KOPACZEWSKI (*Compt. rend.*, 1924, **179**, 628—629).—Certain colloidal solutions give, on dilution, conductivity values greater than would be expected as a result of dissociation. It is suggested that the union between ions and molecules in the solution is not a simple chemical change. Some biological aspects of the experimental results are indicated. H. J. E.

Theory of Elasticity of Colloidal Solutions. E. SZEGVARI (*Z. physikal. Chem.*, 1924, **108**, 175—184; cf. following abstract).—When the elasticity limit in solids is overstepped the tension completely disappears, but in a colloidal solution in motion the tension at the elasticity limit is maintained, and represents a flow-elasticity. The relation between the resistance value, w, the velocity gradient, G, in the liquid, the flow-elasticity, δ, and the true viscosity, η, is expressed by $w=\delta/G+\eta$. This formula is in good agreement with the experimental results obtained using Couette's apparatus, but, for agreement with those obtained by Hess' method, the addition of a constant to G is required. By reference to the experimental data for benzopurpurin and vanadium pentoxide sols it is shown that, whilst true viscosity increases proportionally with concentration, or with addition of electrolyte, and in the latter case only very slowly, the rate of increase of elasticity also increases rapidly. The two quantities therefore appear to be independent of one another. Under the conditions prevailing in the Ostwald

viscosimeter, the influence of the elasticity of the sol on the result is of the same order as that of the viscosity. M. S. B.

Viscosity and Elasticity of Colloidal Solutions. H. FREUNDLICH and E. SCHALEK (*Z. physikal. Chem.*, 1924, **108**, 153—174).—The viscosity of various sols has been examined by Hess' method of comparison of the rate of flow of the sol with that of water through horizontal capillary tubes under the influence of varying pressures (cf. Rothlin, A., 1920, ii, 18) and by Couette's method, as modified by Hatschek (A., 1913, ii, 835), in which an external revolving cylinder drags round an internal concentric cylinder on account of the viscosity of the liquid between. A number of sols, especially hydrophobic sols, for example, arsenic trisulphide, lanthanum oxide, zirconium oxide, calcium fluoride, a sulphur sol, and an aluminium oxide sol, obeyed Poiseuille's law, that is, they behaved like true solutions. A different aluminium oxide sol and a cerium oxide sol showed slight deviations from Poiseuille's law. Greater deviations were shown by an old ferric oxide sol, and much greater divergence by vanadium pentoxide, benzopurpurin, cotton-yellow, gelatin, and sodium stearate. With increasing pressure, or with increasing angular velocity, according to the method of measurement, the apparent coefficient of viscosity, or the resistance value, decreased. This is attributed to a shearing elasticity of the sol which becomes less important relatively to the true viscosity coefficient as the velocity gradient in the sol increases. It has been previously shown by Freundlich and Seifriz (*Z. physikal. Chem.*, 1923, **104**, 233) that most sols displaying deviations from Poiseuille's law possess an extension elasticity. The sols which show the greatest deviations, and therefore the greatest elasticity, appear to be those which consist of non-spherical particles. The elasticity apparently increases with age and with the addition of electrolytes, and decreases with dilution. In the case of vanadium pentoxide sols, the increase in double refraction runs parallel with the increase in apparent viscosity, but does not appear to be related to the size of the particles.

Since only low pressures are operative in the Ostwald viscosimeter, it is evidently not suitable for the measurement of the viscosity of sols. M. S. B.

Colloidal Arsenic Sulphide. A. BOUTARIC and M. VUILLAUME (*J. Chim. Phys.*, 1924, **21**, 247—264; cf. A., 1924, ii, 405).—The absorption of light by arsenic sulphide sols is expressed by the relation $\log I_0/I = k/\lambda^n$, where I_0 and I are the intensities of the incident and transmitted rays of wave-length λ. The constant n increases regularly with diminishing wave-length, being 3·3 for $\lambda = 640\ \mu\mu$ and 12·0 for $\lambda = 530\ \mu\mu$, and it is equal to 4 (the Rayleigh constant for absorption by colourless particles of small size compared to λ) when $\lambda = 620\ \mu\mu$. The absorption is the result of (1) a simple absorption following the law of Rayleigh, and (2) a selective absorption in the region of $\lambda = 620\ \mu\mu$, and due to reflection from the surface of the granules. Absorption due to (1) is increased and that due to (2) is decreased by increase in the size of the granules.

When the sols are prepared by passing hydrogen sulphide into a solution of arsenious oxide, the size of the granules increases with the concentration of the arsenic and with the time of passage of the hydrogen sulphide, a slow current of which gives much larger granules than a rapid one.

The densities and viscosities of sols of different concentration have been determined, and indicate that the viscosity formula of Einstein applies accurately to sols of infinite dilution.

The flocculation of these sols has been studied spectrophotometrically by periodically measuring the coefficient of absorption, which first increases rapidly and then reaches a limiting value. At this point, a gel is produced in an unstable condition, and flocculation may occur at any moment and is favoured by factors such as rapid stirring. The slightest excess of hydrogen sulphide greatly retards the flocculation by alkali chlorides and aluminium chloride, accelerates it in the case of the chlorides of barium, strontium, and calcium, and has little effect with manganese or magnesium chlorides. Rise of temperature produces a similar effect, but the presence of excess of arsenic trioxide has little effect. In all cases, the speed of flocculation increases both with the concentration of the electrolyte after mixing, and with that of the added solution, unless this is very dilute. For a given concentration of electrolyte, increased colloid concentration raises the velocity of flocculation with the chlorides of potassium, barium, magnesium, and manganese, and diminishes the velocity with cadmium and aluminium chlorides. W. H.-R.

Dispersion of Colloidal Electrolytes in Relation to Mineral Exchanges in Cells. W. MESTREZAT and (MLLE.) M. JANET.—(See i, 198.)

Determination of the Size of Invisible Particles in Emulsoid Sols. H. R. KRUYT and H. J. C. TENDELOO (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 377—381).—The conductivity, viscosity, and the cataphoretic velocity of 0·5% sols of starch, to which varying quantities of various electrolytes were added, were measured. This leaves only ϕ, the relative volume of the particles, and r, their radius, undetermined in Smoluchowski's equation for charged particles, $(\eta_s-\eta_0)/\eta_0=\frac{5}{2}\phi[1+\omega/\eta r_2.(\zeta D/2\pi)^2]$, in which η_s and η_0 are the viscosities of the sol and dispersent, respectively, ω is the specific resistance, ζ is the potential difference in the surface double layer, and D is the dielectric constant. By taking the results with different concentrations of electrolytes present in pairs and solving for ϕ and r, it is found that these are constant whichever combination be taken, that is, ϕ and r are not affected by the charge. As a mean, r is found to be, in this case, 7 $\mu\mu$. L. J. H.

Titration Curve of Gelatin. W. R. ATKIN and G. W. DOUGLAS (*J. Soc. Leather Trades Chem.*, 1924, **8**, 584—596).—The p_H values of 1% gelatin solutions to which varying amounts of acid or alkali have been added are plotted against the amount of acid or alkali

combined with the gelatin. From p_H 1·7 the amount of combined hydrochloric acid rises sharply with decreasing p_H. From the isoelectric point p_H 4·7 to p_H 1·7 the curve is rather flatter whilst from p_H 4·7 to p_H 7·7 the amount of sodium hydroxide fixed increases continuously. From p_H 7·7 the curve is an almost perfect sigmoid. Sigmoid curves have been obtained by Harris (A., 1924, ii, 73) for certain proteins, and the authors consider that the gelatin curve is the result of the merging of two sigmoid curves into one another between p_H 4·7 and p_H 7·7. The acid portion of the titration curve represents approximately the titration curve of the free amino groups in gelatin with hydrochloric acid and the alkaline portion represents the titration of the free carboxyl groups with sodium hydroxide. From the first curve the basic dissociation constant is 0·0002 and the acid dissociation constant is found similarly to be 2×10^{-6}. From the alkaline portion of the curve, p_H 4·7 to p_H 7·7, it is found that the equivalent weight of gelatin is 3290. The more alkaline portion of the curve p_H 7·7 to p_H 12·6 gives 2060. A keto–enol transformation appears to be involved in this region. Wilson's second isoelectric point for gelatin (cf. A., 1923, i, 68) is due to neutral salt effects. The point of inflection at p_H 7·7 appears to represent the commencement of the introduction of alkali into the –CO·NH– group, in which there has been a molecular rearrangement into the enol form –C(OH):N–, the hydroxyl then combining with alkali. D. W.

Physico-chemical Examination of Medicinal Silver Preparations. H. Schlee and W. Thiessenhusen (*Z. angew. Chem.*, 1924, **37**, 837—845, 855—860; cf. A., 1924, i, 1262).—Equal concentrations of aqueous solutions of various silver preparations (dispargen, fulmargin, protargol, collargol, iodcollargol, solargyl) have about the same conductivity (about $2·5\times10^{-5}$ for 0·031% solutions and $1·0\times10^{-3}$ for 2% solutions), this being roughly proportional to the silver content. The determination of the conductivity and of the silver-ion concentration affords a means of detecting the presence of electrolytes which do not yield silver ions and of roughly estimating their quantity. The size of the colloidal particles present in the solutions varies between 21 and 27 $\mu\mu$, except for solargyl, in which they measure 59 $\mu\mu$. Their number is, in general, proportional to the silver content, and varies between 1×10^9 and 76×10^9 per c.c. of the 1% solutions. The above determinations were also made on solutions which had been kept for several months. In every case, a sediment had formed, increasing in quantity with increasing concentration of the solutions and causing a diminution in the silver content of the solutions. The silver-ion concentration had diminished (except in the case of collargol and of concentrated solutions of dispargen and solargyl), the conductivity had increased, the number of colloidal particles had decreased, and the size of the latter had remained constant or had increased slightly. Silver hydrosols, freshly prepared in water and $N/1000$ sodium hydroxide by Bredig's electrical pulverisation method, were also examined. The quantity of silver going into colloidal solution

increases with the time of pulverisation, although not always in strict proportion. The same applies to the silver-ion concentration (except in dilute alkaline sols), conductivity, and number of the colloidal particles, the size of which is about 20 $\mu\mu$ in pure water and 29—40 $\mu\mu$ in the alkaline medium. From the high silver-ion concentration of the hydrosols (about 0·1 mg. of ion per litre), it is assumed that part of the silver pulverised goes into colloidal solution in the combined state. These hydrosols rapidly form flocculent precipitates, a phenomenon in which atmospheric carbon dioxide appears to play a part. W. T. K. B.

Influence of Valency on Coagulation and Cataphoresis. H. FREUNDLICH and H. P. ZEH (*Z. physikal. Chem.*, 1924, **114**, 65).—The influence of complex cobalt salts with uni- to sexa-valent cations on the cataphoresis and coagulation of an As_2S_3 sol has been examined. The coagulative power (γ) of the salts increases with increasing valency of the cation. From curves expressing the relation between the electrokinetic potential ζ and the concentration c, the concentrations which correspond with a fixed ζ value have been derived. In agreement with Freundlich's adsorption theory of coagulation, these concentrations (c) vary with the valency of the cations in the same manner as the coagulation values. The adsorption theory is applicable to the uni-, bi-, ter-, and quadrivalent cations, but unexplained deviations occur with the sexavalent cation.

Similar observations were made on the influence of salts with complex cyanide ions on a Fe_2O_3 sol. Here also the parallelism between γ and c is complete. The inference that the different anions are equally adsorbed in equimolar concentration proves, however, to be valid only to a limited extent. In particular, $Au(CN)_2'$ acts more weakly than $Au(CN)_4'$ and $Cu(CN)_4'''$ than $Fe(CN)_6'''$. In contrast to earlier work, the authors' ζ–c curves show no initial rise of ζ potential except where the multivalent anion $Fe(CN)_6''''$ acts on As_2S_3 sol and the multivalent cation

$$[(NH_3)_4CO<\begin{matrix}NH_2\\OH\end{matrix}>CO(NH_3)_4]^{\cdots}$$

acts on Fe_2O_3 sol. The observed behaviour is attributed to the value of the ζ potential possessed by the original pure sol.

N. H. H.

Influence of Colloids on the Cathodic Overvoltage of Hydrogen and Metals. C. MARIE and G. LEJEUNE (*Compt. rend.*, 1924, **179**, 679—682; cf. A., 1909, ii, 124).—The energy required to liberate zinc, nickel, or lead is increased when a colloid such as gelatin is added to the solution. The colloid reduces the amount of the metal deposited by a given current. With copper, mercury, or silver, on the other hand, the energy difference is small. It was to be expected that the addition of colloid to an acid solution of the metal would increase the quantity of the latter deposited. This may be the case for low concentrations of hydrogen ions, but experiment shows that it is not so for greater concentrations. The

phenomenon apparently undergoes inversion at a certain limiting concentration. T. H. P.

Influence of Intensive Drying on Internal Change. II. A. SMITS (*Z. physikal. Chem.*, 1924, **111**, 161—170; cf. A., 1922, ii, 358).—The mechanism of the changes in a unary system, which produce the phenomena observed after intensive drying, has been discussed. Regarding the substance as a mixture of at least two different kinds of molecules, it is possible that the internal equilibrium between these, which would otherwise change with change of temperature, may be fixed by the drying, so that the same equilibrium is thereafter maintained at all temperatures. Alternatively, the position of equilibrium may be moved, after a certain degree of dryness is reached, because the reaction in one direction is delayed by the absence of water more than the reaction in the contrary direction. The latter view appears to be supported by the experiments of Dixon and Baker on the influence of drying on the reactivity of different substances. Their results might be explained by postulating the existence of an internal equilibrium between active and inactive molecules which is shifted by drying in such a way that all the molecules become inactive (Smits, *Versl. Kon. Akad. V. Wet.*, 1923, **32**, 345). The experiments of Coehn (A., 1923, ii, 206) on the effect of drying upon the equilibrium between hydrogen and chlorine on the one side, and hydrogen chloride on the other, when under the influence of ultra-violet light, may probably be similarly explained. M. S. B.

Measurement of the Second Dissociation Constants of Dibasic Acids, with Special Reference to Tartaric Acid. T. PAUL (*Z. physikal. Chem.*, 1924, **110**, 417—434).—The expression of A. A. Noyes (A., 1893, ii, 365), connecting the first and second dissociation constants of dibasic acids with the hydrogen-ion concentration and molarity of dilute aqueous solutions of the corresponding acid sodium or potassium salts, is deduced. The concentration of the hydrogen ion in solutions of sodium and potassium hydrogen tartrates has been determined by conductivity methods at 18°, and by the method of sugar inversion at 76°. Assuming k_1 for tartaric acid to have the value $0{\cdot}97\times10^{-3}$, as determined by Ostwald and Walden from conductivity measurements at both temperatures, values of k_2 are calculated. The k_2 values obtained by the catalytic method diminish with increasing dilution of the acid salt and reach a constant limiting value $2{\cdot}7\times10^{-5}$ at $v=1000$. The k_2 values from conductivity measurements increase with increasing dilution and attain the same limiting value at roughly the same dilution. These variations are ascribed to the incomplete ionisation of the salt in the more concentrated solutions. Measurements of the rates of sugar inversion and of electrical conductivity show that the value of k_1 for tartaric acid is $0{\cdot}97\times10^{-3}$ at 18° and 76°. Values of k_2 for tartaric acid obtained by other investigators are given, the values ranging from $2{\cdot}9\times10^{-5}$ to $7{\cdot}5\times10^{-5}$. J. S. C.

Theory of Binary Electrolytes. W. SEMENTSCHENKO (*Z. physikal. Chem.*, 1924, **112**, 128—134).—An expression is derived which connects the degree of dissociation of an electrolyte with the dilution and with the dielectric constant of the solvent. Ostwald's dilution law and Walden's law result as special cases. The expression is used to develop quantitatively the hypothesis of dissociated complexes in connexion with anomalous conductivity (cf. Steele, McIntosh, and Archibald, A., 1905, ii, 222).

L. F. G.

Dilution Laws and Distribution Coefficients of Strong Electrolytes from the Debye Theory. P. GROSS and O. HALPERN (*Physikal. Z.*, 1924, **25**, 393—397).—The dilution laws for strong electrolytes and the distribution coefficients of such compounds between two immiscible solvents have been treated from the standpoint of the Debye theory. Existing data have been used to verify the relations deduced. S. B.

Electrometric Study of Hydrolysis. P. JOB (*Compt. rend.*, 1924, **179**, 1317—1319).—The hydrolytic equilibrium in salt solution is displaced by the addition of strong acids or bases, and the displacement measured electrometrically (A., 1924, ii, 512). An atmosphere free from carbon dioxide is essential. In the case of solutions of alkali acetates (except at the neutral point), the formula $B=C_H(1+AC_H/K+C_H)$ is used, where B is the concentration of the added hydrochloric acid, C_H the hydrogen-ion concentration, A is the concentration (dilute enough for complete dissociation) of the acetate, and K is the dissociation constant of acetic acid. The value obtained for K is $3{\cdot}5\times10^{-5}$, *i.e.*, almost double that usually adopted. Reasons are given for this discrepancy. The value obtained for the hydrolytic constant of the acetate is $2{\cdot}6\times10^{-10}$. L. L. B.

Affinity Constant of some Organic Bases. M. BOURGEAUD and A. DONDELINGER (*Compt. rend.*, 1924, **179**, 1159—1161).—The affinity constants of twenty-seven amines were calculated from measurements of the degree of hydrolysis of their hydrochlorides. Aniline has a smaller affinity constant than indanylamine and the latter smaller than benzylamine. Qualitatively this order can be explained by the more symmetrical structure of aniline and the closer proximity of the nitrogen atom to the phenyl radical. Substitution of one or two methyl groups lowers the affinity constant although the first only plays the part of a negatifying radical. The positive ethyl group sometimes lowers, sometimes raises the value of the constant. The indanyl group always acts in a negative manner. Substitution in the para position by the methyl group has very slight influence on the value of the constant (cf. Walker, *Z. physikal. Chem.*, 1899, 319). H. T.

Theory of the Isoelectric Point. R. KUHN (*Z. physikal. Chem.*, 1924, **114**, 44–48).—The values obtained for the isoelectric point of amphoteric electrolytes by viscosity minimum and similar physical methods do not always agree with those obtained from Michaelis' formula $h_1=\sqrt{K_aK_w/K_b}$, where h_1 is the hydrogen-ion

concentration, K_a and K_b are the acidic and basic dissociation constants, and K_w is the ionic product for water. The author puts forward the formula $h_0=h_1\sqrt{\tan\alpha_1/\tan\alpha_2}$, where h_0 is the hydrogen-ion concentration determined by the viscosity or other method, h_1 that obtained as above, whilst $\tan\alpha_1$ and $\tan\alpha_2$ are the tangents of inclination of the viscosity etc. curves for points with equal ordinates on both sides of the minimum or maximum. N. H. H.

Electrometric Titration of Acids. F. AUERBACH and E. SMOLCZYK (*Z. physikal. Chem.*, 1924, **110**, 65—141).—Equations are derived representing the change in the p_H value on titration of solutions of monobasic, dibasic, and tribasic organic acids with alkali. It is shown that in the case of a dibasic acid the existence of two sigmoid portions on plotting p_H against c.c. alkali depends on the ratio of the values of the first and second dissociation constants. If $K_1 : K_2<16$, the form of the curve is that of a monobasic acid. The process of electrometric titration may be employed to determine the various dissociation constants. Equations are derived whereby the concentrations of the components of mixtures of two monobasic acids, a monobasic acid and a dibasic acid, two dibasic acids, or a dibasic acid and a tribasic acid, may be determined from a knowledge of the dissociation constants and the results of an electrometric titration. The influence of errors of observation on the final result is dealt with.

A form of the quinhydrone electrode suitable for electrometric titration is described. The total electrolyte concentration must always be kept below 0·1 *M* in order to avoid the inherent "salt error."

The values for the dissociation constants of the various acids at 20° are found to be: benzoic, $6{\cdot}5\times10^{-5}$; acetic, $1{\cdot}86\times10^{-5}$; lactic, $1{\cdot}33\times10^{-4}$; tartaric, K_1 $8{\cdot}96\times10^{-4}$, K_2 $7{\cdot}46\times10^{-5}$; malic, K_1 $3{\cdot}86\times10^{-4}$, K_2 $1{\cdot}39\times10^{-5}$; succinic, K_1 $6{\cdot}86\times10^{-5}$, K_2 $3{\cdot}97\times10^{-6}$; citric, K_1 $1{\cdot}03\times10^{-3}$, K_2 $2{\cdot}53\times10^{-5}$, K_3 $1{\cdot}51\times10^{-6}$. Oxalic acid is too strong an electrolyte to permit of the determination of K_1 and K_2 by this method. Owing to the activity of formic acid as a reducing agent, the quinhydrone electrode cannot be employed for the electrometric titration of this acid.

The applicability of the method to the determination of the individual concentrations in mixtures of two acids has been tested by experiments with known mixtures of the following acid pairs: acetic and lactic, tartaric and acetic, tartaric and lactic, tartaric and malic, citric and tartaric, citric and malic. The concentrations thus found are in excellent agreement with the actual values.

The concentration of an organic acid in presence of its salts may be determined by addition of a small known excess of strong acid, *e.g.*, hydrochloric, followed by an electrometric titration. The occurrence of the first maximum in the value of $\Delta\epsilon/\Delta x$ (ϵ being the potential of the hydrogen electrode and x the amount of added alkali) indicates the neutralisation of the excess of strong acid, and the occurrence of the second maximum, the neutralisation of the total acid. The method has been successfully applied to the

determination of lactic, tartaric, malic, and citric acids in presence of their sodium salts and to the determination of a mixture of tartaric and malic acids in presence of sodium malate and tartrate. J. S. C.

Calculation of the Work of Chemical Changes involving Variable Concentrations. C. FRENZEL (*Z. physikal. Chem.*, 1924, **110**, 547—558).—Mathematical. An expression for the maximum work in homogeneous gas reactions is derived. The expression may be represented graphically. J. S. C.

Equilibrium across a Parchment Membrane in the Case of Sodium Chloride in Presence of Sodium Caseinate. P. A. SPORING (*J. Chem. Soc.*, 1924, **125**, 2316—2319).—Purified sodium caseinate, neutral to phenolphthalein, was selected as an example of an electrolytic colloid of complicated constitution and placed in one compartment of a distribution vessel. Separated from it by a parchment membrane was an equal volume of aqueous sodium chloride. After equilibrium had been attained the two solutions were analysed. The ionic product [Na][Cl], on the caseinate side of the membrane is found to be always greater than on the other side if the caseinate is assumed to be completely dissociated. To give a constant ionic product, a dissociation value of 0·6—0·8 for sodium caseinate must be assumed. The results are in fair agreement with the theory of membrane equilibrium in its simplest form. C. I.

Solubilities of Vanillin. C. E. MANGE and O. EHLER (*Ind. Eng. Chem.*, 1924, **16**, 1258—1259).—Solubility curves for vanillin in aqueous alcohol and aqueous glycerol are drawn. The latter dissolves very little more vanillin than water alone and the solutions exhibit considerable supercooling. Concentrated solutions of vanillin in glycerol or in a mixture of glycerol and alcohol deposit a heavy white precipitate of vanillin glyceride, which is easily hydrolysed into glycerol and vanillin by addition of water and heating. Generally speaking, if the solution contains as much water as vanillin, precipitation of the glyceride will not occur. W. T. K. B.

System Zinc Sulphate–Water. C. R. BURY (*J. Chem. Soc.*, 1924, **125**, 2538—2541).—Data obtained for the solubility of zinc sulphate hexahydrate between 11° and 61° differ (below 25°) from those of Cohen (cf. A., 1900, ii, 184), whose figures must refer to some other hydrate. The latter agree with the data obtained for the monoclinic heptahydrate between 7° and 23°. The transition of the hepta- to the hexa-hydrate takes place at 24·8°. The monohydrate is probably formed when the hexahydrate is warmed at about 60° (cf. A., 1897, ii, 250). S. K. T.

Determination of the Solubilities of Sparingly Soluble Substances. II. Solubilities of the Oxides of Beryllium, Aluminium, Zinc, Cadmium, Lead, Copper, and Silver in Water. H. REMY and A. KUHLMANN (*Z. anal. Chem.*, 1924, **65**, 161—181).—The solubilities of the above oxides were deter-

mined by the conductometric titration and conductivity methods, a correction being applied in the latter case for the carbon dioxide content of the water. The results obtained by the respective methods were (in mg. per litre): aluminium oxide, 0·94, 1·04; zinc oxide, 2·92, 3·06; cadmium oxide, 4·80, 5·00; lead dioxide, 12·39, 12·34; copper oxide, 5·46, 5·39; silver oxide, 25·29, 24·80. The solubility of beryllium oxide, 0·20 mg. per litre (conductometric titration; the conductivity method failed), is very much smaller than that of magnesium oxide (cf. this vol., ii, 30), which is in accordance with the general relationship between the solubilities of the oxides of the metals in the first column of the second group of the periodic table. S. K. T.

Sulphurous Acid and its Salts. II. Decomposition of Sulphites at Red Heat. F. Foerster and K. Kubel (*Z. anorg. Chem.*, 1924, **139**, 261—292).—Calcium and sodium sulphites decompose at 650° and 600°, respectively, according to the equation: $4M_2SO_3 \rightleftharpoons 3M_2SO_4+M_2S$. Above 900°, the dissociation $M_2SO_3 \rightleftharpoons M_2O+SO_2(\alpha)$ disturbs the equilibrium. For the calcium compound, this dissociation is perceptible at 650° and is almost complete at 1100°. The residue contains calcium sulphate besides oxide, probably because the equilibrium $3SO_2 \rightleftharpoons 2SO_3+S$ becomes effective at high temperatures. With sodium sulphite, the equilibrium (α) is not fully established after 2 hours' heating at 1200°. The rate of decomposition of sodium sulphite is much greater than that of the calcium salt at the same temperature. For the former, it increases rapidly between 600° and 700°; for the latter it increases rapidly between 650° and 700°, but only very slowly between 700° and 800°.

Magnesium sulphite decomposes at 300° according to the equation: $4MgSO_3=[2MgSO_4+2MgSO_2]=2MgSO_4+MgS_2O_3+MgO$, the magnesium sulphoxylate being regarded as an intermediate product; partial decomposition of the thiosulphate, $MgS_2O_3=MgSO_3+S$, and dissociation of the sulphite, $MgSO_3 \rightleftharpoons MgO+SO_2$, also take place, especially at higher temperatures. [Cf. *B.*, 1925, 39.] S. K. T.

Sodium and Potassium Salts of Sulphurous Acid. F. Foerster, A. Brosche, and C. Norberg-Schulz (*Z. physikal. Chem.*, 1924, **110**, 435—496).—Sodium and potassium salts of sulphurous acid have been prepared and separated in an atmosphere of hydrogen. Solubility determinations, also in a hydrogen atmosphere, have been made over a range of temperature extending from the cryohydric point almost to the boiling point. Sodium sulphite exists as a heptahydrate and as the anhydrous salt. No evidence for the existence of the reported decahydrate was obtained. Solubility data show that the cryohydric point is −3·45° and the transition temperature of the heptahydrate 33·4°. The retarded transition renders the determination of this temperature by thermometric and dilatometric methods impossible. Sodium pyrosulphite crystallises from acid solutions and there appears to be no evidence for the existence of $NaHSO_3$. The solubility data for sodium

pyrosulphite show that this crystallises out from aqueous solutions as $Na_2S_2O_5$ from the boiling point to 5·5° (stable), or to −4·8° (metastable), as $Na_2S_2O_5,7H_2O$ from +5·5° to the cryohydric point −9·05° (stable), and as $Na_2S_2O_5,6H_2O$ from +3·8° to the cryohydric point −9·79° (metastable). Some evidence was obtained as to the existence of $Na_2S_2O_5,3H_2O$ and $3Na_2S_2O_5,H_2O$ but no conclusive proof.

Potassium sulphite forms no hydrate as recorded in the literature. The cryohydric point is −45·5°. Solubility determinations show that potassium pyrosulphite exists only as the anhydrous salt. A double salt, $K_2S_2O_5,4KHSO_3$, crystallises out from such solutions over the temperature range −4° to +4°. The hydrogen sulphite itself is non-existent. The above salts are perfectly stable in dry air and give off no sulphur dioxide. Cryoscopic measurements show that in aqueous solution the pyrosulphites are hydrolysed according to the scheme $S_2O_5'' + H_2O \rightleftarrows 2HSO_3'$. J. S. C.

Displacement of the Maximum Solubility and the Existence of Solubility Constants. A. Colson (*Compt. rend.*, 1924, **179**, 1399—1404).—Measurements of the solubility of calcium sulphate in dilute nitric and sulphuric acids have been made at different temperatures. The solubility curves show no maxima. Measurements of the heats of solution of calcium sulphate in dilute nitric and sulphuric acids at 16—17° gave 18·5 cal. and 10 cal. per g., respectively. H. T.

Equilibrium $Fe^{\cdot\cdot} + Ag^{\cdot} \rightleftarrows Fe^{\cdot\cdot\cdot} + Ag$. N. A. Tananaev (*Z. physikal. Chem.*, 1924, **114**, 49—58).—The reaction studied in the complete absence of air is shown to be reversible and gives the well-defined equilibrium constants K_0, 0·0018; K_{25}, 0·0061; K_{45}, 0·0110. The heat of reaction is 7868 cal. for 1 g.-atom of silver. Van't Hoff's equation connecting change of equilibrium with temperature is applied and gives satisfactory agreement with the experimental results. N. H. H.

Reciprocal Salt Pair $Na_2Cr_2O_7 + 2KCl \rightleftharpoons K_2Cr_2O_7 + 2NaCl$. J. B. Robertson (*J. Soc. Chem. Ind.*, 1924, **43**, 334—338T).—The equilibrium diagram for the above system at 25°, 50°, and 100° was constructed from investigations on the systems KCl–$K_2Cr_2O_7$–H_2O, $NaCl$–$Na_2Cr_2O_7$–H_2O, $K_2Cr_2O_7$–$Na_2Cr_2O_7$–H_2O and (K,Na)–(Cl,Cr_2O_7)–H_2O, together with Reinders' results for the system $NaCl$–KCl–H_2O (*Z. anorg. Chem.*, 1915, **93**, 202). Potassium dichromate and sodium chloride are the compatible salt pair at all temperatures; as the temperature increases the areas on the diagram representing potassium and sodium chlorides increase considerably at the expense of the area representing potassium dichromate. The sodium dichromate area is always very small. S. K. T.

Binary System Sodium Metasilicate–Silica. G. W. Morey and N. L. Bowen (*J. Physical Chem.*, 1924, **28**, 1167—1179).—The system sodium metasilicate–silica has been investigated by heating a few mg. wrapped in platinum foil at constant temperature until

equilibrium is reached, and quenching by dropping into mercury. The m. p. of the metasilicate is 1088° and the thermal diagram shows a maximum corresponding with sodium disilicate, $Na_2O,2SiO_2$, at 874°. The eutectic metasilicate–disilicate is at 840° and 37·5 mol.-% of silica and the eutectic disilicate–quartz is at 793° and 65 mol.-% of silica. The results are compared with those of previous workers for potassium and lithium metasilicates. M. B. D.

Thermal Analysis of the System Lithium Fluoride–Magnesium Fluoride. G. TACCHINI (*Gazzetta*, 1924, **54**, 777—780).—As the proportion of magnesium fluoride in this system is increased the solidifying point falls gradually from 840°, the value for pure lithium fluoride, to the minimum, 669°, for about 60 mol.-% of magnesium fluoride, and then rises slowly to 690° for 75·71 mol.-% of the latter. The curve then rises steeply to reach 1060° with 86·59 mol.-% of magnesium fluoride. Extrapolation gives for the m. p. of magnesium fluoride the approximate value 1400° (cf. Beck, *Metallurgie*, 1908, **5**, 504). The form of the diagram and the absence of an eutectic in all the mixtures examined would indicate the existence of mixed crystals in all proportions of the components or at least in mixtures containing up to 75 mol.-% of magnesium fluoride. Since the lithium and magnesium salts are of different crystalline forms, being respectively cubic and tetragonal, it is probable that two series of mixed crystals are formed and that the curve of incipient solidification exhibits an angle, with a miscibility gap. T. H. P.

Equilibrium Diagram of the Copper–Tin System. T. ISHIHARA (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **13**, 75—100).—The equilibrium diagram of the copper–tin series of alloys has been reinvestigated by means of the electrical resistance method and microscopical examination. The maximum solubility of tin in copper at the ordinary temperature is 11% and this solid solution undergoes a progressive transformation at temperatures between 480° and 580°, according to the percentage of tin. The β solid solution decompses below 510° into $\alpha+\delta$, whilst the γ constituent decomposes below 580° into an eutectoid mixture of $\delta+\eta$. The constituent δ is the compound Cu_4Sn, η is a solid solution of tin in Cu_3Sn, and ε is the compound CuSn, which apparently exists in two forms having a transformation point at 180° similar to the A2 point in steel. A. R. P.

Secondary Crystallisation of Steel. E. SCHEIL (*Z. anorg. Chem.*, 1924, **139**, 81—107).—From a comparison of the rates of crystallisation and of formation of crystal centres in a carbon–iron alloy as a function of temperature, it is shown that the phenomena observed in the formation of pearlite by the transition of steel in the solid state are interpreted more easily by Vogel's theory (A., 1912, ii, 744) than by that of Howe (*Proc. Amer. Soc. Testing Materials*, 1911, 263). From the same point of view, assuming that martensite is a solution of carbon in an unstable form of α-iron, the equilibrium curve of the austenite–martensite

system is discussed. This curve is of Roozeboom's first type. Benedicks' experiments on the chilling of an austenite steel in liquid air (*J. Iron and Steel Inst.*, 1908, 251) are also satisfactorily explained. Fränkel and Heymann's assumption that austenite first changes to martensite on tempering (A., 1924, ii, 490) is not supported, and the existence of the carbide FeC_{8-10} could not be confirmed. S. K. T.

System Sodium Carbonate–Sodium Sulphate–Water. W. A. Caspari (*J. Chem. Soc.*, 1924, **125**, 2381—2387).—The solid phases characterising this system include the two decahydrates and mixed crystals thereof, anhydrous sodium sulphate, the hydrates, $Na_2CO_3,7H_2O$ and Na_2CO_3,H_2O, and a double salt $Na_2CO_3,2Na_2SO_4$, which latter has a wide field of stability from 26·1° to the b. p. The conditions of equilibrium in which these phases take part have been examined in detail. The double salt, which forms thick prisms (d=2·59) which deliquesce in moist air, is stable in contact with its own solution above 67°. C. I.

Equilibria in the System: Mercuric Chloride, Ammonium Chloride, Potassium Chloride, and Water at 25°. Y. Osaka and K. Ando (*Z. physikal. Chem.*, 1924, **110**, 786—798).—The following double salts and solid solutions have been found and the conditions for their existence determined: $HgCl_2,KCl,H_2O$, $HgCl_2,2KCl,H_2O$, $2HgCl_2,KCl,2H_2O$, $HgCl_2,NH_4Cl,H_2O$, $HgCl_2,2NH_4Cl,H_2O$, $3HgCl_2,2NH_4Cl,H_2O$, $9HgCl_2,2NH_4Cl$, $HgCl_2,(K,NH_4)Cl,H_2O$ (complete), $HgCl_2,2(K,NH_4)Cl,H_2O$ (complete), $3HgCl_2,(K,NH_4)Cl,2H_2O$ (a gap), $3HgCl_2,2(K,NH_4)Cl,H_2O$ (gaps), $(K,NH_4)Cl$ (a gap). For the system $HgCl_2$–KCl–H_2O see Foote and Levy (A., 1906, ii, 231), and the system $HgCl_2$–NH_4Cl–H_2O see Meerburg (A., 1908, ii, 676). J. S. C.

System: Copper Nitrate–Ammonium Nitrate–Water. G. Meijer (*Rec. trav. chim.*, 1924, **43**, 397—398).—At 30·5° the two nitrates form no compound; the diagram shows that addition of solid ammonium nitrate to a saturated solution of copper nitrate at this temperature increases the solubility of the latter, thus indicating the formation of a complex. H. J. E.

System: Cupric Nitrate–Ammonium Nitrate–Water. F. A. H. Schreinemakers, G. Berkhoff, and K. Posthumus (*Rec. trav. chim.*, 1924, **43**, 508—511; cf. Meijer, preceding abstract).—The equilibrium cupric nitrate–ammonium nitrate–water has been studied at 40° and 30° by analysis of the solid phases and corresponding residues. The existence of a hydrate $Cu(NO_3)_2,2·5H_2O$ is inferred from the data at 40°. Evidence for this has also been obtained in the system cupric nitrate–nitric acid–water. The double salt $Cu(NO_3)_2,3NH_4NO_3$, is decomposed by water and cannot coexist with ammonium nitrite. A transition point has been found at 27·1°. F. M. H.

Equilibria between Sodium, Alkaline-earth Metals, and their Chlorides in the Fused State. K. Jellinek and J. Czerwinski (*Z. physikal. Chem.*, 1924, **110**, 192—236).—The equi-

librium, $2Na+ECl_2 \rightleftarrows 2NaCl+E$, where E denotes the alkaline-earth metals, calcium, strontium, or barium, has been investigated at 1000°, the metals being distributed between the two phases, fused salts and molten lead. The actual experimental method consists essentially in the electrolysis of the fused chlorides, the molten lead serving as cathode whilst a carbon rod dipping into the fused salt acts as anode. Employing this electrochemical method, the same state of equilibrium is set up for the reaction $K+NaCl \rightleftarrows Na+KCl$ as was obtained by Jellinek and Tomoff (A., 1924, ii, 658) by purely chemical methods. In the case of experiments with the alkaline-earth metals, application of the experimental numbers to the mass law expression leads to an inconstant value. Constancy is, however, obtained if it be assumed that whilst the alkaline-earth metals and chlorides are present as simple atoms and molecules, respectively, sodium exists in the molten lead phase principally as Na_2 and that sodium chloride exists in the fused salt phase as Na_2Cl_2. The fact that freezing-point curves of lead–alkali metal alloys and lead–alkaline-earth metal alloys exhibit maxima corresponding with $Na_{2x}Pb_y$, Ca_xPb_y, etc., respectively, is interpreted as being in support of this assumption. The temperature coefficient of the equilibrium constant is found to be extremely small. It is shown that the experimental numbers obtained in a study of the equilibrium $Pb+CdCl_2 \rightleftarrows PbCl_2+Cd$ (Lorenz, Fraenkel, and Silberstein, A., 1924, ii, 258) conform to the requirements of the law of mass action.

J. S. C.

Equilibrium between Lithium, Barium, and their Chlorides in the Molten State. K. Jellinek and J. Czerwinski (*Z. anorg. Chem.*, 1924, **139**, 233—236).—By a slight modification of the method previously employed (cf. A., 1924, ii, 658) the equilibrium $2Li+BaCl_2 \rightleftharpoons Ba+2LiCl$ was examined at about 850°. The mass-action law is obeyed; lithium chloride appears to combine with the barium chloride in the fused mass. Metallic lithium dissolved in lead appears to exist as double molecules or as Li_2Pb_n. Using previously published data, the equilibrium constant of the reaction $2Na+Li_2Cl_2 \rightleftharpoons 2Li+Na_2Cl_2$ is calculated. S. K. T.

In-, Uni-, and Multi-variant Equilibria. XXVII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 441—450).—Theoretical (cf. A., 1924, ii, 389, 601). L. J. H.

System Chromium Oxide–Chromium Hydroxide–Chromite-Sodium Hydroxide. E. Müller (*Z. physikal. Chem.*, 1924, **110**, 363—383; cf. A., 1923, ii, 71).—Excess of chromium oxide or hydroxide was shaken with aqueous sodium hydroxide solutions of various concentrations for several days. From time to time samples of the turbid liquid were extracted and centrifuged, the chromium in the clear liquid and the water in the precipitate being determined. In all cases, it was found that the solubility was dependent on the time of agitation, rising to a maximum and then falling to a constant value. Both the maximum and final solubilities attain their highest

values at a sodium hydroxide concentration 14*N*. These facts are interpreted on the assumption that chromium hydroxide is a "solid liquid" in which simple and polymerised molecules are present in homogeneous solution. On account of the magnitude of the internal friction, equilibrium is only slowly attained. The ageing process does not so much consist in the enlarging of single particles as in a progressive change during polymerisation and is thus essentially chemical in character. J. S. C.

System Lead Hydroxide–Lead Oxide–Plumbite–Sodium Hydroxide Solution. E. MÜLLER [with E. REISSMANN and O. BALLIN] (*Z. physikal. Chem.*, 1924, **114**, 129—155).—By treatment of precipitated lead hydroxide with sodium hydroxide solution the following solid phases are formed according to the conditions: yellow and red forms of the oxide, PbO, and a crystalline sodium plumbite. From the solubilities of these substances in sodium hydroxide solutions of varying concentrations, an equilibrium diagram has been constructed which, however, gives uncertain results at low concentrations of alkali. It is doubtful whether the sodium plumbite is Na_2PbO_2 or $NaHPbO_2$. The preparation of a crystalline hydroxide, $Pb(OH)_2$, is also described. The amorphous hydroxides are thought to be supercooled liquids. N. H. H.

Le Chatelier Principle and its Application to the Crystallisation Processes in Binary Systems. R. RUER (*Z. physikal. Chem.*, 1924, **110**, 60—64).—The solidus and liquidus curves for binary mixtures are considered from the point of view of the principle of mobile equilibrium. J. S. C.

Reactivity of Solid Phases. J. A. HEDVALL (*J. Physical Chem.*, 1924, **28**, 1316—1330).—The author summarises previous work on the reactivity, diffusion, and recrystallisation of solid phases and surveys his own results (1913—1924). The heating curves of mixtures composed of the reacting solids in powder form indicate when a reaction is taking place. Metallic oxides can form both compounds and solid solutions, *e.g.*, Rinman's green. The temperature of thermal dissociation of a compound can be determined by this method. The rate of reaction depends on the size of the grains, large grains giving a small rate. Sometimes the reaction product forms an impermeable film; *e.g.*, the reaction between calcium oxide and copper sulphate does not go to completion, but the mixture requires regrinding several times. Very intense reactions occur on heating mixtures of a peroxide of an alkaline-earth with other oxides. The heat of reaction, intensity, and temperature of the beginning of the reaction are tabulated for alkaline-earth oxides with various metallic carbonates and sulphates. M. B. D.

Specific Heats of Aqueous Solutions of Hydrogen Chloride and Ammonia at Various Temperatures. M. WREWSKY and A. KAIGORODOFF (*Z. physikal. Chem.*, 1924, **112**, 83—89).—An apparatus for the determination of specific heats which obviates errors due to evaporation has been employed with aqueous solutions

of hydrogen chloride and of ammonia at 3°, 20°, 40°, and 60° over a range of concentrations varying from very dilute to nearly saturated. At constant temperature, the specific heat of hydrogen chloride solutions decreases with increasing concentration, but with ammonia at low temperatures, the specific heat decreases to a minimum and then increases. At higher temperatures, the minimum becomes flatter and finally disappears, the specific heat increasing approximately linearly with increase of ammonia content. For both solutions, the specific heat for constant composition increases with the temperature, except at very low concentrations, when it first passes through a minimum. The occurrence of such minima is explained by the presence of the minimum, at 40°, in the specific heat of water. From the deviations between the observed specific heats of these solutions and those calculated from the law of mixtures, it is concluded that the temperature coefficient of their heats of formation is a function which decreases with rising temperature. L. F. G.

Specific Heats of Aqueous Solutions of Hydrogen Chloride and Ammonia at Various Temperatures, etc. I—V. M. WREWSKY and others (*Z. physikal. Chem.*, 1924, **113**, 490—491; cf. preceding abstract).—Errata. G. M. B.

True Specific Heats of Salt Solutions (Cadmium Iodide, Ammonium Nitrate, and Zinc Sulphate). E. COHEN, W. D. HELDERMAN, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **112**, 135—140).—The true specific heats of solutions of various concentrations of cadmium iodide (19°), ammonium nitrate (32·3°), and of zinc sulphate (19°) were determined with an accuracy of 0·05% by the use of an adiabatic electrical calorimeter previously described (A., 1920, ii, 584). The values obtained agreed closely with those calculated from an equation in which specific heat is expressed as a function of concentration. L. F. G.

Heats of Formation of Aqueous Solutions of Hydrogen Chloride and Ammonia at Different Temperatures. M. WREWSKY and N. SAWARITZKY (*Z. physikal. Chem.*, 1924, **112**, 90—96).—Heats of solution and dilution have been determined at various temperatures. The results obtained are more complete than those of Thomsen and of Berthelot. The heats of formation of very concentrated solutions vary considerably with the composition, but the variations are relatively small when dilute solutions are formed. At constant temperature, the molecular heat of solution of ammonia is practically constant over a large concentration interval. The molecular heat of solution of hydrogen chloride increases with rise of temperature, whilst that of ammonia decreases. L. F. G.

Heats of Combustion of Normal Substances. W. JAEGER and H. VON STEINWEHR (*Z. physikal. Chem.*, 1924, **114**, 59—64).—The authors criticise as somewhat arbitrary the decision of the

"Commission pour l'Établissement d'un étalon thermochimique" in 1922 to take as the heat of combustion of benzoic acid the value obtained by Dickinson (*Bull. Bur. of Standards*, 1915, **11**, 190) in preference to those of other workers, notably Fischer and Wrede (*Z. physikal. Chem.*, 1909, **69**, 218). The electrical method used by the latter for determining the heat value of the calorimeter is said to be more trustworthy than the calorimetric method used by Dickinson. N. H. H.

Electrical Conductivity of Fused Sodium Hydroxide. K. Arndt and G. Ploetz (*Z. physikal. Chem.*, 1924, **110**, 237—242).—The electrical conductivity of fused sodium hydroxide has been determined at temperatures between 320° and 450° (m. p. of sodium hydroxide, 318°) in a silver apparatus, a brief description of which is given. As the samples of caustic soda were found to contain small amounts of sodium chloride and carbonate, the effect of addition of these substances on the conductivity has been investigated. The value of the conductivity of pure sodium hydroxide was then determined after a small extrapolation, from the values for the impure substance. At temperatures 320°, 350°, 400°, and 450° the values of k are, respectively, 2·12, 2·38, 2·82, and 3·27. J. S. C.

Fused Electrolytes. W. Biltz and W. Klemm (*Z. physikal. Chem.*, 1924, **110**, 318—342).—The electrical conductivities of a number of fused chlorides have been determined over a considerable range of temperature. Descriptions of the various forms of apparatus employed and of the experimental technique are given. With the exception of zinc chloride, the conductivity is a linear function of the temperature. The conductivities of the alkali chlorides decrease with increasing molecular weight. The chlorides of beryllium, zinc, and mercury have very low conductivities, whilst magnesium and cadmium chlorides possess conductivities of the same order of magnitude as those of the alkaline-earths. J. S. C.

Temperature Coefficient of the Mobility of Ions in Liquids. F. A. Lindemann (*Z. physikal. Chem.*, 1924, **110**, 394—398).—From a consideration of the collisions between the ions and the solvent molecules, an equation is derived for the migration velocity which involves the velocities and masses of the solvent molecules and ions, the absolute temperature, and the mean free path. For equal temperatures and free paths the equation requires that the mobilities should be greatest for light ions and constant for heavy ions. The fact that ions of light elements do not obey this rule may be due to hydration or more probably that the free path is not the same for all ions. If by hydration is meant an increase in the density of the solvent in the vicinity of the ions the theory implies its occurrence. If, however, it be understood to mean that solvent molecules are combined with the ion and travel with it, the above considerations are not applicable. J. S. C.

Effect of Boric Acid on the Solubility in Water and on the Conductivity of γ-Pyronecarboxylic Acids. P. E. VERKADE (*Rec. trav. chim.*, 1924, **43**, 879—893).—In opposition to Borsche (A., 1917, i, 117), meconic acid is considered to be 3-hydroxy-4-pyrone-2 : 6-dicarboxylic acid; in aqueous solution, it probably gives an equilibrium mixture of keto and enol forms. Comenic acid (3-hydroxy-4-pyrone-6-carboxylic acid) also gives an equilibrium mixture of keto and enol forms, in which the former predominates. In the presence of boric acid, the solubilities of meconic and chelidonic acids in water are increased, whereas the solubility of comenic acid is unchanged; hence the first two acids form complexes with boric acid, but the last does not (cf. A., 1903, ii, 288; 1910, ii, 275; 1911, ii, 261). The boric acid complex of chelidonic acid is probably an oxonium compound. Sulphuric acid conforms to the rules of Böeseken and Verkade respecting the influence of boric acid on the electrical conductivity of acids in aqueous solution (A., 1916, ii, 595). Meconic and chelidonic acids, however, in the presence of boric acid, show, at high concentration, an abnormally large decrease in conductivity. Although in all other such cases an increase has been observed, the present result is considered to support the conclusion that these acids form complexes with boric acid. W. E. E.

Conductivity and Catalytic Action of the three Strong Halogen Acids in Methyl and Ethyl Alcohol. H. GOLDSCHMIDT and P. DAHLL (*Z. physikal. Chem.*, 1924, **114**, 1—22).—The conductivities of hydrochloric, hydrobromic, and hydriodic acids and of their sodium salts in methyl and ethyl alcohols have been measured at 25°. The increase of Λ with dilution differs in both alcohols, being greatest for sodium chloride and least for hydriodic acid. Kohlrausch's law of independent ionic migration velocities is found to hold. For the three acids the influence of water on Λ_∞ is the same. In both alcohols equally concentrated solutions of the acids catalyse ester formation to the same degree. Consideration of the reaction kinetics shows that in both alcohols complete dissociation of the acids in solutions of finite concentration is not quite reached, this being more evident with ethyl alcohol. N. H. H.

Adsorption and Cataphoresis. C. FROMAGEOT (*Compt. rend.*, 1924, **179**, 1404—1406).—The velocity of cataphoresis of carbon particles in solutions of organic acids and their sodium salts depends only on the hydrogen-ion concentration increasing as the latter decreases. It is not affected by the extent to which the acid or its salt is adsorbed. It is inferred that organic acids are adsorbed in the form of non-dissociated molecules and that adsorption takes place directly on the carbon surface and not through the medium of a double layer. H. T.

Experiments on the Conductivity and Ionisation of Electrolytes. O. SCARPA (*Gazzetta*, 1924, **54**, 860—875).—The experiments illustrate the conductivity of electrolytes without the aid of

electrodes, the electrical resistance of electrolytes in motion, the action of a fixed magnetic field on a moving electrolyte, and the action of a fixed magnetic field on a jet of an electrolyte traversed by an electric current. T. H. P.

Formation and Ionisation of Compounds of Casein with Alkali. I. Transport Numbers of Alkali Caseinate Solutions. II. Conductivities of Alkali Caseinate Solutions. III. Electrochemical Behaviour of Racemic Casein. D. M. GREENBERG and C. L. A. SCHMIDT (*J. Gen. Physiol.*, 1924, 7, 287—301, 303—316, 317—326).—I. In the electrolysis of solutions of the alkali caseinates at constant p_H the quantity of casein deposited is directly proportional to the current and inversely proportional to the amount of the combined alkali. The transport numbers of the ions of alkali caseinate solutions have been measured by Hittorf's direct method, and the results support the view that the current is carried by the alkali metal as cation and by casein as anion.

II. By a method of extrapolation of results at certain dilutions, the conductivity at infinite dilution and at different temperatures has been obtained; from these data, the mobility of the casein ion is calculated. The average value, 45·3 at 30° (that of lithium is 43·7 at 30°), agrees well with the results from the transport number experiments. A linear relationship exists between the conductivity of alkali casein solutions and temperature.

III. The results of experiments on the conductivity of alkali solutions of casein and "racemic" casein, and the nitrogen distribution in these substances, are discussed from the point of view of protein racemisation. From the data obtained, and from the fact that the isoelectric point of "racemic" casein is at p_H 4·3 (that of casein is at p_H 4·55), it is concluded that, save for hydrolysis of amide groups, racemic casein is not a degradation product of casein. H. J. C.

Electro-endosmosis. II. F. FAIRBROTHER (*J. Chem. Soc.*, 1924, **125**, 2495—2501).—The calculation of potential gradient in electro-endosmosis experiments from the observed current flow and the resistance of the electrolyte is inaccurate, since the amount of current flowing through a fine capillary tube or the pores of a powder is influenced by surface effects. Electrolytes in Jena glass powder (grains 0·2—0·25 mm. diameter) show an increased conductivity of several units per cent., the increase being greatest in dilute solutions and negligible in solutions of strong acids. 0·1*N*-Potassium chloride solution is not free from surface conductivity effects. With carborundum powder (grains 0·2 mm. diameter), the alternating current resistance of carborundum–electrolyte mixtures depends on the conductivity of the electrolyte and, in very dilute solutions, the resistance of the electrolyte is of the same order as that of the carborundum. J. W. B.

Electric Transport in a Ferric Oxide Hydrosol. H. PUIGGARI (*I. Congreso Sudamer. Quím.*, 1924; reprint).—The transport of material in a ferric oxide hydrosol (p_H 3·8) is in agreement with

the ordinary laws of electrolysis when the current intensity is less than 0·01 amp. G. W. R.

Influence of Neutral Salts on the Potential of the Hydrogen Electrode in Contact with a Hydrochloric Acid Solution. L. MICHAELIS and M. MIZUTANI (*Z. physikal. Chem.*, 1924, **112**, 68—82).—The change of activity of the hydrogen ions in very dilute hydrochloric acid solution, as influenced by the addition of neutral salts, was examined by a modification of a method previously used (A., 1921, ii, 56; 1923, ii, 824). In general, with increasing salt concentration, the potential difference rises to a maximum in the region 0·2—0·3*N*, and then falls, so much so in some cases that the solution would appear to be more "acid" in the presence of salt than alone. From the results obtained with the alkali chlorides the effect of the different alkali ions is correlated systematically with atomic weight. Data are also given for the effect of various mixtures of chlorides on 0·01*N*-hydrochloric acid. L. F. G.

Electromotive Behaviour of Aluminium. I. A. SMITS (*Z. Elektrochem.*, 1924, **30**, 423—435).—When a pure aluminium electrode, previously immersed in an aluminium sulphate solution, is transferred to another of the same concentration, but saturated also with mercuric chloride, in an atmosphere of nitrogen, its potential first becomes more positive and then more negative than in the original state. At the same time a grey mercury deposit forms on the electrode, and there is probably an equilibrium set up between a liquid and solid amalgam and the electrolyte solution. After remaining at a maximum negative potential for some time, the surface becomes bright, due to the complete covering of the electrode by a liquid amalgam, and the potential begins to fall again. The presence of the mercury makes the aluminium more active. It therefore dissolves in water, leaving the mercury poorer in aluminium, and the potential becomes more positive. The whole process takes place more quickly with a polished electrode than with one etched with hydrochloric acid and washed with distilled water. It is considered that in the second case aluminium hydroxide acts as a retarder. In the presence of the nitrate ion the action on the polished electrode is retarded, whilst the potential of the etched electrode remains positive indefinitely, as if no mercury had been precipitated on it. If, however, it is washed and transferred to a pure aluminium chloride solution, it immediately takes on a large negative potential, which increases on keeping. This shows that mercury has actually been present in the electrode and that the nitrate ion has completely inhibited the usual reactions.

The electromotive behaviour of an aluminium electrode in aqueous aluminium chloride solutions of different hydrogen-ion concentrations has also been studied. The aluminium becomes most passive between the hydrogen-ion concentrations $10^{-0·5}$ and $10^{-3·5}$ but never behaves as a hydrogen electrode, showing that, under the conditions of the experiments, the aluminium is never covered

with an insulating film of oxide, but always behaves as a metallic electrode.

The results are explained in accordance with the author's views on electromotive equilibria, as deduced from his theory of allotropy. M. S. B.

Phase Boundary Potentials. L. MICHAELIS and A. FUJITA (*Z. physikal. Chem.*, 1924, **110**, 266—284).—Theoretical equations for the *E.M.F.* of cells involving immiscible liquids are developed, and the *E.M.F.* of a large number of such cells experimentally determined. The investigations cover concentration cells with the following liquid junctions; (1) benzyl alcohol saturated with water, (2) dilute electrolyte solution saturated with benzyl alcohol, cells consisting of aqueous solutions of different electrolytes at one and the same concentration separated by benzyl alcohol saturated with water, cells containing mixed electrolytes, and cells using toluene saturated with water as liquid junction. J. S. C.

Theory of the Bioelectric Cell. R. HÖBER (*Z. physikal. Chem.*, 1924, **110**, 142—146).—Bioelectric systems are set up in living matter, the protoplasmic membrane separating the protoplasm with its dissolved salts from the exterior solution. Systems consisting of two aqueous electrolyte solutions separated by some immiscible organic liquid are not suitable for purposes of comparison, the *E.M.F.* of the cell thus formed being influenced by the organic or inorganic nature of the dissolved electrolytes, whereas, when living tissue (apple and liver) is used as intermediate substance the resulting *E.M.F.* is independent of the character of the electrolytes concerned. Cells in which gelatin, coated with gelatin tannate (p_H 7·1) and euglobin on the alkaline side of the isoelectric point, replace the organic liquid behave in an analogous manner to the apple and liver systems. Protein cells therefore serve as satisfactory models for bioelectric systems. J. S. C.

Influence of Anions on the "Passivability" of Metals. V. ROTHMUND [with F. EISENKOLB and R. STEINHERZ] (*Z. physikal. Chem.*, 1924, **110**, 384—393).—The passivity of nickel and tin in solutions of acids has been established. A small anode of the metal is set up against a large platinum cathode in acid solution and a current applied. The abrupt fall in the current strength as the applied potential passes through a critical value corresponds with the entry of the metal into the passive state. Under these conditions, the metal may actually go into solution even when passive.

Nickel becomes passive in solutions of sulphuric, perchloric, nitric, acetic, phosphoric, citric, oxalic, tartaric, boric, and hydrofluosilicic acids, the necessary potential (0·34 volt) being practically independent of the nature and concentration of the acid. The metal also becomes passive in solutions of thiocyanic and the halogen acids, the critical potential being, however, much higher.

Tin becomes passive in solutions of sulphuric, hydrofluosilicic, and the halogen acids but not in nitric, iodic, perchloric, or acetic

acid. The metal goes into solution to form stannous salts from both the active and passive states. J. S. C.

Electrolysis of Potassium–Sodium Alloys. R. KREMANN and R. G. VON REHENBURG (*Z. physikal. Chem.*, 1924, **110**, 559—571).—Passage of an electric current through fused sodium–potassium alloys results in an accumulation of sodium at the anode and of potassium at the cathode. Measurements carried out with alloys containing 63—75% potassium show that the percentage separation at first increases rapidly with increasing current density and subsequently approaches asymptotically a limiting value. J. S. C.

Electrolysis of Molten Alloys. III. Lead–Cadmium and Lead–Sodium Alloys. R. KREMANN, H. KIENZL, and R. MARKL (*Monatsh.*, 1924, **45**, 133—139).—A lead–cadmium alloy, containing 57% of lead, was subjected in the molten state (300°), in a capillary tube, to the action of a current of density 0·67 amp./mm.^{2}, for 72 hours, then cooled, the current being maintained until the continuity of the metal in the capillary was broken by contraction. Passing from cathode to anode, the lead content was found to have alternately decreased and increased in the sense that the whole strip formed a series of electrolytes in which cadmium was carried to the cathode, lead to the anode, the lowest lead content observed being 43%, the highest 72%. A lead–sodium alloy, containing 90% of lead, showed no electrolytic effect at the ordinary temperature, but in the molten state at 370° sodium accumulated at the cathode, lead at the anode. F. G. W.

Electrolysis of Molten Alloys. IV. Sodium–Mercury Alloys. R. KREMANN, R. MÜLLER, and H. KIENZL (*Monatsh.*, 1924, **45**, 157—176).—When an electric current is passed through a column (diameter 1·0—1·5 mm.) of molten sodium amalgam at 240°, the sodium content is increased at the cathode and decreased at the anode. The effect increases with current density up to 4·5 amp./mm.^{2}, thereafter being independent of current density, and equilibrium is attained in 3 hours. The greater the original sodium content of the amalgam, the greater the difference between anode and cathode compositions. The effect is also greater, the longer the column of alloy, but a limit is reached at about 35 cm. It is concluded that the final structure of the column is the result of equilibrium between the forces due to the applied current and those of diffusion, which tend to homogenise the alloy column. F. G. W.

Electrolysis of Molten Alloys. V. Potassium, Calcium, and Cadmium Amalgams. R. KREMANN, R. MÜLLER, and H. ORTNER (*Monatsh.*, 1924, **45**, 177—186).—As in the case of sodium amalgam (cf. preceding abstract), passage of an electric current through a column of potassium amalgam at 240° produces an increase in potassium content at the cathode, the effect being similarly influenced by the various factors involved. The magnitude of the effect, however, is about twice as great as for sodium amalgam,

and is attributed to the more electropositive character of potassium and to the lower rate of diffusion which corresponds with the greater atomic volume. With calcium and cadmium amalgams similar, although smaller, variations were observed. F. G. W.

Application of the Method of Electrolysis with the Mercury Dropping Cathode. J. HEYROVSKY (*Compt. rend.*, 1924, **179**, 1267—1268; cf. A., 1924, ii, 598, 599; this vol., ii, 43).—This method is useful for studying ionic relations in solutions in cases where reversible cells cannot be used owing either to the low concentrations of the metals in solution or to the attackability by water or passivity of the electrodes. The solubility product and degree of ionic complexity of alkali zincates and plumbites are readily determinable by this means, which serves also to investigate inorganic or organic reductions in aqueous or non-aqueous solutions. T. H. P.

Electrolytic Polarisation. II. Cathodic Overvoltage of Mercury. S. GLASSTONE (*J. Chem. Soc.*, 1924, **125**, 2646—2656).—The extrapolation method for the determination of the overvoltage of the lead cathode (cf. A., 1924, ii, 600) is extended to the mercury cathode in acid solution. Of the three overvoltage states observed by Newbery (T., 1922, **121**, 7), only the highest state has been obtained with certainty. At low current densities, when the electrolyte is not too dilute, the potential of the mercury cathode measured by the direct method (cf. Lewis and Jackson, A., 1906, ii, 648) is almost equal to the instantaneous back *E.M.F.*, and hence the true overvoltage may be calculated from the former. At high current densities direct and extrapolated overvoltages differ; the divergence increases as the concentration of the electrolyte is decreased, but diminishes with increase of temperature. The cathodic overvoltage of mercury in sulphuric acid at such current densities does not itself vary greatly as the concentration of the electrolyte changes from $N/50$ to $6N$. At 10° the variation of the true overvoltage of mercury in a N-sulphuric acid electrolyte with current density is expressed by the equation $E=0{\cdot}955+0{\cdot}028 \log I$ (I=current density in milliamp./cm.^{2}). The minimum overvoltage is almost independent of the hydrogen-ion concentration of the electrolyte. With dilute electrolytes it is found that oxygen diffusing from the anode may influence the rate of fall of the back *E.M.F.* of the mercury cathode in a manner which depends on the material of the electrode vessel and the current density. Coating the glass surface with paraffin wax or stearic acid, or digestion with concentrated acid reduces the effect, whilst heating with alkali increases it. J. W. B.

Electrochemistry of Non-aqueous Solutions. IV. Attempts to Deposit certain Metals of the Earths and Alkaline-earths from Anhydrous Pyridine. R. MÜLLER, F. HÖLZL, W. KNAUS, F. PLANISZIG, and K. PRETT (*Monatsh.*, 1924, **44**, 219—236; cf. A., 1922, ii, 612; 1923, ii, 287).—The conditions of electrolysis are similar to those described in previous communications (*loc. cit.*),

either platinum or mercury being used as cathode. The potentials given (unless otherwise stated) refer to a silver electrode in 0·1*N*-silver nitrate in pyridine. Using a platinum cathode, magnesium was deposited from a saturated solution of magnesium bromide at 18° and from a solution saturated at 60° at about 1·8 volts. The grey coating of magnesium becomes covered with a coherent skin —a magnesium–pyridine compound—if the current is interrupted. This hinders further passage. Deposition on mercury is more difficult. Calcium is deposited on platinum from a solution of the nitrate saturated at 18°, but the formation of a calcium–pyridine compound rapidly stops the current. Zinc is deposited rather readily, but the measurement of potential is difficult, partly owing to bad conductivity. Solutions of zinc iodide, 0·1*N* and saturated, have the same decomposition potential, 1·60 volts. Cadmium iodide is only slightly soluble in pyridine and the solutions conduct extremely badly. The decomposition potential of a saturated solution at 25° is about 3·3 volts. Similar data are recorded for beryllium and aluminium. A. C.

Electrochemistry of Non-aqueous Solutions. V. Attempts to Deposit certain of the Heavy Metals from Anhydrous Pyridine. R. Müller, R. Hönig, and A. Konetschnigg (*Monatsh.*, 1924, **44**, 237—245; cf. preceding abstract).—Copper is deposited from a solution of cuprous iodide saturated at 25° (17·4 g. CuI per litre of solvent) at a potential of 2·8 volts. A green deposit (cuprous compound) separates at the anode. Solutions of manganous chloride, 0·1 and 0·168*N* (saturated at 25°), show very indefinite decomposition potentials of about 2 volts. A solution of ferrous bromide, saturated at 25° (4·87 g. of salt per litre), shows a decomposition potential of about 1·05 volts. The deposited metal appears to be in the passive state and dissolves only with difficulty in dilute hydrochloric and nitric acids. Other difficulties in the electrolysis of metals of this class in organic solvents arise from the low solubility of the salts, the poor conductivity of the solutions, and the tendency to form complexes with the solvent. The solution of cuprous iodide in pyridine deposits yellow crystals of a compound of the salt and solvent. The compound $MnCl_2$, $2C_5H_5N$, stated by Varet to be rose-coloured, is white when entirely anhydrous. A. C.

Electrochemical Aspects of the Oxidising Properties of Sulphur Dioxide. S. R. Carter and F. James (*J. Chem. Soc.*, 1924, **125**, 2231—2240).—The capacity of sulphur dioxide to act as an oxidising or reducing agent in solutions containing ferrous and ferric ions has been studied electrochemically. Measurements of electrode potentials for the half cells, $Pt|H_2SO_4,H_2SO_3,xN$-HCl, and $Pt|H_2SO_3,S,xN$-HCl show that an increase in acid concentration is accompanied by a rise in the sulphur dioxide potential, whilst under the same conditions there is a diminution in the ferric–ferrous potential. Experiments on the cathodic reduction of sulphur dioxide in acid solution show that hydrogen sulphide is not formed as a primary product. As the cathode potential is

reduced from 0·7 volt to 0·1 volt a very small current passes with separation of sulphur (but not hydrogen sulphide). At 0·1 volt a marked increase in the current density takes place. This is in agreement with Jellinek's work on the electrode potential of mixtures of hydrogen sulphate and hydrosulphite in neutral or faintly acid solution. It is probable therefore that the primary product of reduction of sulphur dioxide in acid solution is hyposulphurous acid. C. I.

"Reaction-influencing" Ions in Light and Dark Reactions. H. VON EULER and E. RUDBERG (*Z. physikal. Chem.*, 1924, **110**, 243—250).—The interpretation of results of previous studies on reaction velocities (A., 1923, ii, 547, 840) is discussed and the question of the existence of active ions in very small concentration raised. It is thought that a study of certain photochemical reactions may throw some light on the problem. J. S. C.

Temperature-coefficients of Thermal and Photochemical Reactions. N. R. DHAR (*Z. anorg. Chem.*, 1924, **139**, 194—204).—A résumé of previous work from which conclusions are drawn contrary to those recently arrived at by van Thiel (A., 1922, ii, 754). S. K. T.

Propagation of the Explosion Wave. P. LAFFITTE (*Compt. rend.*, 1924, **179**, 1394—1396).—The effect of a sudden change in the diameter of the tube on the explosion wave has been examined for mixtures of carbon disulphide and of hydrogen with oxygen (cf. Campbell, T., 1922, **121**, 2483). After a certain interval of disturbance the explosion wave was re-formed. This interval was dependent on the diameter of the second tube, varying in length from 8 cm. for a 13-mm. tube to 100 cm. for a 44-mm. tube, when the diameter of the first tube was constant at 7 mm. H. T.

Influence of Nitrogen Dilution on the Speed of Flame. O. C. DE C. ELLIS (*J. Chem. Soc.*, 1924, **125**, 2674).—If the speed of flame in the author's experiments (cf. Campbell and Ellis, A., 1924, ii, 746; Ellis and Stubbs, *ibid.*, 747) is proportional to one additive constant of the constituent gases, it must be proportional to any other. Thermal conductivity is not accurately additive. J. W. B.

Detonation Limits of Gaseous Mixtures. R. WENDLANDT (*Z. physikal. Chem.*, 1924, **110**, 637—655).—The minimum concentrations of hydrogen and carbon monoxide for the detonation of hydrogen–air, and carbon monoxide–oxygen mixtures are 18—19% and 38—39%, respectively. Carbon monoxide–air mixtures exhibit only pseudo-detonation, the maximum velocity corresponding with a 40% carbon monoxide content. [Cf. *B.*, 1925, 88.] J. S. C.

Formation and Thermal Decomposition of Carbonyl Chloride. M. BODENSTEIN and H. PLAUT (*Z. physikal. Chem.*, 1924, **110**, 399—416).—The equilibrium constant of the reaction $CO+Cl_2 \rightleftarrows COCl_2$ has been determined at temperatures between

349° and 452°. The variation of this with temperature is given by $\log K_c = -5710/T + 5{\cdot}46$. Measurement of the velocities of the direct and opposing reactions indicates that the reaction occurs entirely in the homogeneous gas phase and takes place according to the equation suggested by Christiansen (A., 1923, ii, 62); the rate of formation of carbonyl chloride is given by $v_1 = k_1\sqrt{[Cl_2]}([CO][Cl_2] - K[COCl_2])$ and the rate of decomposition by $v_2 = k_2\sqrt{[Cl_2]}([COCl_2] - [CO][Cl_2]/K)$, K being the value of the equilibrium constant $[COCl_2]/[CO][Cl_2]$. In the case of the latter reaction, certain corrections must be applied to the experimental observations. The value of the ratio k_2/k_1 is in excellent agreement with the value of K at the same temperature. It is shown that the experimental results are in accordance with the following reaction scheme: (i) $Cl_2 \rightleftarrows 2Cl$; (ii) $Cl + Cl_2 \rightleftarrows Cl_3$; (iii) $Cl_3 + CO \rightleftarrows COCl_2 + Cl$. Systems (i) and (ii) remain in a state of equilibrium whilst (iii) determines the reaction velocity. J. S. C.

Transformation of Diamond in a Vacuum at High Temperatures. P. Lebeau and M. Picon (*Compt. rend.*, 1924, **179**, 1059—1061).—The transformation of diamond into graphite is comparatively slow in a high vacuum at 1500—1900°, being incomplete after 1 hour, in marked contrast to the rapid transformation in the presence of gases (cf. Friedel and Ribaud, A., 1924, ii, 474). Above 2000° the change is much more rapid, but the swelling up and disintegration which occur in the presence of gases are not always observed. The speed of transformation of different specimens varies greatly, and is probably influenced by the presence of traces of impurities. W. H.-R.

Kinetics of Macro-crystal Formation in Tungsten by Union of Small Crystals. H. Alterthum (*Z. physikal. Chem.*, 1924, **110**, 1—16).—An aggregate of small crystals tends to pass into the more stable system consisting of a few large crystals. Owing to the small free energy involved and the extremely slow rate of diffusion in solids the velocity of this change is very small at the ordinary temperature. In presence of foreign substances, the small crystals become coated with a film and macro-crystal formation is prevented. Rods consisting of a large number of tungsten crystals were found to consist of a few large crystals after being heated for some time at 3000° in an atmosphere of hydrogen. The time necessary for the production of these large grains is not constant and with the rods employed at 3200° varied from 45 to 70 minutes. The number of crystals produced depends also on the concentration of water vapour in the hydrogen. Various theoretical points are discussed. J. S. C.

Induction Periods in Chemical Reactions. R. P. Sanyal and N. R. Dhar (*Z. anorg. Chem.*, 1924, **139**, 161—193).—The induction period of the reaction between arsenious and iodic acids is curtailed by (1) excess of iodic acid, (2) increase in the concentrations of the reactants, (3) addition of a trace of arsenic acid, (4)

addition of many mineral acids, and (5) exposure to sunlight; it is prolonged by addition of mercuric chloride or by violent shaking. The fraction of the iodine liberated increases with the arsenious acid concentration and passes through a maximum. The iodine appears on the surface of the solution even if the latter is covered with benzene or hydrogen; occasionally it appears at a nucleus on the glass.

The induction period of many reactions was followed by measuring the conductivity of the mixed solutions, which attains a maximum at the termination of the period. Some reactions showed no maximum, *e.g.*, reduction of iodic acid with ferrous sulphate, when insoluble $Fe(OH)SO_4$ is probably formed etc. The reduction with hydroxylamine hydrochloride showed a period of induction, but the conductivity did not attain a maximum until after the appearance of the iodine; this is attributed to decomposition of the hydroxylamine in aqueous solution as well as to oxidation by iodine. Sulphur is deposited from acid solutions of sodium thiosulphate while the conductivity remains fairly constant. No induction period was found for the decomposition of chlorine water, nor for the action of bromine water on oxalic and tartaric acids. With mixtures of sodium thiosulphate, hydrochloric acid, and arsenious acid, the arsenic trisulphide is probably formed immediately but is precipitated only when its solubility limit in presence of hydrochloric acid is reached (cf. Forbes, Estill, and Walker, A., 1922, ii, 271). It is concluded from experiments on the oxidation of organic acids by permanganate that an apparent period in which no reaction takes place can be produced in very slow reactions when the method of following the changes during the period is not very sensitive. Skrabal's conclusions on the reaction between potassium permanganate and oxalic acid could not be supported (cf. A., 1905, ii, 17).

S. K. T.

Velocity of Reaction in Mixed Solvents. VII. Influence of the Base on the Velocity of Saponification of Esters in Methyl Alcohol Mixtures. W. I. Jones, H. McCombie, and H. A. Scarborough (*J. Chem. Soc.*, 1914, **125**, 2590—2595).—The velocity of saponification of methyl *n*-butyrate and *o*-chlorobenzoate by lithium, barium, and tetramethylammonium hydroxides in methyl alcohol–water mixtures is measured and compared with the results obtained for potassium hydroxide (cf. T., 1923, **123**, 2688); the curves are divisible into linear sections. All four bases give points of inflection at compositions corresponding with the complexes, $2MeOH,H_2O$ and $MeOH,3H_2O$, whilst lithium hydroxide gives one corresponding with $2MeOH,2H_2O$, and the other bases at points corresponding with $MeOH,H_2O$ and $MeOH,2H_2O$. The results indicate that the process of saponification is not mainly promoted by hydroxyl ions but by the formation of a complex between the ester and the base and its subsequent decomposition. The ratio k_{KOH}/k_{base} is calculated in each case, and lithium and tetramethylammonium hydroxides yield results which support the view that the velocity of saponification depends on two factors, the

relative proportion of base existing as hydroxide and methoxide, and a steric factor including the influence both of the ester and of the base. J. W. B.

Diazoamino Conversion. H. GOLDSCHMIDT, S. JOHNSEN, and E. OVERWIEN (*Z. physikal. Chem.*, 1924, **110**, 251—265).—The influence of various acids on the rate of the diazoamino conversion in aniline solution has been investigated. In presence of strong acids the rate of reaction is roughly proportional to the acid concentration. With weak acids, there is no such proportionality, the velocity coefficients increasing more rapidly than the acid concentration. The deviations from proportionality apparently become larger as the strengths of the acids diminish. 1 : 3 : 5-Dinitrobenzoic acid, however, behaves abnormally in this respect. In all cases, the variation in reaction velocity with the change in the acid concentration c, may be represented by the expression $k = ac + bc^2$, where k is the unimolecular velocity coefficient and a and b are constants characteristic of the acid. Addition of water causes a diminution in reaction velocity in presence of strong acids, but produces an increase when the catalyst is a weak acid. Conductivity measurements in aniline solution show that the value of the molecular conductivity passes through a minimum as the dilution is increased, and that in all cases the conductivity is increased on addition of water. The effect of addition of various bases on the conductivity of a number of acids in aniline solution has been investigated. The experimental results are interpreted as being in favour of the hypothesis that the active catalyst in the diazoamino conversion is the ion, $C_6H_5 \cdot NH_3^+$. J. S. C.

Velocity of Oxidation of the Metals and the Structure of Coloured Oxide Films. D. H. BANGHAM and J. STAFFORD (*Nature*, 1925, **115**, 83—84).—Despite Mallock's observations (*Proc. Roy. Soc.*, 1918, **A**, **94**, 566), it is considered proved that interference is the true explanation of metallic temper colours since there is a close approximation between the rate of reaction of the metal with oxygen, assuming interference to be the cause (Tammann), and that in the case of zinc directly determined. In the case of copper the primary formation (as required by the interference theory) of a coherent, tightly clinging film must be ascribed to cuprous, and not cupric, oxide (cf. Hinshelwood, A., 1923, ii, 29) on account of the lattice similarity of copper and cuprous oxide, and the consequent formation of the latter with the minimum disturbance. Calculation of the thicknesses of air films corresponding with such cuprous oxide films gives results closely approximating to known colour ranges. Hinshelwood's observations that successive oxidations and reductions of a copper surface led to an intensification of the film colours produced, and to a correspondingly greater rate of fixation of the oxygen; also that the amounts of oxygen required to form purple, blue, and green films remain in constant ratio, are explained if the treatment causes a roughening of the surface, whereby the effective area of the metal is increased (cf. Mason, this vol., ii, 108; Gale, *ibid.*, 109.) A. A. E.

Formation of Nitrous Acid from Nitric Acid and Nitric Oxide. E. ABEL and D. HARASTY (*Z. anorg. Chem.*, 1924, **139**, 1—39).—The velocity of the reaction $HNO_3+H_2O+2NO=3HNO_2$ was followed by bubbling nitric oxide through nitric acid and examining the solution after a series of time intervals by the usual methods (cf. A., 1912, ii, 1093). The reaction is heterogeneous (the velocity of reduction is decreased by decreasing the glass surface of the apparatus) and is autocatalysed by the nitrous acid, which acts as a superposed positive and negative catalyst; it accelerates the reduction when its concentration is small and retards it as the concentration becomes larger. The velocity increases with increasing velocity of the nitric oxide stream and with decreasing volume of the solution of the reactants. The latter effect is mainly due to change in the hydrogen-ion concentration of the nitric acid; the nitrate-ion concentration has only a small influence. Sodium sulphate retards the reaction and in moderately large concentrations practically stops it. S. K. T.

Hydrolysis of Esters of Ketonic Acids. A. SKRABAL, F. PFAFF, and H. AIROLDI (*Monatsh.*, 1924, **45**, 141—155).—A detailed discussion of published data on the hydrolysis of esters of lævulic, acetoacetic, and pyruvic acids. Measurements of the rate of hydrolysis of ethyl lævulate in presence of hydrochloric acid and sodium hydroxide gave values of k, for normal hydrogen- and hydroxyl-ion concentration respectively, of 0·00156 and 7·7, whilst corresponding values for ethyl pyruvate, derived from similar measurements in presence of hydrochloric acid, water, and phosphate buffer solutions, were 0·00816 and $1·1\times10^5$. F. G. W.

Rate of Hydrolysis of Ethyl Orthocarbonate. A. SKRABAL and M. BALTADSCHIEWA (*Monatsh.*, 1924, **45**, 95—104).—The hydrolysis of ethyl orthocarbonate takes place in the two stages: (i) $C(OEt)_4+H_2O=CO(OEt)_2+2EtOH$; (ii) $CO(OEt)_2+H_2O=CO_2+2EtOH$. The velocity of (ii) is small in presence of hydrogen ions (cf. A., 1918, ii, 11), but is proportional to the concentration of hydroxyl ions present. Measurements made in presence of sodium carbonate gave $k=1·6$ for $[C]_{OH'}=1·0$. For methyl carbonate, the corresponding constant is 7·0. The rate of reaction (i) is not influenced by hydroxyl ions, and $k_w=3·4\times10^{-4}$. Measurements in potassium dihydrogen phosphate/disodium hydrogen phosphate, and sodium acetate/acetic acid buffer solutions showed the rate of reaction (i) to be proportional to the concentration of hydrogen ions present, and for $[C]_{H'}=1·0$, $k=1·2\times10^4$. F. G. W.

Acceleration of the Catalysis of Mixtures of Hydrogen and Oxygen by Oxygen Carriers and by the Alternating Current. K. A. HOFMANN and A. DOLDE (*Ber.*, 1924, **57**, [*B*], 1969—1976; cf. A., 1922, ii, 276, 490).—The rate of formation of water from mixtures of oxygen and hydrogen at platinum contacts continuously wetted by an aqueous electrolyte is diminished by the formation of a comparatively inactive platinum hydride from the hydrogen originally dissolved in the atomic state and of platinum oxide which

is produced even when ozone is present in the gaseous mixture. The formation of these substances can be avoided by the aid of an alternating current. After a short induction period, the platinum develops its maximum activity. The union of absorbed hydrogen atoms with oxygen molecules at a platinum surface occurs instantaneously, but time is required for the passage of the hydrogen and oxygen molecules to the metal. Since hydrogen diffuses about four times as rapidly as oxygen through the liquid, the union is delayed for lack of oxygen, and a platinum contact, even if previously primed with oxygen, rapidly becomes a strong Pt—H pole in the presence of electrolytic gas. This defect may be obviated by the introduction of a rapidly reducible and quickly oxidisable oxide which is adsorbed by platinum. For this purpose, the addition of a small amount of vanadium sulphate to 0·1*N*-sulphuric acid is effective; titanium sulphate, uranyl sulphate, and ferric ammonium sulphate are unsuitable. In all probability an oxide containing quadrivalent vanadium is produced. By this means a given platinum contact is brought to its maximum activity, which is developed with mixtures containing 33% of oxygen and not, as in the case of *N*-sulphuric acid alone, with 40% of oxygen. H. W.

Heterogeneous Catalysis. W. E. GARNER (*Nature*, 1924, **114**, 932).—A brief discussion of the bearing of results already published (Blench and Garner, T., 1924, **125**, 1288) on the mechanism of heterogeneous catalysis. Differences in the heats of absorption of oxygen by carbon at various temperatures are held to indicate a widely differing energy content of the surface carbon atoms, of which the valencies are far from being saturated by neighbouring carbon atoms. The effect of surface atoms lying in an exposed position in initiating or maintaining chemical processes is considered. A. A. E.

Corrosion of Metals. E. MAASS and E. LIEBREICH (*Z. angew. Chem.*, 1924, **37**, 897—899).—A theoretical survey of the principal factors, both chemical and electrochemical, concerned in the corrosion of metals in contact with electrolytes. Feeble polarisation of either sign favours corrosion, up to the point at which protection is afforded by actual evolution of hydrogen. Electrochemical effects are, however, often masked by the formation of a protective coating of some insoluble compound of the metal. W. T. K. B.

Action of Salt Solutions on Iron and Steel in the Presence of Oxygen. U. R. EVANS (*J. Soc. Chem. Ind.*, 1924, **43**, 315—322T).—The corrosion of iron and steel by drops of 0·1*N*-aqueous salt solutions was observed. The area under the centre of the drop becomes anodic and is attacked, whilst the outer portions, which are exposed to the air, become cathodic. Salt solutions (*e.g.*, potassium chloride) which yield soluble anodic and cathodic products (*e.g.*, ferrous chloride and potassium hydroxide, respectively) tend to increase the velocity of corrosion; where the products mix, a ring of ferrous hydroxide is formed which is oxidised to ferric hydroxide and spreads as a membrane over the surface. Outside

this membrane the iron is unattacked. When the cathodic product only is insoluble, as in the case of zinc sulphate, the cathodic area is protected from diffused oxygen and the rate of corrosion is slightly diminished; insoluble anodic products cling to the metal surface and practically prevent corrosion, although the edges of the protecting skin may fail to adhere in places and localised corrosion then takes place. Potassium chromate causes passivity, but localised corrosion is caused by the presence of large quantities of chlorides and to some extent by sulphates and more especially nitrates.

S. K. T.

Anodic Oxidation of Gold. III. F. JIRSA and J. JELINEK (*Chem. Listy*, 1924, **18**, 334—337).—The ionic product of auric hydroxide deduced from its solubility in nitric acid was found to be $[Au^{\cdots}][OH']_3=5{\cdot}5\times10^{-46}$, a value that is in fair agreement with that previously deduced from its solubility in sulphuric acid (9×10^{-46}). The solubility of auric hydroxide in water is $2{\cdot}4\times10^{-12}$ mol. per litre and its affinity constant, calculated on the assumption that in sulphuric acid solution it exists as $HAu(SO_4)_2$, is $1{\cdot}1\times10^{-6}$; it is therefore about as strong a base as hydrazine hydrate. The potential of gold in a solution of auric nitrate was found to be 1·37 volts, which agrees closely with previously calculated figures.

A. R. P.

Photochemistry of the Halogens. Action of Light on the Reactions of Iodine or Bromine with Potassium Oxalate. A. BERTHOUD and H. BELLENOT (*J. Chim. phys.*, 1924, **21**, 308—350). The reaction of iodine with potassium oxalate ($K_2C_2O_4+I_2=2KI+2CO_2$) has been investigated, the course of the reaction being determined by titration of the unchanged iodine. In the dark, the velocity of the reaction is proportional to the concentrations of the oxalate and of the iodine, and inversely proportional to the concentration of potassium iodide. The temperature coefficient of the velocity constant in the dark ($k_{t+10}:kt$) is 4·36 for the range 69·5° to 78°, the high value being partly due to the increasing dissociation of the complexes I_3' as the temperature rises. The reaction is due entirely to the I_2 molecules and not to the complexes. The reaction is accelerated by light of all visible wave-lengths and does not follow the law of Grotthus. In the case of red light where the absorption is weak, the velocity of the reaction is proportional (1) to the concentration of oxalate, (2) to the square root of the concentration of iodine, (3) to the square root of the intensity of the incident light, and (4) inversely proportional to the concentration of potassium iodide. In blue light where the absorption is almost total, (1), (3), and (4) still apply, but the velocity in this case is inversely proportional to the square root of the concentration of iodine. A complicated explanation of these facts is possible if it is assumed that the light activates only the I_2 molecules, causing these to split up into atoms which may either react with the oxalate, recombine to form I_2 molecules, or combine with I′ ions to form complexes according to the scheme $2I+I'\longrightarrow I_3'$. The temperature coefficient of the reaction in light is 3·18 for the range 25—40°; if account is taken of the

increased dissociation of the complexes as the temperature rises, the coefficient becomes 2·90, which is still a very high value.

In the dark, the reaction with bromine is similar to that with iodine, the temperature coefficient being 5·99 for the range 0—11·5°. The reaction is accelerated only by light of shorter wave-length than green, and the velocity is again proportional to the concentration of oxalate and to the square root of the intensity of the light. The concentration of potassium bromide, however, has little effect, indicating that the light activates the complexes Br_3' and Br_3K', as well as the Br_2 molecules. In dilute solutions of bromine in which the absorption is weak, the velocity of the reaction is again proportional to the square root of the concentration of bromine, but in concentrated solutions in which the absorption is complete the velocity is independent of the bromine concentration. If traces of ammonium salts are present, a period of induction occurs until the ammonium ions are destroyed. The temperature coefficient is again high, 2·04 for the range 0—15°. W. H.-R.

Influence of Aqueous Vapour Pressure and Wave-length on the Photochemical Formation of Hydrogen Chloride. A. COEHN and G. JUNG (*Z. physikal. Chem.*, 1924, **110**, 705—724).—Mixtures of hydrogen and chlorine containing water vapour equivalent to 10^{-7} mm. of mercury exhibit no photochemical combination on exposure to rays of the visible spectrum. On raising the water content to the equivalent of 10^{-5} mm. mercury, an 88% yield of hydrogen chloride is obtained. Perfectly dry gaseous mixtures on exposure to the short ultra-violet rays, $\lambda > 300\mu\mu$, react quantitatively in a few minutes. The maximum wave-length producing the photochemical combination of moist gaseous mixtures is found to be $540\mu\mu$. J. S. C.

Example of Photochemical Reaction-coupling ($COCl_2+H_2$) and the Photochemical Decomposition of Formaldehyde. G. BREDIG and A. VON GOLDBERGER (*Z. physikal. Chem.*, 1924, **110**, 521—546).—Exposure of mixtures of carbonyl chloride and hydrogen to ultra-violet light results in the 97% decomposition of the carbonyl chloride according to the scheme $COCl_2 \rightarrow CO+Cl_2$, followed by $Cl_2+H_2 \rightarrow 2HCl$. In the absence of hydrogen, the equilibrium mixture under similar conditions contains about 4% of carbon monoxide and chlorine. It was hoped to obtain formaldehyde according to the scheme $COCl_2+2H_2 \rightarrow CH_2O+2HCl$. At 10°, minute traces of this substance were obtained and none at all at 80°. The walls of the reaction vessel were observed to be coated with a white to brown deposit. The photolysis of pure gaseous formaldehyde was therefore studied at 80° and 195°. Carbon monoxide and hydrogen were the chief decomposition products. Small amounts of methane and carbon dioxide were observed and at the higher temperature a sugary substance was formed on the walls. The decomposition cannot apparently be represented by any simple stoicheiometric expression. At 80°, the decomposition follows the unimolecular law but at 195°, and for high concentrations of vapour, all light is absorbed and the rate of reaction is independent of

concentration. The failure to obtain formaldehyde from carbonyl chloride is explained on the assumption that on formation it undergoes a polymerisation to solid products and also suffers a photochemical decomposition. J. S. C.

Quantity of Ultra-violet Light Energy required to render developable a Grain of Photographic Silver Bromide. P. S. HELMICK (*J. Opt. Soc. Amer.*, 1924, 9, 521—540).—For 2537 Å., the average quanta per grain is 731±14, for 2653 Å. 514±11; for 3131 Å. 510±16, for 3650 Å. 555±13. Thus small energies are more efficient in producing developable grains than large energies. Determinations are made of the absorption of the silver bromide and the gelatin in an ordinary photographic emulsion. C. W. B.

Photographic Blackening Curve. W. MEIDINGER (*Z. physikal. Chem.*, 1924, **114**, 89—113).—The dependence of the velocity of development on the concentration of the components of a "metol" developer has been studied and the law of mass action thereby demonstrated. Addition of bromide ion retards development up to a limiting value, from which it is inferred that development is a surface reaction and that the grains adsorb bromide ion which forms a protection against the developer. Addition of iodide ion eventually stops development, whilst chloride ion is without effect. The relation between constitution and developing properties is discussed for the hydroxy-benzenes and -naphthalenes. It is shown that in a developer the hydroxyl groups must be arranged so as to allow the quinone structure to be formed on oxidation. Blackening increases with duration of development up to a limiting value. In making these last measurements a correction for fog is applied. The results obtained by "physical" development are discussed and compared with the ordinary process. The action of α-rays is approximately proportional to the mass of the silver bromide in the plate layer.

In an examination of three types of plate (Agfa "Spezial," "Reproduktion," and "Diapositiv") the covering power of the emulsions was determined. For the same emulsion, the same degree of blackening corresponds with a constant separation of silver irrespective of the times of development and exposure. Grain size alone is not a criterion of sensitiveness, which may be altered considerably in the same plate by treatment with acids and alkalis. The blackening curve for the "Spezial" and "Reproduktion" plates was determined by grain counting and titration and the light absorption is interpreted in terms of the quantum theory. N. H. H.

Latent Photographic Image. I. Relation between Light Frequency and Number of Developable Centres. F. C. TOY (*Phil. Mag.*, 1924, [vi], 48, 947—961).—By applying the laws of reflection and absorption to the case of a "single layer" photographic plate, the relative quantities of light energy, of different frequencies, absorbed by the grains when equal intensities of each are incident, are calculated; hence the number of quanta absorbed

is determined. It is shown experimentally that, except at low exposure, the relative number of developable centres produced by different frequencies is equal to the relative number of quanta absorbed. It is suggested that the departure from this equality at low exposures is due to the fact that the development does not then give a true record of the extent of the light action.

C. W. B.

Action of Ultra-violet Light on "Dye and Textile Fibre" Systems. P. HEERMANN (*Chem.-Ztg.*, 1924, **48**, 813—814, 834—835).—It is proposed to classify "dye and textile fibre" systems into four classes according to their susceptibility to light of various wave-lengths. The behaviour has been examined with reference to sunlight transmitted through glass (3500—30000λ), direct sunlight (3000—40000λ) and ultra-violet light such as that obtained by means of a mercury vapour lamp (1800—6000λ). These classes, termed "micro-," "macro-," "homo-," and "meso-tropic" are, respectively, most susceptible to light of short wave-length, long wave-length, all wave-lengths, and to the ultra-violet light present in sunlight. The majority of synthetic organic dyes are included in the "microtropic" class. The action of ultra-violet light on textile materials such as cotton, artificial silks, linen, jute, wool, and silk is closely related to the fading of dyed materials. The action of sunlight and weathering cannot, however, be satisfactorily determined by means of artificial sources of illumination. [Cf. *B.*, 1925, 68.] A. J. H.

Chemical Combination of Helium. E. H. BOOMER (*Nature*, 1925, **115**, 16; cf. Manley, this vol., ii, 57).—Mixtures of helium with mercury, iodine, sulphur, and phosphorus vapours have been examined under the influence of electron bombardment and in the presence of surfaces cooled by liquid air. The helium disappears much more quickly than under the ordinary conditions in a discharge tube. Solid substances, believed to be compounds of helium, were obtained which suddenly liberate the original amount of helium when warmed to −70° in the cases of mercury and iodine, and −125° in the cases of sulphur and phosphorus. A. A. E.

Compounds of Gold with Nitrogen. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 46—49; from *Chem. Zentr.*, 1924, ii, 18; cf. Weitz, A., 1915, ii, 39).—Explosive gold ("knallgold") is held by the author to be a mixture of gold amidine, $NH{:}Au{\cdot}NH_2$, and gold iminochloride, $NH{:}AuCl$. G. W. R.

Isomorphous Relations between Beryllium and Magnesium Compounds. F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 218—222).—Magnesium lanthanum nitrate, $Mg_3La_2(NO_3)_{12},24H_2O$, forms, with the corresponding beryllium lanthanum compound, mixed crystals containing as much as about 19% of the latter. In their simple compounds, however, beryllium and magnesium appear to be isomorphogenous only in special cases,

Such slight tendency towards isomorphism is in accord with the different atomic structures proposed for these two metals by Bohr.
T. H. P.

Reduction of Magnesium Sulphate. W. ALTHAMMER (*Kali*, 1924, **18**, 112—114; from *Chem. Zentr.*, 1924, ii, 165).—Magnesium sulphate is quantitatively reduced when heated with an equivalent amount of carbon at 750°. About 40% of the sulphur is obtained in the free state. Even with a fivefold excess of carbon no magnesium sulphide is obtained but simply an increase in the yield of free sulphur. The primary reaction is according to the equation $MgSO_4+C=MgO+SO_2+CO$. The production of sulphur follows the reversible secondary reactions: $2CO+SO_2=S+2CO_2$ and $CO_2+C=2CO$. Illuminating gas, hydrogen, carbon dioxide, benzene vapour, acetylene, and producer gases all reduce magnesium sulphate at 650—700°. The effect of producer gases depends principally on their hydrogen content. In the case of reduction with hydrogen, over 70% of the sulphur present is obtained in the free state.
G. W. R.

Crystal Structure of Mercuric Sulphide. II. N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSSEN (*Rec. trav. chim.*, 1924, **43**, 894—896; cf. *ibid.*, 677).—The agreement between the Debye–Scherrer photographs of cubic (black) and trigonal (red) mercuric sulphides is due to identity in the dimensions of the octahedral and basal planes respectively. Neither β′ mercuric sulphide nor any other modification described by Allen and Crenshaw is distinct from the black and the red forms.
W. E. E.

Double Nitrates of Metals of the Cerium Group with Copper and with Cadmium. G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 246—250).—*Lanthanum copper nitrate*, $2La(NO_3)_3,3Cu(NO_3)_2,24H_2O$, forms hygroscopic, pale blue, trigonal crystals, d^{10} 2·227, which are melted in their water of crystallisation by the heat of the hand, and form mixed crystals with the analogous lanthanum magnesium nitrate. *Cerium copper nitrate*,

$$2Ce(NO_3)_3,3Cu(NO_3)_2,24H_2O,$$

forms highly deliquescent, pale blue crystals, d^{10} 2·237.
T. H. P.

Allotropy of Germanium Dioxide. J. H. MÜLLER and H. R. BLANK (*J. Amer. Chem. Soc.*, 1924, **46**, 2358—2367).—An allotropic form of germanium dioxide, quantitatively insoluble in boiling water and stable towards acids (*e. g.*, hydrofluoric) and alkalis, is prepared by heating at 200—1100° for 4 hours the oxide obtained by the evaporation of an aqueous solution of the oxide. The maximum yield under these conditions, and probably also the maximum velocity of transition, occurs when the heating is carried out at 380°. This insoluble variety, which must be the stable modification at the ordinary temperature, is reconverted into the soluble form by fusion. The yields obtained by heating the soluble oxide at 280° increase with duration of heating up to a maximum conversion of about 15%; this probably indicates the presence of

a second soluble allotropic form in the soluble oxide obtained by evaporation. The m. p. of any variety is between 1090° and 1100°. The oxide may be purified from sulphates by ignition above 950° for about 36 hours; chlorides are removed by repeatedly moistening the oxide with water, evaporating, and igniting at 950° (cf. Nichols, A., 1923, ii, 571). S. K. T.

Pharmacological Properties of Tin Hydride and Germanium Hydride. F. PANETH and G. JOACHIMOGLU.—(See i, 197.)

New Oxides of Nitrogen. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 20—33; from *Chem. Zentr.*, 1924, ii, 17—18; cf. A., 1914, ii, 39).—When nitrogen is burnt in the high-tension flame arc or when ammonia is burnt with a platinum catalyst at low red heat, nitrogen *iso*dioxide, N=O=O is the primary product. This is in contradiction to the assumption that nitric oxide is the only oxide of nitrogen stable at high temperatures. The lighter colour which is observed when nitrogen peroxide is passed through a hot tube is not to be attributed to decomposition into nitric oxide and oxygen but to the formation of the lighter coloured nitrogen *iso*dioxide. G. W. R.

Reactions between Nitrous and Sulphurous Acids. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 1—19; from *Chem. Zentr.*, 1924, ii, 16—17; cf. A., 1907, ii, 23, 700).—The reactions of sulphites and hyposulphites can be explained on the assumption that they are differently constituted. For the sodium salts, the accompanying formulæ are given. The fact that normal sulphites do not react with nitrites is explained by steric hindrance, owing to the central position of the sulphur atom. The reactions of nitrites and nitrous acid with sulphites and sulphurous acid are discussed from this point of view. The different reactions are best explained by assuming for nitrous acid the formula $N(OH)_3$. By successive replacement of the hydroxyl groups by sulphonic acid groups, dihydroxylaminesulphonic acid, hydroxylaminedisulphonic acid, and nitrilosulphonic acid are formed. In the presence of an indifferent acid, nitrososulphonic acid tends to form with nitrous acid, nitrosisulphonic acid, $O{:}N(OH){\cdot}SO_3H$, with liberation of nitric oxide. This acid is stable in sulphuric acid solution. It is also formed by reduction of nitrosulphonic acid by copper or mercury in sulphuric acid solution. It yields nitric oxide and sulphuric acid on decomposition. Nitrosulphonic acid is decomposed according to the equation $O{:}N{\cdot}SO_3H+H_2O=NOH+H_2SO_4$. The hyponitrous acid thus formed rapidly decomposes, yielding nitrous oxide and water. G. W. R.

Monochloroamine. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 50—78; from *Chem. Zentr.*, 1924, ii, 162—163; cf. A., 1909, ii, 232; Marckwald and Wille, A., 1923, ii, 558).—In the reaction whereby monochloroamine is formed from sodium hypochlorite and aqueous ammonia, ammonium hypochlorite is

not produced. Monochloroamine may be distilled in a vacuum without decomposition from the products of the above reaction in the presence of 50% zinc chloride solution. Concentrated aqueous solutions of monochloroamine on being kept at low temperatures deposit yellow crystals which appear to be chlorine hydrate. Monochloroamine is decomposed by strong ammonia solution, yielding ammonium chloride and nitrogen. In the presence of strong alkalis, hydrazine is produced according to the equation $NH_2Cl+NH_3+NaOH=N_2H_4+NaCl+H_2O$. The yield of hydrazine is increased by the presence of formaldehyde, sugars, gum, or gelatin. The chlorine of monochloroamine may be replaced by the sulphonic acid group, using sodium sulphite. With sodium hydrogen sulphite, however, sulphonation does not take place even in the presence of sodium hydroxide. In the reaction between sodium hydroxide and monochloroamine, it is probable that some tri-imide, N_3H_3, is formed. G. W. R.

Composition of Nitrogen Iodide. F. Raschig (*Schwefel- u. Stickstoffstudien*, 1924, 34—45; from *Chem. Zentr.*, 1924, ii, 18).—The precipitate obtained by the reaction of potassium iodide solution with aqueous ammonia, which has the composition NH_3,NI_3, when washed with water yields ammonia and nitrogen iodide. The original precipitate on being dried loses half its ammonia, yielding the explosive compound, NHI_2, considered by the author to be a molecular compound of 2 mols. of nitrogen iodide and 1 mol. of ammonia. The ammonia–nitrogen iodide compound reacts with sodium hydroxide according to the following equations: (i) $NH_3,NI_3+4NaOH=NH_3+3NaI+2H_2O+NaNO_2$; (ii) $NH_3,NI_3+3NaOH=N_2+3NaI+3H_2O$. With sodium sulphite the following reaction takes place: $NH_3,NI_3+3Na_2SO_3+3H_2O=2NH_3+3HI+3Na_2SO_4$. The precipitate obtained by the action of potassium iodide on chloroamine solution in the presence of ammonium chloride is similar to that obtained from the action of iodine on aqueous ammonia. G. W. R.

Ozone from Flames. H. von Wartenburg (*Z. physikal. Chem.*, 1924, **110**, 285—290; cf. Riesenfeld and Beja, A., 1924, ii, 470).—Manchot's criticism (A., 1924, ii, 543) of the author's assumption that the formation of ozone in flames containing oxygen and hydrogen is preceded by the formation of hydrogen peroxide and its decomposition into water and oxygen atoms (A., 1921, ii, 107) is considered. Oxygen atoms are certainly present in such flames and these in some way form ozone, since Riesenfeld (A., 1924, ii, 470) has shown that the quantities of ozone are far too large to be explained on the assumption of thermal formation from oxygen. Atomic oxygen may result from some partial reaction following a primary addition of molecules, or by means of molecular collisions whereby translational energy is converted into chemical energy. The question of an electron effect in the absence of an accelerating electric field is also discussed.

J. S. C.

Formation of Ozone and Hydrogen Peroxide in the Oxyhydrogen Flame. E. H. RIESENFELD (*Z. physikal. Chem.*, 1924, **110**, 801—807).—Dry mixtures of hydrogen and oxygen have been burned at the end of a silica tube 0·2—0·4 mm. in diameter, and the gases immediately cooled, the amounts of ozone and hydrogen peroxide formed being determined. The small dimensions of the flame permit a much more efficient cooling than was obtained by other investigators, the amounts of ozone and hydrogen peroxide being consequently much greater. The ratio $[O_3]/[H_2O_2]$ is found to decrease as the hydrogen content of the burning gases increases, becoming zero when a gas mixture of the composition $H_2{:}O$ is attained. With mixtures richer in hydrogen much more hydrogen peroxide is obtained and it therefore seems unlikely that this latter substance is to be regarded as the precursor of ozone. A more plausible hypothesis is that ozone is produced by collisions between ionic or atomic oxygen and molecular oxygen and that the presence of hydrogen peroxide is due to collisions between oxygen ions or atoms and hydrogen molecules. J. S. C.

Reduction of Sulphuric Acid to Hydrogen Sulphide. A. VILA (*Compt. rend.*, 1924, **179**, 1163—1165).—When sulphuric acid vapour mixed with hydrogen is passed over silica heated at 700—900° quantitative reduction to hydrogen sulphide takes place. H. T.

Formation and Decomposition of Polythionates. F. FOERSTER (*Z. anorg. Chem.*, 1924, **139**, 246—260).—Criticism of Josephy's work (A., 1924, ii, 470) in the light of previous work by the author (cf. A., 1923, ii, 23) and others. S. K. T.

Reaction between Arsenious Anhydride and Chlorine. L. CAMBI [with P. M. VOLTOLIN] (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 527—532).—The experimental results show that the products of the interaction of chlorine and arsenious anhydride in presence of water represent the resultant of the two reversible reactions, $AsCl_3+Cl_2+(2{\cdot}5+n)H_2O \rightleftarrows 0{\cdot}5As_2O_5,nH_2O+5HCl$; and $0{\cdot}5As_2O_3+3HCl \rightleftarrows AsCl_3+1{\cdot}5H_2O$. The final result corresponds with the former equation when the proportion of water present is high and approximately with the latter when little water is used, liquid trichloride being formed in this case. Application of the reaction to the preparation of calcium and lead arsenates is considered. [Cf. *B.*, 1925, 97.] T. H. P.

Reaction between Ferrous Salts and Cuprous Salts. R. C. WELLS (*Amer. J. Sci.*, 1924, **8**, 428—433).—In the reduction of cuprous salts with ferrous hydroxide the main reaction corresponds with the equation, $3FeO+2CuCl=2Cu+Fe_2O_3+FeCl_2$, especially when cuprous chloride is present in excess. With decrease of the latter, the reaction is: $4FeO+2CuCl=2Cu+Fe_3O_4+FeCl_2$. Investigation of the effect of the hydrogen-ion concentration shows that the reaction $Cu^{\cdot}+Fe^{\cdot\cdot\cdot} \rightleftharpoons Cu+Fe^{\cdot\cdot\cdot}$ results in the separation of copper at $p_H>5{\cdot}0$. H. T.

Ruthenium Oxides. L. Wöhler, P. Balz, and L. Metz (*Z. anorg. Chem.*, 1924, **139**, 205—219).—The methods previously proposed for the preparation of ruthenium pentahydroxide are shown to be erroneous. Debray and Joly's method (A., 1888, 559, 920) yields the tetrahydroxide; reduction of the tetroxide and of potassium ruthenate with alcohol gives the dioxide mixed with an explosive organic compound of ruthenium; Remy's method (A., 1923, ii, 329) gives the sesquioxide mixed with more or less dioxide. Pure ruthenium dioxide may be prepared by heating ruthenium sesquichloride, Ru_2Cl_3, at 600—700° in oxygen; the sesquichloride is obtained by the action of chlorine on finely divided ruthenium at 400—600°, or by the reduction of sodium ruthenium chloride, Na_2RuCl_5, at 400° in hydrogen. Hydrogen peroxide solution reduces ruthenium tetroxide solution, and oxidises ruthenium trihydroxide to the tetrahydroxide, which when heated (<800°) in a vacuum yields the pure dioxide. Treatment of potassium ruthenate with carbon dioxide or nitric acid gives a mixture of ruthenium tetroxide and tetrahydroxide. Ruthenium is the most easily oxidised of the noble metals; the vapour pressure of the dioxide is 15 mm. at 1000°, decomposition into metal and tetroxide taking place at higher temperatures. Ruthenium trihydroxide loses oxygen and water when placed in a vacuum; when carefully dehydrated in carbon dioxide it yields a mixture of dioxide and metal. The monoxide is not formed by the direct oxidation of the metal, nor by the reduction of the tetroxide in hydrogen. S. K. T.

Compounds of Carbon Monoxide with Ruthenium Salts. W. Manchot and J. König (*Ber.*, 1924, **57**, [*B*], 2130—2133).—Ruthenium tri-iodide is converted smoothly by carbon monoxide at 240—250° into the *compound*, $RuI_2(CO)_2$, in which the carbon monoxide is retained with remarkable firmness. Ruthenium tribromide is less readily transformed at 270—290° into the *substance*, $RuBr_2(CO)_2$, whereas the corresponding chloro *compound* is formed only slowly and incompletely from ruthenium trichloride at 270°. Aqueous or alcoholic solutions of ruthenium trichloride or tribromide absorb carbon monoxide slowly.

The facilitation of the chlorination of ruthenium at 360—440° by the presence of carbon monoxide depends on the formation of the compound just described and its decomposition with the production of finely-divided ruthenium. H. W.

Ozone. G. M. Schwab (*Z. physikal. Chem.*, 1924, **110**, 599—625).—A convenient form of apparatus for the preparation of pure ozonised oxygen by the customary silent discharge method is described. The gas so obtained contains about 15% of ozone. On cooling by means of liquid air two liquid phases result, the upper light blue layer being a saturated solution of ozone in oxygen and the lower dark blue layer a saturated solution of oxygen in ozone. At −183° the latter phase contains 70% of ozone, and on fractionation pure ozone is obtained. The critical solution temperature is −158°.

The mean value for the molecular weight by volumetric methods (determination of iodine liberated from potassium iodide in presence of boric acid) is 49·1 and the value given by the Dumas vapour density method 47·9. The following physical constants have been determined: b. p. −112·3°, m. p. −251·4°, critical temperature −5°, critical density 0·54, critical volume 89·4 c.c./mol., d^{-183} 1·71±0·05. The expansion between −192° and −80° is given by $v_T=0·512+0·000456T+0·0000039T^2$, T being the absolute temperature. The calculated critical pressure is 67 atm. The question of the structure of ozone is discussed and it is shown that the most probable formula is O=O=O. [Cf. Riesenfeld and Schwab, A., 1922, ii, 761.] J. S. C.

Formation of Nitric Oxide by purely Electrical Means. G. M. Schwab and S. Loeb (*Z. physikal. Chem.*, 1924, **114**, 23—43).—An apparatus is described in which nitrogen and oxygen are made to react at 6 mm. pressure in a cold direct current discharge with an oxide cathode. The velocity of formation of nitric oxide is constant for nitrogen percentages of 20 to 80, outside which limits it falls towards zero. The velocity of decomposition depends on the form of discharge but in an unreproducible manner. Interpreted kinetically, the results show that the optical absorption law can be closely applied to the activation of a component without regard to the energy distribution in the discharge. It is concluded that the greater part of the energy taken from the oxygen serves to activate the nitrogen by impact of the oxygen ions on the nitrogen molecules, whilst the energy absorbed by the latter for which the absorption law applies is, under the experimental conditions, only a small part of the current energy, which is mainly lost by reflection from the electrodes. N. H. H.

Test of the Efficiency of a Stirring Contrivance. W. A. Roth (*Z. physikal. Chem.*, 1924, **110**, 57—59).—The efficiency of a stirring device may be determined by embedding a little coloured salt (*e.g.*, potassium permanganate) in sodium sulphate which is introduced into the agitated liquid, the time necessary for the solution to assume a homogeneous tint being noted. Quantitative determinations may be carried out by measurement of the electrical conductivity in various parts of the solution or by titration of small samples with oxalic acid. Alternatively, the permanganate may be enclosed in silver gauze or "cellon" paper. J. S. C.

Trustworthy Shaking Machine. A. G. Milligan (*J. Chem. Soc.*, 1924, **125**, 2674—2675).—The bottle carrier is supported on four springy laths of straight-grained ash allowing a limited horizontal displacement and exerting a strong restoring force at the end of each stroke, and thus very little power is needed and the danger of stoppage at a dead point eliminated. J. W. B.

Apparatus for Physical Chemistry Laboratories. O. Scarpa (*Gazzetta*, 1924, **54**, 876—887).—Descriptions are given of apparatus for measuring coefficients of diffusion in liquids and

surface tension of liquids, and of a tonometer for measuring dissociation pressures and the depression of the vapour pressures of liquids. T. H. P.

Modifications in Laboratory Apparatus. T. S. PATTERSON (*J. Soc. Chem. Ind.*, 1924, **43**, 281—283T).—The following apparatus is described and figured: (*a*) A water condenser which can be suspended in the neck of a flask and containing a centre tube down which additions may be made to the contents of the flask during a reaction. (*b*) A simple extractor working at the b. p. of the solvent, and less fragile than the Soxhlet type. (*c*) A simple pressure equaliser. (*d*) A device for absorbing fumes, consisting of a modified calcium chloride tower packed with pumice; a suitable absorbent, contained in a dropping funnel at the top, is allowed to trickle down the tower. (*e*) A simplified vacuum distillation receiver of the rotating type. (*f*) A test-tube stand with a wedge-shaped base, enabling moisture from the tubes to drain away rapidly. A large number of holes in the die of a sodium-wire press hastens the preparation of sodium-wire. S. K. T.

Apparatus for the Accurate Determination of Solubilities. E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **112**, 150—155).—An apparatus is described and figured which is similar to one previously used (cf. A., 1923, ii, 386), but suitable for determinations carried out at normal pressure and higher temperatures. The solubilities of thallium sulphate at 30°, 40°, and 60° and of silver nitrate at 30° have been determined by this method. The former values are within about 0·2% of those of Berkeley (A., 1904, ii, 648), but the solubility of silver nitrate is 73·82 g. per 100 g. of solution, compared with 73 obtained by Schreinemakers and de Baat (*Arch. Néerland.*, 1910, [ii], **15**, 415). L. F. G.

Calorimeter for the Electrical Adiabatic Determination of Heats of Solution. E. COHEN, A. L. T. MOESVELD, and W. D. HELDERMAN (*Z. physikal. Chem.*, 1924, **112**, 141—149).—An improved form of an apparatus previously used (A., 1920, ii, 584) is described and figured; it has given results reproducible to within about 0·3%. The method of employing it where a negative heat of solution occurs is explained. Three determinations of the molecular heat of solution of ammonium nitrate gave the values —3579, —3583, and —3589 cal., respectively. L. F. G.

Apparatus for the Catalytic Dehydrogenation of Alcohols. S. G. WILLIMOTT (*Analyst*, 1925, **50**, 13—16).—The usual laboratory methods for preparing aliphatic aldehydes were found unsatisfactory, never giving yields of more than, *e.g.*, 20% of the theoretical quantity for propaldehyde, but by dehydrogenating the alcohol, using an improved form of Neave's apparatus (A., 1909, ii, 835), an average yield of 30% was obtained in this case. The alcohol vapour is passed at a controlled speed through a pre-heater into the dehydrogenation tube (at 300°) containing the copper catalyst; for small operations copper-bronze may be used. D. G. H.

Theories of Strong Electrolytes and their History. J. J. VAN LAAR (*Z. anorg. Chem.*, 1924, 139, 108—134).—A mathematical paper in which Debye's theory (cf. A., 1923, ii, 459, 617, 724, 827) is correlated with the Rudolphi–van't Hoff laws (cf. *Archives Teyler*, 1900, [ii], 7, 1). S. K. T.

Mineralogical Chemistry.

Constitution of the Silicates. Chlorites. V. ISKYUL (*Private Pub.*, Petrograd, 1917).—Analyses of the following minerals are given, together with data regarding the solubility of the silica in acid and alkali, and considerations of constitution: forsterite, olivine, glinkite, enstatite, bronzite, anthophyllite, actinolite, serpentine, chrysotile, antigorite, melanite, and pyrope garnet, clinochlore, leuchtenbergite, penninite, rhodochrome, tabergite, corundophyllite, and prochlorite. Olivines are classed as orthosilicates; on ignition, the reactions, (*a*) $Fe_2SiO_4+O=Fe_2O_3+SiO_2$; (*b*) $Mg_2SiO_4+SiO_2=2MgSiO_3$, occur. The solubility of amphibole silica is twice as great as that of pyroxene silica. Experiments with serpentine indicate the occurrence of the reaction, $H_4Mg_3Si_2O_9=2H_2O+Mg_2SiO_4+MgSiO_3$. The serpentines are classed as metasilicates. The experiments support Vernadsky's theory that the chlorites are salts, and complex compounds of these salts, of the acids of the formula $Al_2Si_{m+2}O_{2m-n+7}(OH)_{2n}$.

CHEMICAL ABSTRACTS.

Composition of Melilite. A. N. WINCHELL (*Amer. J. Sci.*, 1924, 8, 375—384).—It is suggested that all minerals of the melilite group conform to the general type R_5O_7 (R including silicon), the dominant members being gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$). In substituted members, Fe'' replaces part of the magnesium and Fe''' part of the aluminium. Alkalis present may be assigned either to $Na_2Si_3O_7$ or $NaAl_3SiO_7$. Contrary to the views of Buddington and Schaller, grossularite and andradite are not miscible with melilites. Excess of silica may exist in the interatomic spaces of the molecules. This increases the density but has little effect on the index of refraction. H. T.

Sincosite, a New Vanadium Mineral. W. T. SCHALLER (*Amer. J. Sci.*, 1924, [v], 8, 462—480).—A new vanadium mineral, sincosite, from Sincos (Peru), is described. It probably belongs to the uranite group; its chemical composition is V_2O_4,CaO,P_2O_5,xH_2O (x=4 or 5). Traces of selenium are also present. It occurs as small, brittle, green crystals (d 2·84), which closely resemble crystals of torbernite in shape, habit, and optical properties. Most of the crystals are uniaxial, but some are biaxial; nearly all become biaxial on keeping, this form probably corresponding with a lower hydrate. They revert to the uniaxial form when stored in a desiccator over dilute sulphuric acid. S. K. T.

Analysis of the New Germanium-Gallium Mineral Germanite. F. W. KRIESEL (*Chem.-Ztg.*, 1924, 48, 961—963).—The finely-ground mineral is dissolved in a mixture of nitric and sulphuric acids and the solution is evaporated until the former is expelled; hydrochloric acid is added and the germanium distilled off as tetrachloride while a current of chlorine is passed through the apparatus. The distillate is treated with hydrogen sulphide, the germanium sulphide dissolved in ammonium sulphide, reprecipitated by the addition of sulphuric acid, collected, washed with dilute acid, dried, and ignited; the oxide residue is reoxidised with nitric acid and heated repeatedly with ammonia until of constant weight. Arsenic is removed from the residue in the distillation flask by a second distillation in the presence of a stream of sulphur dioxide and the remaining liquid is used for the determination of lead, copper, iron, and zinc. A second but much larger portion of the mineral is dissolved as before and the solution is repeatedly evaporated with hydrochloric acid to remove germanium, then electrolysed to remove copper and arsenic, and finally evaporated with nitric and sulphuric acids to dryness. Iron, aluminium, and gallium are precipitated in the aqueous solution of this residue by the basic acetate process, cadmium, cobalt, nickel, manganese, magnesium, and calcium being determined in the filtrate. The iron precipitate is dissolved in dilute sulphuric acid, the solution reduced with hydrogen sulphide, the excess of which is boiled off, and, after neutralisation with sodium carbonate, the gallium is precipitated by boiling with cuprous oxide. The precipitate is dissolved in nitric acid, the copper removed with hydrogen sulphide, and the gallium separated from aluminium by addition of sodium acetate and arsenite followed by saturation of the solution with hydrogen sulphide. The gallium–arsenic sulphide precipitate is dissolved in nitric acid, which is removed by evaporation with hydrochloric acid and the arsenic is precipitated as sulphide, the gallium being recovered from the filtrate by addition of ammonia. For the determination of molybdenum, a third portion is dissolved in nitric acid, the solution filtered, treated with ferric nitrate, neutralised with sodium carbonate, diluted considerably, and boiled, the precipitate of basic iron salts dissolved in hydrochloric acid, and the molybdenum precipitated as sulphide, which is dissolved in ammonium sulphide, reprecipitated, and subsequently dissolved in nitric acid. The solution is evaporated with hydrochloric acid and sulphur dioxide to expel arsenic and the molybdenum eventually precipitated as lead molybdate. Tungsten trioxide, silica, titanium dioxide, and barium sulphate are determined in the material insoluble in aqua regia. An analysis of a clean specimen of germanite by the above process gave the following (percentage) figures: Cu, 45·39; Pb, 0·66; Zn, 2·58; Fe, 4·56; Ge, 8·70; S, 30·65; As, 4·13; Ga, 0·76; SiO_2, 0·23; WO_3, 0·18; TiO_2, 0·004; Mo, 1·282; Mn, 0·02; Ni, 0·001; Co, 0·013; Cd, 0·07; CaO, 0·12; MgO, 0·055; C, 0·136; Ag and Au, 0·005. The mineral occurs fairly intimately mixed with tetrahedrite, which itself contains 0·14% Ge. A. R. P.

Analytical Chemistry.

Multiple Gas Analysis Apparatus. M. N. J. DIRKEN (*J. Scientific Instruments*, 1924, 2, 55—60).—The ordinary apparatus is modified so that the rate of working is doubled whilst the same accuracy is attained. The absorption vessel, which is an improved Shipley and Henderson type, can be readily detached from the burette and placed in a shaking machine while another is put in its place. By this means four or five sets of absorption vessels may be used in rotation. A new sampling tube containing no stopcocks and a new method of collecting and transferring gas samples are described. S. K. T.

Hæmoglobinometer. K. BÜRKER.—(See i, 177.)

Economic Anode for Rapid Electro-analysis. A. LASSIEUR (*Bull. Soc. chim.*, 1924, [iv], 35, 1530—1532).—The anode described by Bertiaux (A., 1924, ii, 695) is criticised partly on account of the inferior deposits obtained, especially with antimony, zinc, and lead, on the perforated foil, but mainly on account of the cost of the heavy platinum–iridium foil and of the possibility of errors introduced by the use of silver supports. The latter source of error may be eliminated by substituting special steel for the silver. A more economic rotating anode is described in which a thin platinum wire is attached to a suitable glass agitator. This anode cannot be used for the analysis of brasses and bronzes containing lead in which the lead is deposited on the anode as lead peroxide, but the conditions have now been determined for the successive deposition of copper and lead in the metallic state. Anodes with large surfaces and oxidising powers are not always advantageous in electro-analysis. R. B.

Automatic Gas Analysis. L. LÖWENSTEIN (*Z. physikal. Chem.*, 1924, 110, 799—800).—A method is described for the accurate determination of small quantities of hydrogen, methane, etc., in presence of a large excess of oxygen (or *vice versa*), in which the gases, after passing through a combustion chamber, enter a hair hygrometer, the alterations in the length of the fibre being an indication of the water content (*i.e.*, of the hydrogen or oxygen content of the original gas). J. S. C.

Gasometric Determinations by Combustion with Copper Oxide. I. J. ŠVÉDA (*Chem. News*, 1925, 130, 1—5).—Hydrogen and carbon monoxide are completely burnt to water and carbon dioxide, respectively, whilst methane remains unchanged when brought into contact with copper oxide at 280—290°. In order to analyse a mixture of these gases confined over mercury in a eudiometer, a miniature platinum-wound electric furnace containing a mixture of 3 parts of cupric oxide and 1 part of ceric oxide is introduced into the gas and the temperature adjusted by a pre-

determined external resistance to 280—290°. A slight error is introduced into the analysis by the adsorption of a certain amount of carbon dioxide by the furnace, but the volume after combustion of pure carbon monoxide is practically the same as before. The furnace is made by winding a few turns of platinum wire, 0·16 mm. thick, around a narrow porous crucible made of Marquardt paste, covering the wire with a further quantity of the paste, packing the crucible with the oxide mixture, and drying by heating it to redness. After use, the cupric oxide may be regenerated by heating the furnace at a red heat in air. A. R. P.

Determination of the Hydrogen-ion Concentration of the Soil. (1) W. R. G. ATKINS. (2) R. M. BARNETTE, D. J. HISSINK, and J. VAN DER SPEK.—(See i, 220.)

Acid-Base Titrations and Equilibria of Weak Bases and Acids. L. J. HARRIS (*Nature*, 1925, **115**, 119—120).—By determining the volume of standard alkali or acid required to titrate a solute over a given p_H range or to a given p_H end-point, substances with feebly acidic or basic properties can be determined to an accuracy of the same order as that of an ordinary acid–base titration. It is possible to resolve a compound titration curve into its components and determine a number of acids and bases or ampholytes present simultaneously in a mixture, even when partial overlapping occurs. The method has been applied to determinations of proteins in solution, to determinations of molecular weights and dissociation constants, and to the detection of chemical changes. For glycine and arginine, accurate values of α in the equation $[H^{\cdot}]=\alpha$[free HCl] have been calculated. A. A. E.

Use of Aminosulphonic Acid as a Standard in Volumetric Analysis. L. HERBOTH (*Arch. Pharm.*, 1924, **262**, 517—519).—Aminosulphonic acid is easily prepared (cf. Hofmann, "Lehrbuch der anorg. Chemie," 4th ed., 1922, 174) by saturating a concentrated solution of hydroxylamine hydrochloride with sulphur dioxide. The crystals (decomp. 205°) are anhydrous and quite stable in air. The compound yields ammonia when treated with sodium hydroxide and its barium and mercurous salts are sparingly soluble. It can be satisfactorily used as a standard in alkalimetry in either 0·1*N*- or 0·01*N*-solution, with dimethylaminoazobenzene, methyl-red, phenolphthalein, or rosolic acid as indicator. W. A. S.

Conductivity of Water. F. BORDAS and F. TOUPLAIN (*Ann. Falsif.*, 1924, **17**, 516—524).—The conductivity of a water affords the best physical test of its composition. The presence of even small numbers of hydrogen and hydroxyl ions allow of the passage of a current, and dissolved gases, particularly carbon dioxide, appreciably increase the conductivity. If, however, as much as 300 mg. of a salt per litre is present the effect of the dissolved gas disappears. D. G. H.

Determination of Water in Mixtures of Ether, Alcohol, and Water. R. K. NEWMAN (*J. Soc. Chem. Ind.*, 1924, 43, 285—287T). —A measured volume of the mixture is boiled and the vapour passed over calcium carbide and then through concentrated sulphuric acid. The acetylene formed from the water is collected in a Schiff nitrometer over potassium hydroxide solution and measured. The other constituents are retained by the acid. The apparatus is swept out with a stream of carbon dioxide, which is also used to remove any acetylene dissolved in the acid. From the results of experiments made by this method, it is concluded that ether dried over sodium for six months still contains 0·14% by weight of water. S. K. T.

Determination of Minute Quantities of Iodine in Biological Material. F. C. KELLY and A. D. HUSBAND.—(See i, 183.)

Use of Iodic Acid and Potassium Hydrogen Carbonate for the Preparation of Standard Solutions. M. RUSZKOWSKI (*Roczniki Farmacji*, 1924, 2, 108—109; from *Chem. Zentr.*, 1924, ii, 215).—For the volumetric determination of thiosulphate the author recommends the use of iodic acid. The iodic acid is allowed to react with potassium iodide solution and the iodine thus liberated is titrated with the thiosulphate solution. G. W. R.

Determination of Oxygen in Organic Compounds. II. H. TER MEULEN (*Rec. trav. chim.*, 1924, 43, 899—904).—Modifications of the catalytic hydrogenation method of determining oxygen (A., 1922, ii, 717) are described, which render it applicable to organic compounds containing one or more of the elements nitrogen, sulphur, and halogens. W. E. E.

Rapid Determination of Sulphur. F. KÜHL (*Z. anal. Chem.*, 1924, 65, 185—186).—The sulphur is dissolved in a known volume of hot standard sodium hydroxide solution, and, after cooling, is oxidised to sodium sulphate by addition of hydrogen peroxide; the excess of alkali is then titrated with standard hydrochloric acid. S. K. T.

Detection of Sulphur Dioxide, Nitrogen Dioxide, and some Acids. E. EGGRIWE (*Z. anal. Chem.*, 1924, 65, 182—185).—Well-known qualitative reactions are modified so as to increase their sensitivity. Sulphur dioxide is detected by lowering into the gas a rod thinly coated with a layer of moist zinc nitroprusside which has been rendered transparent by exposure to ammonia (test for ammonia). The coating turns rose to deep red, according as the concentration of sulphur dioxide is small or large. If the rose-coloured layer is allowed to dry, it becomes white and the change is then more readily observed. Nitrogen dioxide is detected by holding in the gas a drop of 1% aqueous benzidine hydrochloride solution on a glass rod and then adding it to a drop of 0·04% aqueous β-naphthol solution. A red colour develops which changes to rose- or dark red-violet on addition of ammonia. A drop of 20% aqueous ammonium molybdate solution held in silicon tetra-

fluoride on a piece of paper turns yellow, first on the edges, then throughout, in the absence of hydrogen sulphide. Tests, based on this reaction, are described for silicates and fluorides. S. K. T.

Colorimetric Determination of Ammonia in Urine. A. P. ORR.—(See i, 184.)

Determination of Silica in Plant Material. D. R. NANJI and W. S. SHAW.—(See i, 214.)

Colorimetric Determination of the Inorganic Phosphorus of Serum. R. ESSINGER and P. GYÖRGY.—(See i, 178.)

Colorimetric Determination of Phosphorus. C. RIMINGTON. —(See i, 183.)

Sources of Error in the Determination of Phosphoric Acid by the Molybdate-Magnesia Method. J. M. MCCANDLESS and J. Q. BURTON (*Ind. Eng. Chem.*, 1924, **16**, 1267—1270).—Discrepancies in the gravimetric analysis of materials with a high phosphoric acid content (*e.g.*, superphosphates with 45—50% of phosphoric acid) are avoided by carefully testing the neutrality of the ammonia solution of the yellow precipitate prior to adding the magnesia mixture. A solution which is neutral to litmus gives correct results, an excess of acid giving high, and an excess of ammonia low results. If the solution is neutral or slightly alkaline before adding the magnesia, the precipitate remains white after strong ignition and contains only faint traces of molybdenum, but when hydrochloric acid is in excess the ignited precipitate is blue and contains an appreciable amount of molybdenum oxide. The origin of the latter is discussed, and exact details are given for carrying out the analysis. W. T. K. B.

Determination of Small Quantities of Arsenic and its occurrence in Urine and in Fish. H. E. COX (*Analyst*, 1925, **50**, 3—13).—Preliminary digestion of the organic material is best carried out by the Swedish method, where sulphuric and nitric acids are added in such a way as to preclude the formation of any large quantities of carbon which may retain or adsorb arsenic. Subsequent determination may be by Ramberg's process when not less than 0·01 mg. of arsenic is present. All traces of nitrous acid must first be removed, ammonium oxalate is then added, and the mixture boiled to expel sulphuric acid fumes. Hydrochloric acid, ferrous sulphate, and potassium bromide are then added before distilling into water, with subsequent titration of the distillate with potassium bromate solution. For quantities of arsenic less than 0·01 mg. the Marsh-Berzelius method is more trustworthy. Normal urine was found to contain up to 0·58 mg. of arsenic per litre, and fish, especially plaice, up to 3 parts per million. D. G. H.

Distillation of Arsenious, Antimonious, and Stannic Chlorides. K. RÖHRE (*Z. anal. Chem.*, 1924, **65**, 109—128).—The distillation of arsenious chloride from solutions strongly acid with hydrochloric acid is accelerated by the addition of calcium or aluminium chloride, but zinc, copper, and cadmium chlorides

have little effect. Phosphoric and sulphuric acids, whilst accelerating the volatilisation of the arsenic, tend to retain part as sulphate or phosphate. The most favourable procedure for the distillation of arsenious chloride solutions which do not contain antimony consists in slowly heating the solution containing calcium chloride and much hydrochloric acid at 130°, cooling somewhat, adding more hydrochloric acid, and again distilling up to 130°. If antimony is present, the distillation is effected at water-bath temperature while a current of carbon dioxide is passed through the apparatus for 2 hours. Quinquevalent arsenic is most satisfactorily reduced by means of pyrogallol previously to distillation. Antimonious chloride may be distilled from solutions containing much sulphuric acid provided that hydrobromic acid is slowly dropped into the flask during the distillation, which is conducted at 180°. Stannic chloride may also be distilled under these conditions. A. R. P.

Electrical Determination of Soil Alkali. A. F. JOSEPH, F. J. MARTIN, and J. S. HANCOCK.—(See i, 222.)

Iodometric Micro Determination of Sodium. M. BÁLINT (*Biochem. Z.*, 1924, **150**, 424—443).—The sodium is precipitated by the addition of an alkaline solution of potassium pyroantimonate, centrifuged in the presence of 20% alcohol, and washed with 50% alcohol. It is then treated with 2% potassium iodide solution and the liberated iodine is titrated. Serum is first ashed (cf. Bálint and Petow, A., 1924, ii, 500; Kramer and Tisdall, A., 1921, ii, 463). J. P.

Determination of Sodium in Serum. B. KRAMER and I. GITTLEMAN.—(See i, 180.)

Separation of Small Quantities of Calcium from Large Amounts of Magnesium. V. RODT and E. KINDSCHER (*Chem.-Ztg.*, 1924, **48**, 953—954, 964—965).—Details are given of a critical study of the oxalate and sulphate methods of separating calcium from magnesium. In the former method, the calcium may fail entirely to precipitate under any conditions when its actual amount is small and a preponderating quantity of magnesium is present, the precipitate obtained consisting entirely of magnesium oxalate. Precipitation of calcium sulphate by addition of alcohol to a solution of the mixed sulphates, evaporation to dryness of a solution of the mixed chlorides with sulphuric acid followed by an alcohol extraction, and digestion of the dried chlorides with sodium sulphate solution containing alcohol all gave very low figures. The best results (1 to 5% low) were obtained by evaporating the chloride solution to dryness with just sufficient dilute sulphuric acid or lithium sulphate to convert the calcium present into sulphate and extracting the moistened residue with methyl alcohol containing 10% of ethyl alcohol. The residual calcium sulphate is dissolved in dilute hydrochloric acid and converted to oxalate in the usual way. [Cf. *B.*, Mar.] A. R. P.

Simplification in the Detection of Certain Cations. P. SACCARDI (*Annali Chim. Appl.*, 1924, **14**, 303—305).—Separation

of copper from cadmium in qualitative analysis may be effected by taking advantage of the fact that the electrolytic solution tension of iron is intermediate between those of copper and cadmium, the former, but not the latter, being displaced from its salt solutions by iron. The blue ammoniacal solution remaining after removal of the bismuth is rendered acid with hydrochloric acid and then shaken with iron filings, the copper being deposited in a few minutes; without removal of the filings, hydrogen sulphide is passed into the liquid and precipitates the cadmium.

To separate tin from antimony, the mixed sulphides are dissolved in hydrochloric acid and the solution is treated with a little magnesium and divided into two parts. (1) If tin is present, addition of mercuric chloride solution causes the formation of a brown or white precipitate of mercurous chloride and metallic mercury; another method of detecting tin consists in rendering the solution strongly acid with concentrated hydrochloric acid and boiling it with a trace of arsenious anhydride, brownish-black arsenic being precipitated. (2) With excess of chlorine water, antimony is precipitated as the pentoxide. T. H. P.

Separation of Cadmium from Zinc by Means of Hydrogen Sulphide. G. LUFF (*Z. anal. Chem.*, 1924, **65**, 97—109).—Ammonium sulphate assists, whilst ammonium chloride retards, the precipitation of cadmium and zinc as sulphides from acid solutions. For the separation of cadmium from zinc by this procedure, a minimum amount (7 to 8 c.c.) of strong hydrochloric acid (*d* 1·18) or sulphuric acid (*d* 1·836) per 100 c.c. of solution is necessary; cleaner separations are effected if the solution contains ammonium sulphate and is saturated with hydrogen sulphide at 80° and then somewhat diluted with cold water. Under these conditions, the cadmium sulphide is precipitated in the form of orange-red, microscopic, six-sided tablets and rosettes. Cadmium sulphide is usually converted into sulphate for weighing, but it may also be converted into cadmium diammonium ferrocyanide, which is dried at 110° and weighed. The salt forms hexagonal prisms insoluble in dilute ammonia and is obtained by precipitation of a warm ammoniacal solution of cadmium and ammonium chlorides with potassium ferrocyanide. [Cf. *B.*, Mar.] A. R. P.

Electrolytic Separation of Copper, Antimony, and Bismuth from Lead. A. LASSIEUR (*Compt. rend.*, 1924, **179**, 632—634).—Under the conditions recommended by Schoch and Brown (A., 1916, ii, 578), the lead deposit is too heavy owing to the presence of hydroxide. This may be obviated by working with a solution containing 15—20% of concentrated hydrochloric acid, using an auxiliary potential of 440 millivolts, or preferably with a 2·5% solution of hydrofluoric acid and 400 millivolts. In presence of lead, bismuth may be quantitatively deposited in presence of nitric acid and hydroxylamine hydrochloride with an auxiliary potential of 200—240 millivolts. The separation of lead from copper presents little difficulty; antimony, when present in the quinquevalent condition, furnishes a good deposit in presence of hydrochloric

acid, but, from its tervalent compounds, adherence is usually poor. The auxiliary potential needed for antimony is 240 millivolts; deposition of lead does not begin below 350 millivolts and is, in presence of antimony, satisfactory only when the concentration of lead is less than 0·2 g. per 100 c.c. H. J. E.

Conversion of Cupric into Cuprous Sulphide by Heating in a Current of Hydrogen. F. L. HAHN (*Z. anal. Chem.*, 1924, 65, 134—137).—Polemical. The temperature range for the conversion of cupric sulphide into cuprous sulphide by heating in hydrogen is at most only 60°, and correct results cannot be obtained by the method recommended by Wilke-Dörfurt (A., 1924, ii, 785). Good results are obtained only when a mixture of hydrogen and hydrogen sulphide is employed and the cuprous sulphide cooled in an atmosphere of carbon dioxide containing methyl alcohol vapour (cf. Hahn, A., 1917, ii, 543). A. R. P.

Determination of Small Quantities of Copper in Tissues. A. N. CURRIE.—(See i, 183.)

Oxidimetric Determination of Manganese in Hydrofluoric Acid Solution. II. J. HOLLUTA and J. OBERIST (*Monatsh.*, 1924, 44, 209—218; cf. A., 1921, ii, 522).—Some important differences between the authors' method (*loc. cit.*) and that of Metzger and Marrs (A., 1912, ii, 94; 1913, ii, 344) are pointed out. The method is shown to be trustworthy in the presence of large or small quantities of most of the important metals with the exception of calcium, aluminium, chromium, and bismuth. Copper must be in the cupric form, whilst antimony retards the reaction considerably. The presence of arsenate ions accelerates it, and it is thought possible that under suitable conditions arsenic may be substituted for hydrofluoric acid. Magnesium in larger amounts causes the formation of a white precipitate and lengthens the reaction period somewhat. The presence of bismuth disturbs owing to separation of basic salts at the low acidity required by the method. Aluminium in small quantities may be present, but not calcium. Less permanganate is required as the quantity of calcium increases, the probable cause being the formation of a double fluoride of calcium and manganese as well as adsorption effects, especially when large amounts of calcium are present. The colour of the chromium ions hinders a correct spectroscopic determination of the end-point under the conditions prescribed. Attempts to substitute hydrofluosilicic, phosphoric, or arsenic acid for hydrofluoric did not show promising results. Methods of modifying the reaction by making it the basis of electrometric and potentiometric processes are suggested (cf. Müller and Wahle, A., 1923, ii, 881). A. C.

Determination of Manganese. G. BERTRAND.—(See i, 223.)

Determination of Iron in Small Quantities of Biological Substances. M. M. MURRAY.—(See i, 183.)

Analysis of Germanite. F. W. KREISEL.—(See ii, 153.)

Determination of Bismuth. W. AUTENRIETH and A. MEYER.—(See i, 182.)

Bromometric Determinations. W. MANCHOT and F. OBERHAUSER (*Z. anorg. Chem.*, 1924, **139**, 40—50).—Ferrous iron in solution is determined by adding standard hypobromite solution, acidifying, adding excess of arsenious acid solution, and titrating back with bromine (or bromate) after adding phosphoric acid. Nitrites are oxidised to nitrates with a known excess of bromine in presence of sodium hydrogen carbonate, a reaction which is complete in 5 minutes. Excess of alkali arsenite is added and titrated back with bromine after acidification. Cobalt may be determined similarly after precipitation as potassium cobaltinitrite. Tin is oxidised in hydrochloric acid solution with bromine, and hydrogen peroxide with hypobromous acid, the added reagent being titrated back in the usual manner. Carbamide is determined in the same way as ammonia, but the hypobromite mixture is allowed to react for 10—15 minutes. Sulphurous acid, hydrogen sulphide, and thiosulphates are now determined by allowing the solution to flow under the surface of a hypobromite solution, which is then titrated as above. Hypochlorites may also be determined bromometrically. Solutions of arsenious acid acidified with hydrochloric acid may be used in these titrations when the latter are carried out in acid solution.

[With H. WETTSTEIN.]—The bromine-vapour pressures of 0·1*N*-solutions of bromine in hydrochloric acid, potassium bromide, and acetic acid solutions decrease with increasing concentration of the latter solutions, and are greater in hydrochloric acid solutions than in potassium bromide solutions of the same normality. Bromine solutions in *N*-potassium bromide are the most suitable for general use (cf. A., 1924, ii, 274, 507). S. K. T.

Selective Determination of Vanadium in Presence of Iron and Chromium. I. Determination of Vanadium in Presence of Iron. K. SOMEYA (*Z. anorg. Chem.*, 1924, **139**, 237—245).—The vanadium in a vanadium steel may be determined by a modification of Knop's method of determining iron (cf. A., 1924, ii, 351). The alloy, which must not contain tungsten, but may contain manganese, chromium, molybdenum, small amounts of copper, etc., is dissolved in sulphuric acid; a slight excess of potassium permanganate is added and the solution decolorised with a few drops of sulphurous acid solution; 15 c.c. of phosphoric acid mixture and 3 drops of diphenylamine sulphate solution (*loc. cit.*) are then added, the whole is diluted to 120—200 c.c. and titrated at 100° with 0·1*N*-ferrous sulphate solution in dilute sulphuric acid until the violet-blue solution becomes bright greenish-blue. With very large proportions of iron the end-point is not distinct. Allowance must be made for oxidation of the indicator. The end-point is practically independent of the acid concentration, although hydrochloric acid must not be used. Kelley and Conant's method (A., 1916, ii, 274) may also be used with the diphenylamine internal indicator. S. K. T.

Colour Reaction for Glycerol. I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 1497—1498).—By oxidation with permanganate

and treatment with Schiff's reagent, glycerol gives a positive coloration in 0·04% solution. The common organic acids do not interfere. S. I. L.

Determination of Sugar in Blood. (1) M. GILBERT and J. C. BOCK. (2) E. G. B. CALVERT.—(See i, 179.)

Determination of Free Sugar in Total Blood. H. BIERRY and L. MOQUET.—(See i, 179.)

Colorimetric Determination of Sugar in Blood. F. J. PATON.—(See i, 180.)

Differentiation of Citric from Tartaric Acid. W. PARRI (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 537—538).—With a sulphuric acid solution of phosphomolybdic and vanadic acids, citric acid gives a deep blue coloration, which becomes green on heating but resumes its original colour on cooling. This reaction, which is disturbed to some extent by the presence of other compounds, serves for the detection of a small proportion of citric acid in tartaric acid. [Cf. *B.*, 1925, 114.] T. H. P.

Colour Reaction, Supposed Specific for Formaldehyde, Produced by Glyoxylic Acid. FOSSE and A. HIEULLE (*Compt. rend.*, 1924, **179**, 636—638).—Glyoxylic acid yields with Schryver's reagent an intense magenta-red; this coloration has hitherto been considered specific for formaldehyde. The reaction is extremely sensitive, being given by 0·001 mg. of glyoxylic acid at a concentration of 1 in 10^6. The author considers that the presence of formaldehyde in green leaves cannot be regarded as proved. H. J. E.

Effect of different Ammonium Salts in Rothera's Reaction. H. W. VAN URK (*Pharm. Weekblad*, 1925, **62**, 8—10).—Saturated solutions of many ammonium salts containing acetone were treated with ammonia and sodium nitroprusside; the test is most sensitive in presence of ammonium sulphate. There is no relation between the solubility and the sensitiveness. S. I. L.

Action of Sodium Nitroprusside on Acetone and Acetaldehyde. H. W. VAN URK (*Pharm. Weekblad*, 1925, **62**, 2—8).—The colorations given by pure acetone and pure acetaldehyde in presence of sodium nitroprusside in alkaline and acid solutions are tabulated; acetone gives an orange-yellow colour in alkaline solution, changing to purplish-red on acidifying, acetaldehyde reddish-purple in alkaline solution, nearly discharged on acidifying. The latter reaction is attributed to aldol formation, which is reversed in acid solution. Both reagents give green colorations on warming the alkaline solution. In ammoniacal solution acetaldehyde gives no coloration, acetone a violet ring; for testing for acetone in urine, ammonium salts should be present, but alkali tartrates or acetates are not necessary. S. I. L.

Colour Test for Aniline and Toluidine. H. D. MURRAY (*Chem. News*, 1925, **130**, 23).—The amine is dissolved in warm 50% sulphuric acid and a saturated solution of potassium dichromate is added. When no further change in colour takes place, the solution is poured into a large excess of water, and rendered alkaline with ammonia. Three colour stages are noticed, (i) on the addition of the dichromate, (ii) on pouring into water, and (iii) on making alkaline. Aniline gives purple, purple, and dark purple; *o*-toluidine, blue, purple to orange-yellow, and bright blue; *m*-toluidine, green, brown, and dark purple; *p*-toluidine, reddish-brown, straw-colour, and later darkens slightly. The di-substituted tertiary amines give no colour change on pouring into water. I. E. B.

Interference of Ammonia with the Hypochlorite Reaction for Aniline. E. S. WEST (*Ind. Eng. Chem.*, 1924, **16**, 1270—1271).—The inhibitory effect of a relatively low concentration of ammonia and its salts on the formation of a violet coloration when calcium hypochlorite is added to an aqueous solution of aniline is due to its reaction with the hypochlorite and to its effect on the coloured product. The effect is largely avoided by acidifying the solution or by removing the ammonia by aëration (after making alkaline, if ammonium salts are present) before adding the hypochlorite. Sodium chloride and other salts also interfere with the reaction if present in very high concentrations. W. T. K. B.

Directive Influence of Substituents in the Benzene Ring. I. Chemical Determination of the Meta Isomeride in some Disubstituted Derivatives of Benzene. A. W. FRANCIS and A. J. HILL (*J. Amer. Chem. Soc.*, 1924, **46**, 2498—2505).—When bromine in aqueous solution (or acidified bromate–bromide solution) is added to a mixture of an *o*-, *m*-, and *p*-derivative of aniline or phenol, the *m*-derivatives are completely converted into tribromo compounds, whilst the *o*- and *p*-derivatives yield dibromo compounds. The consumption of bromine by a mixture of isomerides is therefore a measure of the proportion of *m*-isomeride present. The method can be extended to nitro compounds by subjecting these to a preliminary reduction with titanous chloride, and is accurate to 0·5%. In the case of *o*- and *m*-toluidines, *o*-phenylenediamine, *o*-aminophenol, and *p*-phenetidine, the bromine titration must be carried out below 0° to prevent formation of deeply coloured oxidation products which mask the end-point. Precipitation of partly-brominated products can be avoided by the use of sufficient solvent (alcohol); this difficulty is greatest with *p*-compounds. The carboxyl, sulphonic, and aldehyde groups are readily displaced by bromine, except at low temperatures, from *o*- and *p*-amino and hydroxy derivatives, the last-named group giving rise to carbon monoxide. Quinol does not absorb bromine at ordinary temperatures, and pyrocatechol, *p*-phenylenediamine, and *p*-aminophenol are indifferent at 0°. Resorcinol is brominated quantitatively, but mixtures of it with quinol give low results unless a large excess of bromine is present. *m*-Phenylenediamine decomposes on bromination, but if mixed with an equal amount of resorcinol,

both compounds are tribrominated quantitatively, without decomposition. Phloroglucinol yields first a precipitate of the tribromo derivative, which then redissolves with formation of the compound $C_6Br_3(OBr)_2 \cdot OH$, and this is finally converted into the compound $C_6Br_3(OBr)_3$. Both of these are reconverted into the tribromo derivative by potassium iodide, so that they do not interfere with the determination of phloroglucinol by this method. F. G. W.

Detection and Determination of Indican in Urine. S. N. GORE.—(See i, 186.)

The Tryptophan–Aldehyde Reaction. E. KOMM (*Z. physiol. Chem.*, 1924, **140**, 74—79).—In the reaction previously described (A., 1923, ii, 194), the maximum intensity of colour is attained only after 5 days in the case of pure solutions of tryptophan, but is reached in a few hours in the presence of gelatin. The following substances also accelerate the intensification of the colour; oxidising agents, proline, proteins, and polypeptides containing proline or proline derivatives. E. S.

Determination of Uric Acid by Benedict's method. H. COHEN.—(See i, 184.)

Determination of Uric Acid in Urine. AUFRECHT.—(See i, 187.)

Colour Reactions of Cryogenine with Heavy Metals. L. BORNET (*J. Pharm. Chim.*, 1924, [vii], **30**, 356—358).—Saturated aqueous solutions of cryogenine react with neutral solutions of certain metallic salts as follows. Copper salts give a red coloration; mercury salts give a peach colour followed by a violet precipitate which, if the solution is shaken with benzene or ether, collects as a violet ring at the junction of the liquids. Ferric salts give a reddish-brown coloration, and a red colour is given by moderate quantities of chromates and dichromates in presence of hydrochloric acid. The sensitiveness is increased if one or two drops of hydrogen peroxide are added after the reagents are mixed. S. K. T.

Determination of Urobilin in Human Excreta. OPITZ and BEHME.—(See i, 187.)

Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in Tests for Urobilin. K. H. BARKENSCHEEN and O. WELTMANN.—(See i, 187.)

Determination of Cholesterol and its Esters in Tissues. II. J. A. GARDNER and F. W. FOX.—(See i, 182.)

Colorimetric Determination of Lycopin. S. J. B. CONNELL.—(See i, 214.)

General, Physical, and Inorganic Chemistry.

Law of Variation with Temperature of the Conductivity of Solid Salts, and Possible Relationship to the Characteristic Spectrum of the Metal of the Salt. P. VAILLANT (*Compt. rend.*, 1925, **180**, 206—208).—If the liberation of electrons which carry the current which flows when an *E.M.F.* is applied to a layer of a solid salt (cf. A., 1924, ii, 456) is caused by the absorption of radiant energy produced by a monochromatic radiation of wave-length λ, then the coefficient K which connects the densities of the liberated electrons, n_1, with that of the particles giving rise to them, n, ($Kn=n_1^2$) should vary with temperature and follow the same law as this radiation, viz., $K=K_0e^{-hc/\nu T\lambda}$, where h=Planck's constant, c=velocity of light. The wave-lengths, λ, calculated in this way for the salts of sodium, potassium, and lithium are, within the limits of experimental error, those of the chief lines in the spectra of the elements. J. W. B.

Exceptionally Intense Absorption of a Radiation by the Emitting Atom. M. DE BROGLIE and J. THIBAUD (*Compt. rend.*, 1925, **180**, 179—180; cf. A., 1922, ii, 104).—Electrons arising from the re-absorption of fluorescent rays emitted in the radiator itself yield more intense rays than those directly emitted under the influence of exciting rays. This is demonstrated by a comparison of the K-radiation of tungsten (double α) and the K-fluorescent rays of the ionised element (copper, mercury, iodine, and barium). The relative intensity of the second increases with the atomic number, *i.e.*, in a reverse sense to that required by the laws of Bragg and Moseley. Atoms which emit γ-rays show the greatest probability of absorbing this radiation and converting it into photo-electrons. (Cf. Ellis, A., 1921, ii, 422.) J. W. B.

Excitation of Spark Spectra. S. WERNER (*Nature*, 1925, **115**, 191—192).—The vapour of the element under investigation is allowed to escape into a high vacuum from a small hole in a crucible heated to 1000°, the vapour being exposed to bombardment by a strong current of electrons (200—500 ma.). Besides the arc spectra, the spark spectra of sodium, potassium, cadmium, and zinc were observed with considerable intensity. In the case of lithium, few only of Morand's lines (A., 1924, ii, 509) were verified, but most of Schüler's results (*Naturwiss.*, July 11, 1924) were confirmed. A scheme is given of the terms of the doublet spectrum, in which the effective quantum numbers of the various terms are very similar to those for helium. With an accelerating potential of 150—200 volts, the intensity of the line 5485 Å. decreased very rapidly relatively to the arc lines. The spark spectrum of lithium was also excited, but with a smaller relative intensity, together with the arc spectrum, by means of an arc between the crucible and anode. A. A. E.

Line Spectrum of Nitrogen and Ionised Oxygen. F. CROZE (*Compt. rend.*, 1925, **180**, 277—279).—In an earlier paper (*ibid.*, 1924, **179**, 1603) it was shown that in the spectrum of ionised nitrogen the most important triple combination terms are multiplets p_3d_3, pp'_3, $p'_3d'_3$, $d_3d'_3$. In the present paper, p_3s_3, d_3f_3 are added. Following the rule of alternation, the line spectrum of ionised oxygen (O+) should be due to combinations of pairs of terms. The author's work on the Zeeman effect (A., 1914, ii, 600) using Landé's rules (*Z. Physik*, 1923, **15**, 189) gives quadruple combinations in the visible region. They are, as in nitrogen, of the type *ps* (Landé), *pd*, *df*, *pp'*, *p'd'*, *dd'*. R. A. M.

Conditions for Appearance, and Structure, of Bands of Silver between λ=3330 and λ=3358. E. BENGTSSON and E. SVENSSON (*Compt. rend.*, 1925, **180**, 274—276; cf. A., 1924, ii, 78).—The arc spectrum of silver chloride in an atmosphere of hydrogen has been photographed in the second order, using a concave grating. It can be expressed as two Deslandres series *P* and *R*. The absent member $m=0$ is taken as origin. If *F* and *f* are initial and final energy states of the molecule, *n* and *m* correspond respectively with nuclear and rotational vibrations; $P(m)=F(nm)-f(n'm+1)$ and $R(m)=F(nm+1)-f(n'm)$. Two relations are given corresponding with the initial and final states of the molecule emitting light: $h/8\pi^2A'=6{\cdot}3$, and $h/8\pi^2A''=6{\cdot}6$, where *h* is the Planck constant, *A'* and *A''* are moments of inertia. Similar results were obtained with gold and copper (A., 1924, ii, 78).

The conditions for appearance of the bands and the size of the moment of inertia lead to the view that a dipole AgH is present. R. A. M.

Excitation of Forbidden Spectral Lines. P. D. FOOTE, T. TAKAMINE, and R. L. CHENAULT (*Nature*, 1925, **115**, 265).—The mercury line $1S-2p_1$ (Paschen's notation), the corresponding line of zinc, and both $1S-2p_1$ and $1S-2p_3$ of cadmium have been excited in the positive column of a hot-cathode discharge. The spectrum observed was of the arc type, only a few spark lines appearing. The cadmium lines 2239, 2267, 2307, and 2329 Å. (belonging to the group $2p-2p_1$) were sharply absorbed by the positive glow. An unknown absorption line at 3086·7 was observed. A. A. E.

Mercury Line 2270 Å. ($1S-2p_1$). T. TAKAMINE and M. FUKUDA (*Physical Rev.*, 1925, [ii], **25**, 23—29).—The mercury line 2270 Å. was excited with an intensity intermediate between that of 2302 ($2p_2-9d_2$) and 2323 ($2p_2-8d_2$) by means of the branched arc of a mercury lamp of suitable form. In a heavy condensed discharge the lines 2270 and 2345 ($2p_3-5s$) are shifted about 0·1 Å. towards the red whereas 2564 ($2p_2-4S$) is displaced by an equal amount in the opposite direction. A. A. E.

Cathode Spectra of Metals and their Salts. M. KIMURA and G. NAKAMURA (*Japan. J. Phys.*, 1924, **3**, 29—41).—The spectra

were obtained by using a vacuum tube with an aluminium anode and a cathode consisting of salts, chiefly chlorides, of the metals. The tube was excited by an induction coil or high-tension transformer and the glow at the cathode was focussed on the slit of the spectroscope. The results for magnesium, tin, and lead are shown in plates. The spectra resembled those of the spark. Zinc, cadmium, and bismuth presented the characteristics of the arc. Calcium, strontium, and barium gave only a few lines of their spectra. Tin gave both long and short lines, the former being ascribed to Sn^{+}, the latter to Sn^{++}. E. B. L.

Cathode Spectra of Metals. M. KIMURA and G. NAKAMURA (*Japan. J. Phys.*, 1924, **3**, 43—44).—Similar results to those obtained with tin (cf. preceding abstract) were found for cadmium, aluminium, zinc, and lead. Long lines were attributed to singly ionised atoms and shorter lines to atoms with two positive charges. E. B. L.

Regularities in the Arc Spectrum of Niobium. W. F. MEGGERS (*J. Washington Acad. Sci.*, 1924, **14**, 442—446).—The data for the arc spectrum of niobium have been examined from the point of view of certain properties of spectral lines in multiplet structures, such as constant wave-number differences, temperature classification, intensity rules accompanying transitions of azimuthal and inner quantum numbers, and Zeeman effect. The spectrum appears to possess structures similar to that of vanadium (Meggers, A., 1923, ii, 673; 1924, ii, 365). The ultimate rays which are most sensitive for the purposes of chemical analysis are 4100·99, 4079·73, and 4058·99 Å. M. S. B.

Spectrum of Iron. M. A. CATALÁN (*Anal. Fís. Quím.*, 1924, **22**, 398—408; cf. A., 1924, ii, 435).—Six new multiplets formed with terms previously known have been found in the spectrum of iron. Ten new levels, only partially classified, originating two sets of multiplets, are also shown. Complete data, including also the results of Laporte (A., 1924, ii, 364), are given in tabular form. G. W. R.

Spark Spectrum of Potassium. W. DAHMEN (*Z. Physik*, 1924, **29**, 264—266).—Measurements of wave-lengths in the spark spectrum of potassium between 3400 and 7000 Å. have been made. Potassium electrodes in argon at a few mm. pressure were employed. The mean error in measurement was 3/1000 Å. The resemblance of the spark spectrum of potassium to the arc spectrum of argon shows at least a qualitative agreement with Kossel and Sommerfeld's displacement law (A., 1919, ii, 378). M. S. B.

Connexion between the Spectra of Argon and Ionised Potassium. T. L. DE BRUIN and P. ZEEMAN (*Nature*, 1925, **115**, 116—117).—An examination of the results of Dahmen (cf. preceding abstract) with ionised potassium. The difference of about 847 is not characteristic, but that of about 1696 is present as 1712; also, 418·2 replaces 414. Some groups have been found

of regularly distributed lines exhibiting a regular distribution of intensities. Five examples of "quintets" are given. A. A. E.

Spark Spectra of Tungsten and Mercury in the Extreme Ultra-violet. BAYEN (*Compt. rend.*, 1925, **180**, 57—59).—The spark spectra of tungsten and mercury in the region between 1850 and 2100 Å. have been investigated and a large number of new lines are tabulated. W. H.-R.

Spark Spectrum of Tungsten in the Schumann Region. L. and E. BLOCH (*Compt. rend.*, 1925, **180**, 133—135).—A list is given of some 360 lines in the spark spectrum of tungsten between 1826 and 1453 Å. G. M. B.

Electromagnetic Analysis of Positive Rays. R. DÖPEL (*Ann. Physik*, 1925, [iv], **76**, 1–28).—The positive rays were produced in the usual manner, the gas streaming through a fine capillary into the discharge bulb or cylinder and thence through the cathode into the inspection chamber maintained at the highest possible vacuum. The parabolas obtained by combined electric and magnetic deflection were observed on a willemite screen, and the energy along the line obtained when the magnetic field alone was used was measured by a sensitive thermo-couple. With a sufficiently high discharge potential energy curves for hydrogen show maxima on the positive side at distances approximately in the ratio $1 : \sqrt{2} : 2$ and are attributed to molecules, fast atoms, and slow atoms. On the negative side, only fast and slow atoms are obtained, the negatively charged molecules being less stable. Addition of oxygen increases the relative number of molecules.

In addition to the usual features, the parabolas showed H_2^- cules and He^- atoms. From the nature of the beading on the bolas the author deduces the existence in the dark space of N_4, and He_2. E. B.

Asymmetric Emission of Electrons by *X*-Rays. W. S (*Physikal. Z.*, 1924, **25**, 547—550).—The asymmetrical emiss of electrons from a metal film placed in a beam of *X*-rays was examined by means of thin films of five different metals, sputtered on celluloid. The number of electrons emitted from the surface from which the *X*-rays emerged was always greater than from the surface on which the *X*-rays were incident, but the ratio of these two quantities decreased with increasing atomic weight. By retaining the slowest electrons by means of a retarding electric field or by means of a thin layer of a non-conductor painted on the film, the asymmetry was increased, being greater the smaller the atomic weight. Further, the magnetic spectra of the incident and emergent beams of electrons from a thin copper foil were simultaneously photographed. The maxima in both spectra corresponded with the same electron velocities, and the intensity of slow electrons was greater on the incident side, whilst that of the fastest electrons was greater on the emergent side. The asymmetry thus appeared to depend chiefly on the fast photo-electrons and not, or only to a small extent, on the slower Compton electrons. L. F. B.

Electronic Bombardment of Metal Surfaces. H. E. FARNSWORTH (*Physical Rev.*, 1925, [ii], **25**, 41—57).—Curves constructed to show the ratio of secondary (emergent) to primary (incident) electron current as a function of the primary velocity depended on the previous heat treatment of the metals copper, silver, gold, tungsten, platinum, palladium, magnesium, and aluminium, but characteristic curves were obtained after heating the metals of higher m. p. to redness for some time. Velocity distribution curves of the secondary electrons are also given. Variation in the treatment of the copper surface and the effect of simultaneous exposure to radiation from a silica mercury arc were also studied.

A. A. E.

Resonance Radiation and the Correspondence Principle. C. G. DARWIN (*Nature*, 1925, **115**, 81—82).—A discussion of the effect of the results of Wood and Ellett (*Proc. Roy. Soc.*, 1923, **A**, **103**, 396) on the validity of the quantum theory, and a consideration of modifications. A well-known classical theorem, on application of the correspondence principle, specifies that if an atom can emit circular waves of equal frequency in either sense, then it can also emit linear waves. There is, however, no direct evidence for the emission of purely circular or linear waves from a single atom in the absence of a magnetic field; in presence of such a field, the degeneracy disappears. The theorem is not consonant with the physical reality of Bohr's orbits, but a new conception arises that a definite statement of phase is required; if this is so, it is not surprising that the older theory fails. Modifications concerning the conception of emission without disturbance of the existing ideas of quantised orbits of the electrons are considered and a serious difficulty in the hypothesis is specified. A. A. E.

Simple Method for Quantitative Studies of Ionisation Phenomena in Gases. I. LANGMUIR and H. A. JONES (*Science*, 1924, **59**, 380—383).—A simple type of tube contains no grid, the filament being mounted axially within a cylindrical electrode and passing through holes in the centres of end plates within, but not touching, the cylinder. The current–voltage curves obtained yield practically full information regarding the number and distribution of velocities of the electrons in the ionised gas. Experiments with argon and mercury vapour permit the recognition of five distinct classes of electrons in the ionised gas: (*a*) Primary electrons from the cathode. (*b*) Electrons scattered through small angles by elastic collisions (for mercury, none were observed). (*c*) Electrons which suffer a definite loss of energy; for mercury vapour, Eldridge's results (*Physical Rev.*, 1922, **20**, 456) are confirmed. (*d*) Secondary electrons of moderate velocity, probably due to photo-electric emission from atoms of gas, ultra-violet radiation being produced from atoms excited by primary electrons. (*e*) Secondary electrons of low velocity, produced in by far the greatest number. Experiments are in progress using hydrogen, helium, nitrogen, neon, and carbon monoxide. A. A. E.

Width of Rays in the Balmer Series in the Oscillating Discharge. (MLLE.) M. HANOT (*Compt. rend.*, 1925, **180**, 54—56).—The width of the H_β and H_γ rays in the Balmer series in hydrogen has been determined. If the capacity and potential are C and V, respectively, and if the period of the oscillating discharge is T, the wave-length of the latter may be written $\lambda = VT$. The width of the lines increases with increasing C and V, and with decreasing T (or λ). No change in the width of the lines occurs if C and T are simultaneously changed so that C/T remains constant, or if V and T are simultaneously changed so that V/T is constant. The maximum intensity of the current $I_0 = 2\pi CV/T$, and, if C, V, and T are all varied, a smooth curve is obtained if the width of a given line is plotted against I_0. The curve for the one line may be derived from that for the other by multiplying the ordinate (representing width of line) by a constant factor. W. H.-R.

Mobilities of the Positive Ions in Helium. H. B. WAHLIN (*Proc. Nat. Acad. Sci.*, 1924, **10**, 475).—The value of the mobility observed depends on the time that elapses between the formation of the ion and the instant it enters the field in which the mobility is measured. Having checked the results of previous workers in the case of air, the author has applied the same method to a monatomic gas, helium, and finds the ratio of the mobilities of the aged to the unaged ion to be approximately $1:\sqrt{3}$, which, on the assumption that the mobility varies inversely as the square root of the mass, indicates a cluster of three helium atoms. E. B. L.

Mobility of Negative Ions in Flames by the Hall Effect Method. J. S. WATT (*Physical Rev.*, 1925, [ii], **25**, 69—74).—For a flame containing potassium carbonate, the mobility of negative ions decreased from 26 m./sec. for 1 volt/cm. when the potential gradient was 1 volt/cm., to 16 m./sec. for a gradient of 30 volts/cm. For a salt-free flame the values were 26·5 m./sec. for 5 volts/cm. and 16 m./sec. for 50 volts/cm. The mobility was scarcely affected by wide variation of concentration. The Hall effect varies slightly with the direction of the magnetic field, the asymmetry being greater the greater the amount of salt in the flame. A. A. E.

Disturbing Influence of an Electric Field on the Zeeman Effect in Spectral Lines. H. C. UREY (*Z. Physik*, 1924, **29**, 86—90; cf. *Kgl. Danske Videnskab. Selsk. math.-fys. Medd.*, 1924, **6**, 2).—In continuation of previous work on the Zeeman effect in hydrogen, the degeneration of the atomic or ionic system for certain values of the magnetic field, in the absence of an electric field, has been discussed mathematically. The state under consideration is reached when certain frequencies in the motion of the atom, namely, the frequency of precession of the orbit of the electron in its plane, and the frequency of precession of the plane of the orbit round an axis parallel to the magnetic field, become equal to one another. The difficulties and limits are considered of an experimental study of the phenomenon by examining the behaviour with a varying magnetic field, combined with an electric field at right-

angles, too weak to affect appreciably the energy of the system composed of the positive nucleus and negative electron.

M. S. B.

Distribution of Electric Field in Metal Arcs and the Stark Effect observed in Arcs of Silver, Copper, Magnesium, Chromium, Nickel, Cobalt, Iron, and Ten other Metals. H. NAGAOKA and Y. SUGIURA (*Japan. J. Phys.*, 1924, 3, 45—73).—The authors produced a stable arc by using a 500 volt d.c. generator with a large inductance and capacity across the electrodes. The potential drop across the arc was measured and from it the electric field and its gradient were deduced. For obtaining Stark effect they found a small drop of metal the preferable form of anode; in the case of silver, copper, magnesium, zinc, cadmium, and aluminium the lines belonging to the same series are similarly affected. In iron there are six types of change due to the electric field, but it is the spark and not the arc lines which are affected. This method can be employed for sorting the lines as in the Zeeman effect. Many new lines were observed, due to the presence of the strong electric field. The spectra are reproduced in a set of plates.

E. B. L.

Life of Metastable Helium. F. M. KANNENSTINE (*Astrophys. J.*, 1924, 59, 133—141).—The life of metastable helium atoms is 1/140 second. The critical frequency was independent of the pressure over a large range of pressure, a condition which is considered to be caused by a long-lived abnormal atom. The departure of the critical frequency–pressure curve from a straight line at low pressures is interpreted from the point of view of diffusion of the atoms from the arc space. The abnormal atoms are stable in pure helium, but revert to the normal atoms in the presence of impurities, *i. e.*, in circumstances in which the selection principle is violated.

A. A. E.

Life of Metastable Helium. A. J. DEMPSTER (*Astrophys. J.*, 1924, 59, 142—147; cf. preceding abstract).—A mathematical consideration of Kannenstine's experiments (*ibid.*, 1922, 55, 345) supports the view that at the higher pressures the metastable state is destroyed only by collision with some impurity, and tends to discredit the suggestion that radiation is handed on from atom to atom.

A. A. E.

Life Periods of Excited Atoms. W. GERLACH and W. SCHÜTZ (*Physikal. Z.*, 1925, 26, 33—35).—On a basis of measurements of thermal energies and of the energy of the Zeeman separation, the limiting values of 10^{-7} to 10^{-9} second are deduced for the periods of existence of mercury and sodium atoms in the excited states Na $2p$ and Hg $2p_2$.

F. G. T.

Electric Field of Ions and Neutral Salt Action. P. DEBYE and J. MCAULAY (*Physikal. Z.*, 1925, 26, 22—29).—Continuing previous work (A., 1924, ii, 387), it is shown that neutral salt action and the salting-out effect are to be attributed to changes in the

dielectric constant on dissolving solutes in a solvent. The electrical work term in the previously deduced expression for the osmotic pressure of dilute electrolyte solutions is a function of the dielectric constant of the solution. This latter is generally decreased by the addition of a non-electrolyte with a consequent variation in the electrical work term and so of the osmotic pressure. In the salting-out effect a rise of dielectric constant is produced by the precipitation of the non-electrolyte to counteract the increase of the electric field due to the addition of an electrolyte.

A mathematical treatment on this basis leads to an expression for the total osmotic pressure of a mixed solution of electrolyte and non-electrolyte of the form $P=P_N+P_E+p$, where P_N,P_E are the osmotic pressures of the non-electrolyte and electrolyte singly, and p is a term involving the dielectric constant of the solvent, the radius of the ions, and a coefficient in an interpolation formula for the effect of the non-electrolyte on the dielectric constant of the solvent. By use of cryoscopic data of Rivett for mixed solutions of sugar and electrolytes, it is shown that values are obtained from the above expression for ionic radii agreeing with accepted values.

An expression is also obtained for the activity of a non-electrolyte in the presence of an electrolyte. Application of this gives a calculated increase of 19% in the activity of a sugar solution on the addition of 0·4 mol. of potassium chloride per litre, which is in agreement with the rise of inversion velocity (15%) found by Arrhenius. F. G. T.

Possibility of Reproducing the Electrical Conditions of the Nitrogen Afterglow. W. H. B. Cameron (*Nature*, 1925, **115**, 122).—Photographs through a neutral wedge of the spectrum of the afterglow at points 17·8 cm. apart in a tube through which glowing nitrogen was pumped showed no pronounced energy displacement. The β-group of the afterglow spectrum cannot be reproduced from discharge tubes containing nitrogen and argon; neither does the spectrum of the light from discharges through ammonia in high-pressure argon yield evidence of the occurrence of α- or β-groups. Further, the band spectrum of iodine in the presence of high-pressure argon did not display the relative intensity changes characteristic of the afterglow. Thus, although there are several points of resemblance between the electrical conditions of the afterglow and those existing when a mild discharge is passed through high-pressure argon, specific effects in the former appear incapable of reproduction in the latter case. A. A. E.

Influence of Temperature on the Photo-electric Effect. J. R. Nielsen (*Physical Rev.*, 1925, [ii], 25, 30—40).—Millikan's suggestion that in the photo-electric effect the energy of the light is transferred to the free electrons of the metals as well as to the bound electrons is discussed. The expression $h\nu_0=\phi_p-E_k$ is deduced, where ν_0 is the threshold frequency, ϕ_p is the gain in potential energy accompanying the transference of a free electron from the metal to the surrounding electron atmosphere, and E_k the average kinetic energy of a free electron within the metal. The

temperature variation of the threshold frequency or of the long wave-length limit is proportional to the Thomson coefficient. The photo-electric current from aluminium for 2537 Å. remained constant within 0·5% when the target was cooled from 400° to 100°.
A. A. E.

Thomson Circuit in the Study of Magnetic Spectra. N. NIKITIN (*Z. Physik*, 1924, 29, 288—293).—A method has been devised for the determination of the apparent magnetic permeabilities, μ_k and μ_n, of iron wire. This can be used for very thick wire and for very small quantities of material. μ_n is less than μ_k and the μ_n-spectrum is much more complicated than the μ_k-spectrum. The results are in agreement with the viscoso-elasticity theory (Arkadiev, *ibid.*, 1924, 27, 37). M. S. B.

Reversible Permeability. R. GANS (*Z. Physik*, 1924, 29, 270—271).—Polemical against Uller (*Verh. deut. physikal. Ges.*, 1924, [iii], 5, 2). M. S. B.

The Constant Δ in the Weiss-Curie Law. B. CABRERA (*Anal. Fis. Quím.*, 1924, 22, 463—475).—Theoretical. The author discusses the theories of paramagnetism of Langevin and Ehrenfest. The reality of the magneton of Weiss as a natural unit implies that in any suggested organisation of electrons in the atom the resulting magnetic moment must always be a whole multiple of the magneton. The significance of the constant Δ in the Weiss–Curie law is also discussed. G. W. R.

Thermo-magnetic Studies of certain Solutions. A. DUPERIER (*Anal. Fis. Quím.*, 1924, 22, 383—397).—Determinations have been made of the value Δ in the Weiss–Curie law $\kappa(T+\Delta)=C$, where κ is the molecular susceptibility, using solutions of nickel nitrate and manganese nitrate, respectively. For nickel the value of Δ obtained is −2, and for manganese, −25. In each case the value is approximately constant. From these values and previous measurements of κ, the magneton number for nickel is found to be $15{\cdot}96\pm0{\cdot}05$ and for manganese $28{\cdot}06\pm0{\cdot}08$. The magneton number thus found for nickel is identical with that found for the solid salts, whilst for manganese it is less by unity than that obtained for solid salts. G. W. R.

Magnetisation Numbers of the Rare Earths. S. MEYER (*Physikal. Z.*, 1925, 26, 51—54).—The magnetic susceptibilities of a number of rare earth elements have been determined and agree with values obtained independently by B. Cabrera (private communication). Plotted against atomic number the values lie on two parabolic curves, maxima being occupied by the pairs Pr, Nd, and Dy, Ho. An attempt is made to correlate these values with the Bohr structure of these atoms. La, Lu, and Hf, in which the 6.6.6. and 8.8.8.8. electron groups are completed, are diamagnetic. Paramagnetism occurs in those atoms in which the 8.8.8.8. group is in course of completion. Ladenburg's view (A., 1920, ii, 301) that magnetic susceptibility is determined by the

arrangement of the inner rather than the valency electrons is confirmed. F. G. T.

Chemical Studies on the Isotopes of Lead. H. BRENNEN (*Compt. rend.*, 1925, **180**, 282—284).—Dillon, Clarke, and Hinchy (A., 1922, ii, 710) recorded a partial separation of the isotopes of radioactive lead by means of the Grignard reaction on lead chloride, using the method of Soddy and Hyman (T., 1914, **105**, 1402) for atomic weight determination. The author has repeated the work using the method of Richards (A., 1908, ii, 281) for the atomic weight of lead. The fractionation through lead tetraethyl gave mean values 207·15 and 207·155 for ordinary lead and 206·87 and 206·88 for a mixture of equal parts of ordinary lead and radioactive lead (atomic weight 206·55). The method does not therefore result in a separation of the isotopes. R. A. M.

Atomic Weight of Silicon. Analysis of Silicon Chloride. O. HÖNIGSCHMID and M. STEINHEIL (*Z. anorg. Chem.*, 1924, **141**, 101—108).—The silicon tetrachloride was purified by repeated fractional distillation in a high vacuum, and the purity tested by measurement of the vapour pressure at 0° (76·6 mm.). The resulting chloride was free from hydrochloric acid and higher chlorides. It was decomposed by sodium hydroxide solution, and the chlorine precipitated with silver nitrate. From the ratio $SiCl_4:4Ag$ (Cl= 35·457; Ag=107·88) a mean of four analyses gave Si=28·105, with a mean deviation of ±0·003. The authors regard this as in favour of Baxter's value Si=28·063, and against the generally-accepted former value 28·3. L. L. B.

Atomic Weight of Chlorine. (MLLE.) E. GLEDITSCH (*J. Chim. physique*, 1924, **21**, 456—460).—No difference could be detected in the atomic weights of chlorine contained in carefully purified silver chloride prepared from (*a*) volcanic ammonium chloride produced in an eruption of Vesuvius, (*b*) water from a depth of 1573 m. in the Calumet and Hecla mines near Lake Superior, and (*c*) ordinary barium chloride. W. H.-R.

Atomic Weight of Zirconium. O. HÖNIGSCHMID, E. ZINTL, and F. GONZÁLEZ (*Anal. Fis. Quím.*, 1924, **22**, 432—462).—The occurrence of hafnium together with zirconium has necessitated a revision of the atomic weight of zirconium. After removal of the greater part of the hafnium by fractional crystallisation of the potassium double fluorides and correction for the small amounts of hafnium remaining, as shown by *X*-ray examination, the mean value for the atomic weight of zirconium, determined by way of the bromide, is given as 91·22. This is in good agreement with the value obtained by Venable and Bell (A., 1924, ii, 690) and deducible from Aston's data for the isotopes of zirconium (A., 1924, ii, 690), assuming that the fourth isotope (96) is present in inappreciable amount. G. W. R.

Determination of the Atomic Weight of Selenium. P. BRUYLANTS, F. LAFORTUNE, and L. VERBRUGGEN (*Bull. Soc. chim. Belg.*, 1924, **33**, 587—612).—Selenium was purified by several

repetitions of the following treatment: solution in nitric acid, evaporation of the solution to dryness, sublimation of the selenium dioxide obtained, and reduction of the sublimate with dry ammonia. The element was converted into hydrogen selenide by direct combination with hydrogen at 700° and by means of the action of water on aluminium selenide prepared by fusing the two elements together. In all cases the gas was purified by condensation in a mixture of solid carbon dioxide and alcohol. By direct weighing, a litre of hydrogen selenide was found to weigh at 0° and 760 mm. 3·6624 g. (mean of 53 determinations); the atomic weight of selenium is, therefore, 79·23. A. R. P.

Atomic Weight of Bismuth. A. CLASSEN and G. STRAUCH (*Z. anorg. Chem.*, 1924, **141**, 82—94).—The atomic weight of bismuth has been determined by means of the combustion of bismuth triphenyl, previously purified by distillation in a high vacuum. In contact with oxalic acid, the oxalate is formed (cf. Classen and Ney, A., 1921, ii, 119), which, by heating in a stream of oxygen, yields an oxide free from carbon. The apparatus employed was a modification of that devised by Richards, in which the initial weighing out, the combustion, and the final weighing all take place in the same vessel. As a mean of fifteen experiments, the value 208·989 was obtained for the atomic weight. This confirms the value 209 found by Classen and Ney, and contradicts that (208) given by von Schneider and Gutbier. L. L. B.

Distribution of Length of α-Particles of Polonium in Oxygen and Nitrogen. I. CURIE and N. YAMADA (*Compt. rend.*, 1924, **179**, 761—763).—About four hundred particles were measured from nitrogen, a somewhat smaller number from oxygen; the general form of the curves of distribution of length is similar to that found with air by Curie (A., 1923, ii, 207). The difference in the actual values is attributed to the use of radiation from a greater mass of polonium than that employed hitherto, so that absorption at the surface of the radiation source may have occurred. The conclusion is reached that the difference in form between Bragg's oxygen and nitrogen curves is due to the law of variation of ionisation with length of the α-particle. H. J. E.

Secondary β-Rays produced in a Gas by *X*-Rays. P. AUGER (*Compt. rend.*, 1925, **180**, 65—68; cf. A., 1924, ii, 286, 440).—When *X*-rays are passed into pure argon only secondary β-rays are produced, but, if the argon is diluted with hydrogen, tertiary β-rays of a few millimetres range are also formed. In krypton diluted with hydrogen, the tertiary rays have a range comparable with that of the secondary rays, and there are traces of quaternary β-rays. The tertiary rays start from the same origin as the secondary and are distinguished from the latter in that they are not affected by changes in the tension of the exciting *X*-rays. Their production is explained as follows: if the initial *X*-ray ionises an atom deeply (*e.g.*, in the *K* shell) the vacant space is very soon taken by an electron from one of the outer shells (*e.g.*, the *L* shell) with liberation of

energy. This energy may be given off as electromagnetic radiation, but generally this radiation is reabsorbed by the same atom with the loss of an electron from one of the outer layers, and this produces the tertiary β-ray. The process may be repeated, with emission of quaternary or β-rays, until the outermost shell of electrons is reached.
W. H.-R.

Magnetic Spectrum of the High Speed β-Rays of Thorium-*B*+*C*. D. K. Yovanovitch and J. d'Espine (*Compt. rend.*, 1925, **180**, 202—203).—The magnetic spectrum of the β-rays of thorium-*B*+*C* is found to contain, in addition to those discovered by Meitner (A., 1922, ii, 732), a band of rapid, but feeble, rays extending to $H\rho$ (gauss per cm.)=6800 with a strong doublet at 5480. In addition, there are two rays at 11,000 and 18,000 and probably another at 40,000. The values of the other rays are in good agreement with those obtained by Meitner. J. W. B.

Absorption of β-Rays by Matter. G. Fournier (*Compt. rend.*, 1925, **180**, 284—287).—A mixture of radium-*D* and -*E* in equilibrium was used as a source so that the experiments were concerned only with the β-radiation from radium-*E* and with a small quantity of a more absorbable β-ray. The coefficient of absorption, μ/ρ, was measured for carbon, aluminium, copper, molybdenum, silver, and tin, using the expression $I=I_0e^{-\mu/\rho \cdot m/s}$ where m/s is the mass of absorbing material per sq. cm., μ the ordinary absorption coefficient, and ρ the density of the material. μ/ρ is independent of experimental arrangement and varies with the absorbent and with the velocity of the β-rays absorbed. The linear relation $\mu/\rho=a+bN$ (a=15, b=0·142, N=atomic number) holds accurately for the principal β-radiation of radium-*E* with the above elements absorbing. For the other β-rays the expression found to hold is $\mu/\rho=65+0{\cdot}615\,N$, *i.e.*, the constants are 4·33 times greater than before. R. A. M.

Study of Characteristic Spectra of γ-Rays by Crystal Diffraction. J. Thibaud (*Compt. rend.*, 1925, **180**, 138—140).—The results obtained previously for the frequencies of γ-rays, by the examination of the secondary β-radiations they excite, have been confirmed by a direct examination of their diffraction by a crystal by de Broglie's method. Examination of the radiation from radium in equilibrium with its products confirms the two lines found by Rutherford and Andrade near 1° 30′ (A., 1914, ii, 698). The present experimental method has, however, extended the range of the observations to rays of an energy of at least 236,000 volts. The radiation from radiothorium showed four lines of wave-lengths 0·168, 0·145, 0·062, and 0·052 Å. Of these lines the last mentioned was also found by the examination of the β-spectrum excited in lead, together with two others of energy 2·73 and $2{\cdot}98\times10^5$ volts respectively which were not detected by the diffraction method. Confirmation of two of the lines enumerated is also found in the measurements of Meitner (A., 1922, ii, 416) and of Ellis (*ibid.*, 466).
G. M. B.

High-Energy γ-Ray from Thorium Disintegration Products. D. H. BLACK (*Nature*, 1925, **115**, 226).—New measurements have been made of the spectra of thorium-*B*, -*C*, and -*D*. Two lines of high energy, viz., 2·55 and $2·62\times10^6$ volts, and possibly a third of slightly greater energy, have been observed. No lines appear between these and those of an energy of about $0·8\times10^6$ volts.

A. A. E.

Capacity for Emanating of Finely-divided Precipitates as a means of Determining Surface Variation. O. HAHN (*Annalen*, 1924, **440**, 121—139).—The capacity for emanating possessed by a compound when mixed with an appropriate radioactive substance, *i.e.*, the ratio of the amount of emanation diffusing out at the ordinary temperature to the total amount the active material can theoretically give, increases with the degree of subdivision of the compound (cf. *Z. Elektrochem.*, 1923, **27**, 189). The procedure previously described, which gave qualitative results, is now combined with Paneth and Vorwerk's method (A., 1922, ii, 618), so that, when large quantities of active material are used, quantitative results are obtained. Investigations on ferric hydroxide hydrogels and alcogels are recorded. Gels precipitated in the cold have a higher emanation capacity than those precipitated in the hot, and moist gels than dry gels, although the reason of the latter is probably not the increase in the size of the crystals. The emanation capacity tends to zero on heating and its original value is not attained on cooling; it decreases rapidly with dry gels on ageing, whereas for moist alcogels it is constant and, for moist hydrogels, nearly so. The ageing phenomena in dry and moist hydrogels are reversible. The emanation coefficient of nickel hydroxide gels sinks extremely rapidly on drying; it is very sensitive to traces of impurities in this case. S. K. T.

Thoron. B. BATSCHA (*Z. physikal. chem. Unterr.*, 1924, **37**, 117—118; from *Chem. Zentr.*, 1924, ii, 1149).—An experiment is described for demonstrating the exponential character of the decay of thoron, showing that its half-value period is about 53 seconds.

G. W. R.

Determination of Radium. (MME.) P. CURIE.—(See ii, 241.)

Decomposition of Mercury Atoms. L. KAUL (*Metallbörse*, 14, 1432; from *Chem. Zentr.*, 1924, ii, 1049).—The conversion of mercury into gold (Miethe and Stammreich, *Naturwiss.*, **12**, 597) is attributed to the loosening effect of the ultra-violet rays on the hydrogen atoms in the mercury atom, which is regarded as built up of hydrogen, helium, and carbon atoms. The hydrogen atoms are unable to resume their place in the system when the ultra-violet light is withdrawn, and by the removal of four hydrogen atoms the gold atom is formed. R. B.

Theory of the Periodic System. A. SOMMERFELD (*Physikal. Z.*, 1925, **26**, 70—74).—A theoretical paper in which is discussed the distribution of electrons among atomic levels according to the

scheme suggested by Stoner (this vol., ii, 85). This is compared with the Bohr distribution and its bearing on the optical and magnetic properties of the elements considered. F. G. T.

Application of the Correspondence Principle to Degenerate Systems and the Relative Intensities of Band Lines. E. C. KEMBLE (*Physical Rev.*, 1925, [ii], **25**, 1—22).—In an attempt to harmonise the Kratzer half integral quantum numbers with the symmetry in the intensities of the two branches of the hydrogen chloride band at 3·46 μ, treatment of the molecule as a degenerate system with but one quantum condition for two degrees of freedom led to an unsatisfactory formula. A modification is proposed and justified by treating the molecule as a non-degenerate system. Comparison between theory and experiment is fairly satisfactory if it is assumed that the lines possess a fine structure. A. A. E.

Lack of Correspondence between Spectroscopic and Spectrophotometric Absorption Maxima. H. GOMBOS (*Biochem. Z.*, 1924, **151**, 7—14).—Absorption maxima of permanganate solutions determined spectroscopically and spectrophotometrically do not correspond. J. P.

Photometric and Spectrophotometric Studies. IV. The Influence of Temperature on the Absorption Spectra of Borax and Phosphate Beads. K. SCHAUM and M. FUNCK (*Z. wiss. Phot.*, 1924, **23**, 73—78).—Study of the absorption spectra of borax and phosphate beads characteristically coloured with copper, nickel, cobalt, iron, chromium, and manganese shows that in most cases increase in temperature (cold to 800—850°) brings about a shift of the absorption band towards the red. In some individual cases, *e.g.*, copper–borax, chromium–phosphate, and manganese–borax and –phosphate, the shift is very marked. In certain other cases, *e.g.*, cobalt, the effect of temperature is very small. The results give no reliable information about the broadening of the bands nor the increase in the maxima on elevation of temperature. Considerable alteration in temperature brings about no constitutive change in the absorbing complex, although it considerably modifies the absorption spectrum. The investigation was carried out with a König–Martens spectrophotometer. Beads were prepared on a platinum wire, and could only be used for about 2 hours on account of their hygroscopicity. Beads having an accurately known content of colouring metal salt can be produced, but the preparation of such beads is useless, since they cannot be made plane-parallel. The influence of thickness and concentration was eliminated by using Weigert's " typical colour curve " method (cf. A., 1916, ii, 545). W. C.

Influence of the CH-group on the Absorption of certain Organic Compounds below 3μ. T. DREISCH (*Z. wiss. Phot.*, 1924, **23**, 102—110).—Observations were made with a mirror spectrometer using benzene and chloroform in both the liquid and vapour states, and acetylene gas. Between 2·486μ and 1·179μ benzene and chloroform show four comparable bands in the liquid

state, and two comparable gaseous bands. An acetylene band at 2·47μ agrees with the benzene band at about 2·48μ, but a second acetylene band at 1·56μ was previously unknown, and falls between the benzene bands at 1·688μ and 1·45μ. There is no acetylene band corresponding with the benzene band at 2·18μ, which is characteristic of aromatic compounds. With one exception, due probably to insufficient resolution, the four liquid and the two vapour bands of benzene and chloroform show the same numerical relationship. The ratio of the absorption coefficients of similar bands due to benzene and chloroform is as 3 to 1. The acetylene band at 2·47μ fits in with the above proportion. W. C.

Ultra-violet Absorption Spectra of Hæmoglobin Derivatives. Chemical Constitution of Blood Pigments. H. FRIEDLI (*Bull. Soc. Chim. biol.*, 1924, **6**, 908—934).—An account is given of the ultra-violet absorption spectra (as far as 2000 Å.) of pyrrole, indole, α- and β-methylindole, hæmin, α- and β-bromohæmin, hæmatin in acid and alkaline solution, hæmatoporphyrin dimethyl ether, mesoporphyrin, and of the anhydride and imide of hæmatic acid. The relation between the chemical constitution and the absorption spectra of these compounds is discussed. It is found that indole has a totally different spectrum from either pyrrole or benzene, from which it is derived. The methylindoles possess spectra very similar to that of indole itself; the position of the substituent methyl group has a small effect. Hæmin (on account, it is suggested, of the four pyrrole rings it contains) shows a strong ultra-violet absorption. Although no difference can be detected chemically, there is a marked difference spectroscopically between α- and β-bromohæmin. The absorption in the ultra-violet of the compounds not containing an atom of iron (*e.g.*, hæmatoporphyrin) is considerably diminished. The spectra of the imide and anhydride of hæmatic acid are very different. L. F. H.

Absorption of [Ultra-]Violet Light by Organic Substances. V. E. KĘPIANKA and L. MARCHLEWSKI (*Bull. Soc. chim.*, 1924, [iv], **35**, 1613—1618).—The coefficient of extinction, for a given wave-length, of an aqueous solution containing equimolecular quantities of benzoic acid and phenol is equal to the sum of the coefficients for solutions of the separate substances of the same concentration, in most cases to within 5%. The maximum deviation was 15%. S. K. T.

Absorption of Ultra-violet Rays by Methyl Derivatives of Naphthalene. H. DE LÁSZLÓ (*Compt. rend.*, 1925, **180**, 203—206).—The absorption spectra of mono- and di-methylnaphthalenes in the vapour state and in hexane solution are plotted. The introduction of the methyl group into the naphthalene causes a displacement of the spectrum towards the red which is greater with β- than α-mononaphthalene derivatives, and with 2 : 6- than 2 : 7-dimethylnaphthalene. The spectra resemble generally those of naphthalene itself, consisting of a region A between 3250 and 2950 Å., a region B between 2950 and 2500 Å., and a very strong band in the

ultra-violet, at 2200 Å. In the state of vapour, the A region consists of continuous bands (resolution into lines being observed only in the case of β-methylnaphthalene) which can be grouped into several series with almost constant intervals. In the B region the bands are fused together, the absorption curve showing three maxima for the β-derivative and four for the α-, whilst, in the vapour state, the β-derivative shows seven and the α-derivative four continuous bands.

J. W. B.

Spectrum of Carbon Monoxide at Very Low Pressures, and its Relation to the Spectrum of the Tails of Comets. F. BALDET (*Compt. rend.*, 1925, **180**, 271—273; cf. A., 1924, ii, 438).—The spectrum was obtained by the impact of slow electrons from an incandescent filament. Thirty bands are given between 5700 and 3080 Å., each having four principal edges. The positions are given sufficiently accurately by the Deslandres expression, $\nu=(27{\cdot}83/2.n^2+2197{\cdot}24n)-(26{\cdot}57/2.p^2+1493{\cdot}66p)+23529{\cdot}0$, where n varies from -3 to 0 and p from $+3$ to -9. The origin is taken at the most intense band beginning at 4248·55 with stronger edges at 4251·27, 4271·31, 4273·87. All the bands are similarly subdivided. The wave-number differences between the first and third, the second and fourth edges of the same band are practically constant ($\Delta\nu=-126$). Between the first and second, $\Delta\nu$ varies regularly but not linearly from $\Delta\nu=-17$ at $\nu=18{,}000$ to $\Delta\nu=-10$ at $\nu=31{,}000$. The spectrum resembles closely the third group in that of air. Since the one may be due to a molecule N+O and the other to C+O, it seems possible that the influence of oxygen preponderates in both spectra. The spectrum is characteristic of comet-tails and may be called the third negative group of carbon. The first group was recorded by Deslandres (A., 1904, ii, 105) and the second by Deslandres and d'Azambuja (*ibid.*, 1905, **140**, 917). R. A. M.

Infra-red Absorption Spectrum of Ammonia. K. SCHIERKOLK (*Z. Physik*, 1924, **29**, 277—287).—The absorption spectrum of ammonia in the region from 0·589μ to 14·4μ has been studied by means of an apparatus of high dispersive power. In the short-wave portion of this region strong bands have been found at 1·493μ and 1·935μ, with a weaker one at 1·643μ. A strong band at 2·22μ shows two sharp maxima at 2·202μ and 2·239μ. The bands previously found by Coblentz ("Ultra-red Investigations") in the neighbourhood of 3·0μ, 6·0μ, and from 7·8μ to 15μ, have been further resolved. The last forms a double band. Mean values for the moment of inertia of the ammonia molecule have been calculated from the absorption bands and compared with Eucken's value calculated from the vapour-pressure curve (*Jahrb. Radioakt.*, 1920, **16**, 401). M. S. B.

Structure of the so-called Ultra-violet Bands of Water Vapour. G. H. DIEKE (*Nature*, 1925, **115**, 194).—Results of a consideration of published data, to be given in detail elsewhere, are summarised. With the aid of the combination principle it is

possible to obtain the relative values of the rotational terms without any theoretical assumption concerning the structure of the molecule. A. A. E.

Ultra-violet Absorption Spectra of Ketens and their Dimerides. II. G. C. LARDY (*J. Chim. physique*, 1924, **21**, 353—385; cf. this vol., ii, 87).—Details of the experimental data (*loc. cit.*) are given. Using solutions in hexane and, in some cases, in alcohol, the ultra-violet absorption spectra of the following substances are described in detail; keten, diethyl-, dipropyl-, and diphenyl-keten; tetraethyl-, tetrapropyl-, and tetra-allyl-diketo*cyclo*butane; diphenyldimethyldiketo*cylo*butane; diketo*cyclo*butane; diphenyldiketo*cyclo*butane; the diethyl ester of 1 : 3-dimethyl-2 : 4-diketo*cyclo*butane-1 : 3-dicarboxylic acid; *aci*dimethyldiketo*cyclo*butane; ethyl- and phenyl-carbimides; diethylcarbodi-imide; diacetyl. No difference exists between the absorption spectra of aldoketens of the type $H_2C{:}C{:}O$ and ketoketens of the type $R_2C{:}C{:}O$. The absorption spectrum of keten has also been examined in the state of vapour, and consists of a number of fine bands occupying the same position as that of the wide band given by the substance in solution and corresponding with the group C:O. W. H.-R.

Fluorescence of Benzene Vapour by Monochromatic Excitation. P. PRINGSHEIM and A. L. REIMANN (*Z. Physik*, 1924, **29**, 115—124).—The ultra-violet band fluorescence of benzene vapour, excited by different monochromatic radiations from the mercury, zinc, and cadmium arcs, has been examined. At the saturation pressure of 25 mm. at 0°, any active wave-length excites the same spectrum as that previously obtained under excitation by electrical discharge, or by light from the iron arc (McVickers and Marsh, T., 1923, **123**, 642, 817, 820). At lower pressures, less than 1 mm., some of the feeble bands, which do not stand in any clearly recognised series relation with the exciting line, or with one another, become intensified, whilst the stronger bands almost disappear. Raising the temperature to increase the saturation pressure, or adding another gas, gradually restores the original spectrum. At still higher pressures, for example 75 mm., and also in liquid benzene and concentrated solutions, the fluorescence appears to be a surface phenomenon, owing to the strong absorption of the exciting radiation. This accounts for the negative results of earlier investigators. M. S. B.

Phosphorescent Powers of Fluorescein. B. BATSCHA (*Ber.*, 1925, **58**, [*B*], 187—193; cf. Trede and Wulff, A., 1922, ii, 245).—Fluorescein is brought into a highly phosphorescent condition when a small quantity of it is melted with tartaric or citric acid and the molten mass is allowed to cool. The phenomenon is excited by exposure to bright, diffused daylight, but persists only for 8—10 seconds. It appears to be connected with the viscosity of the mixture, since the citric acid preparations require to be cooled to −12° (when they become hard instead of viscous) before the effect is obvious and, further, phosphorescence is no longer observed if the

mixtures are heated to about 45°. Mixtures of fluorescein and dextrose are, at most, faintly phosphorescent, but this property is acquired if acidic substances (oxalic or salicylic acid, potassium hydrogen oxalate, sodium hydrogen sulphate) are added. Pyrocatechol, quinol, normal sodium sulphate, sodium hydroxide, barium hydroxide, sodium carbonate, and disodium hydrogen phosphate do not produce this effect, but the action of the alkaline materials is rendered somewhat obscure by their behaviour towards dextrose itself. It is, however, established definitely that the phosphorescence of fluorescein is activated by substances with free hydrogen ions. Phosphorescence is excited in tartaric acid or dextrose which has been melted and cooled if exposed to the arc light, and the effect disappears if the specimens are warmed at 45°; the phenomenon is much less readily excited and less intense in character than that observed in the presence of fluorescein. H. W.

Examination of the Classical Dispersion Formula in the Case of Monatomic Gases and Vapours. K. F. HERZFELD and K. L. WOLF (*Ann. Physik*, 1925, [iv], **76**, 71–105).—A study of experimental results for the variation of refractive index with wave-length in the case of helium, neon, and argon, shows that they can be expressed satisfactorily by a dispersion formula of only one term in which the specific ("dispersion") frequency lies further in the ultra-violet than the long wave-length end of the absorption spectrum. The attempt to base a formula on the resonance frequency failed, but a formula with two terms, one of which involved the resonance frequency and the other the dispersion frequency, satisfied the cases of argon and helium.

The number of electrons in each atom causing the dispersion is much larger for argon than for neon, but the further increase for krypton and xenon is small. The authors consider that there is a real deviation from the classical formula and favour that of Wentzel. An integral relationship is established between the refractive indices for helium, neon, argon, krypton, and xenon, for very long wave-lengths. Mercury vapour shows a peculiarity at λ7000 Å. in that there is anomalous dispersion but no absorption. E. B. L.

Theory of Constitutive Colour. E. ZINTL and A. RAUCH (*Ber.*, 1925, **58**, [*B*], 234; cf. A., 1924, ii, 806).—The colour of all inorganic substances, including the elements, has been ascribed by Biltz (A., 1923, ii, 809) to the presence of incompletely saturated or weak electro-valency forces. H. W.

Ionisation in the Wave of Propagation of Explosions. A. E. MALINOWSKI (*J. Chim. physique*, 1924, **21**, 469—478).—A rapid current of air mixed with hydrogen or hydrocarbon vapour was passed through an iron tube and the variations of pressure and ionisation were measured when the explosive wave proceeded normally, and when it was made to pass through a strong electric field. The explosion proper is preceded by an initial wave in which ionisation takes place, the degree of ionisation being reduced if the

wave passes through a strong electric field owing to the latter removing the ions or electrons. In the case of a mixture of air with benzene vapour, the explosion can be completely stopped if the initial wave passes between plates charged to a potential difference of about 110 volts. The degree of ionisation is greater in those places in which the velocity of the wave is increasing than where it is decreasing. Of the total number of ions (n_1) produced, the greater number recombine and the resulting liberated energy maintains the explosion. But a small fraction (n) of the ions ($n/n_1 < 3{\cdot}6 \times 10^{-5}$) are carried forward by the explosive wave from one layer to the next, and it is these ions that accelerate the explosion and can be removed by an electric field. W. H.-R.

Evolution of the Molecule of Nickelic Hydroxide in Contact with Water. (MLLE.) S. VEIL (*Compt. rend.*, 1925, **180**, 211—213; cf. A., 1924, ii, 557).—Nickelic hydroxide and nickel sesquioxide show exactly similar, but slightly smaller, variations of the molecular coefficient of magnetisation on successive re-dissolution and re-precipitation as do the corresponding compounds of bivalent nickel. J. W. B.

Relation between the Critical Temperature and the Molecular Volume at Absolute Zero. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **141**, 375—379).—Theoretical. Previous work (this vol., ii, 25; Van Laar, "Die Zustandgleichung von Gasen und Flüssigkeiten," 1924, 140) is used to deduce the relation $V_0\gamma p_k/T_k = 5{\cdot}13$, where V_0 is the molecular volume at absolute zero, p_k and T_k the critical pressure and temperature, and $\gamma = b_k/2b_0$, where b is the constant of Van der Waals. For most normal substances $\gamma = 0{\cdot}9$, and the relation reduces to $V_0 p_k/T_k = 5{\cdot}7$, whilst more accurately $2\gamma = 1 + 0{\cdot}038\sqrt{T_k}$. The above relations have been tested for a number of organic and inorganic compounds and the agreement is very satisfactory; in the case of elements the values of $V_0 p_k/T_k$ are considerably greater than the theoretical value, but the values of $V_0\gamma p_k/T_k$ are in better agreement. W. H.-R.

Wave-length of Maximum Energy in the Sound Spectrum of an Explosion. A. DUFOUR (*Compt. rend.*, 1924, **179**, 759—761).—Evidence is adduced in support of the relation established by Villard (*ibid.*, 1924, **179**, 617) between the wave of maximum energy and the mass of explosive used. H. J. E.

Double Refraction of Amorphous Liquids and Molecular Constitution. D. VORLÄNDER and R. WALTER (*Physikal. Z.*, 1924, **25**, 571—573).—The double refraction of about 120 organic substances was measured when they were placed in a rotating cylinder apparatus at nearly constant temperature. The results for various types of molecules are given in terms of the "specific double refraction," which in the case of amorphous oils is given by $D/u\eta$, where D is the double refraction observed when the cylinder rotates with a velocity u, and η the coefficient of viscosity of the substance referred to water as unity. A curve is given showing

the connexion between the specific double refraction and the length of chain in the case of the fatty acids. L. F. B.

Rotatory Power of Cholesteric Substances. M. ROYER (*Compt. rend.*, 1925, **180**, 148—150; cf. A., 1923, ii, 223).—The enormous rotatory power of the cholesteric phase is due to a strong helical torsion in the substance, the rotatory power being smaller the larger the torsion. In a mixture of amyl cyanobenzylideneaminocinnamate with cholesteryl benzoate (2·75 parts : 1) this torsion diminishes as the temperature rises from the lower transition point to the higher temperature at which the cholesteric phase passes into the nematic phase. At the same time the rotatory power increases to seven times its initial value. The direction of the spiral torsion becomes reversed at this point, the rotatory power on either side of it for 5100 Å. being +135·8 and −135·8 turns per mm. In all other cases, optical rotatory power falls with rise of temperature. The cholesteric rotatory power differs in this from molecular rotation in crystals, which often rises with the temperature. On the other hand, cholesteric rotatory power is quite analogous to magnetic rotation and especially with respect to the dispersion, the passage from a large value $+R$ to an equally large $-R$ for adjacent wavelengths being paralleled only in magnetic rotatory dispersions. The light is in both cases circularly polarised. G. M. B.

Ammonium Dimolybdomalate. E. DARMOIS and A. HONNELAITRE (*Compt. rend.*, 1924, **179**, 629—632).—Ammonium dimolybdomalate reacts with substances which can combine with molybdic acid and these produce variations in its rotatory power. Hydroxy-acids, polyhydric alcohols, polyphenols, and phenolic acids exert marked influence. This appears to depend on the possession of two hydroxyl groups in adjacent positions (cf. Böeseken, A., 1921, i, 843). H. J. E.

Varying Valency of Gold with Respect to Mercaptanic Radicles. (SIR) P. C. RÂY (*J. Indian Chem. Soc.*, 1924, **1**, 63—73).—Various products obtained as precipitates by addition of gold chloride to solutions of sulphur compounds in alcohol, ether, and acetone are formulated as containing bi-, quadri-, and sexa-valent sulphur together with bi-, ter-, quadri-, and quinque-valent gold. From diethyl disulphide two *compounds*, Et_2S_2,Au_2Cl_4 and Et_2S_2,Au_4Cl_2. From monopotassium dithioethylene glycol, $C_4H_8S_4Au_2Cl$. *Disodium dithioethylene glycol* gave $(C_2H_4S_2)_4Au_3Cl$ in ether, $(C_2H_4S_2)_5Au_2$ in acetone. The following *compounds* are described from benzylidenediethylene tetrasulphide: $2[PhCHS_4(C_2H_4)_2],Au_3Cl_4,Et_2O$, $6[Ph\cdot CHS_4(C_2H_4)_2]Au_4Cl_3$, $5(C_2H_4)_2S_2,Au_3Cl_5,1\cdot5Et_2O$, $4[(C_2H_4)_2S_2]Au_3Cl_4,0\cdot5Et_2O$, $4[(C_2H_4)_2S_2],Au_3Cl_2$, $3[(C_2H_4)_2S_2]Au_3Cl_2,EtOH$, $3[(C_2H_4)_2S_2],Au_2Cl_2,EtOH$, $3[(C_2H_4)_2S_2],Au_2Cl_2,EtOH$. Triethylene trisulphide gave $(C_2H_4S)_3,2AuCl_3$ and $(C_2H_4S)_3,AuCl_2$. G. M. B.

Calculation of Molecular Diameters from Heat of Vaporisation and Surface Tension Data. H. SIRK (*Physikal. Z.*, 1924, **25**, 545—546).—A formula is deduced connecting the diameter of a

molecule of a substance with its internal heat of vaporisation, and is used to calculate the molecular diameters for seventeen different substances. The values obtained are compared with those calculated from a modified form of an equation given by Ostwald and with values obtained by Kuenen from kinetic theory data. On the average the author's values are about 30% larger than those of Kuenen. L. F. B.

Crystal Structures of Ammonium Fluoferrate, Fluoaluminate, and Oxyfluomolybdate. L. PAULING (*J. Amer. Chem. Soc.*, 1924, **46**, 2738—2751).—Cubic crystals of ammonium fluoferrate, fluoaluminate, and oxyfluomolybdate have been examined by the spectral, Laue, and powder *X*-ray methods. The units of structure, based on a face-centred lattice, contain 4 mols. The values of *d* found are: ammonium fluoferrate 9·10 Å., fluoaluminate 8·40 Å., and oxyfluomolybdate 9·10 Å. The results closely resemble those for the chlorostannate. In oxyfluomolybdate oxygen and fluorine atoms are taken as crystallographically equivalent. G. M. B.

Electrical Conductivity of Rock Salt Crystal. D. VON SEELEN (*Z. Physik*, 1924, **29**, 125—140).—The electrical conductivity of natural rock salt crystals has been determined at temperatures from 15° to 500°. No experiments were made on chemically pure single crystals, and the material used could only be regarded as presenting roughly a crystal lattice structure. The conductivity varies with different specimens, with the direction of the current in relation to the crystal axes, and with the thickness of the layer. At low temperatures, it is very small. The results are affected to a slight extent by a dielectric polarisation, and after long passage of the current electrolytic polarisation is observed. Ohm's law is valid up to differences of potential of 200 volts. Transport measurements show that the conduction is electrolytic and that the current is carried solely by the sodium ion. The sodium separated at the cathode rapidly changes into hydroxide and carbonate, or bicarbonate. By determining the potential at different points inside the crystal, it has been shown that the fall of potential between the electrodes is not expressed by a straight line graph. The form of the curve does not change with the potential difference applied, but only with temperature. The effect therefore appears to be due to a variable resistance of the material. Charging and discharging phenomena have been studied and are in agreement with Maxwell's theory. The results show that conduction takes place by the formation of volume charges and not of electrical double layers. M. S. B.

Free-space Numbers. I. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **141**, 304—308; cf. A., 1923, ii, 801; 1924, ii, 520, 823).—The "free-space number," χ, is calculated by subtracting the "filled-space number," ψ, from unity. Since ψ has been determined for a great number of compounds, the values of χ have only to be tabulated; the figures obtained vary from 0·3601 for bromobenzene to 0·5401 for ethylene. S. I. L.

Hardening Phenomena in Metals as Revealed by *X*-Rays. E. SCHIEBOLD (*Z. Metallk.*, 1924, 417—425, 462—480).—A critical discussion and review of the work and theories of previous investigators on the effect of cold work in hardening metals and the use of *X*-rays in revealing the changes undergone by metals during plastic deformation is given and the opinion expressed that no satisfactory theory which will account for all the known facts of the mechanism of the hardening of metals by cold work has yet been advanced. Laue and Debye–Scherrer röntgenograms show that plastic deformation takes place as the result of pure translation of the crystals in an orderly geometric manner along slip or twinning planes combined with bending or tearing of the individual crystal grains, and, by observing the symmetry of the diagrams, it is possible to tell approximately the extent and nature of the deformation which the metal has undergone, as the symmetry of the figures is greater the severer the deformation. [Cf. *B.*, 1925, 103.]

A. R. P.

Structure of Metals and its Physical Investigation. J. CZOCHRALSKI (*Z. Metallk.*, 1925, **17**, 1—11).—A description is given of an attempt to elucidate the phenomena that occur during the deformation of a metal by investigating the behaviour of a single crystal of aluminium during distortion. Specimens in the shape of round or square rods exhibited after twisting about the long axis and after coiling characteristic reflection figures when polished and etched, the shape of the figures depending to a great extent on the deformation the metal had undergone. Laue photograms also showed this, but not nearly so clearly. A single crystal of aluminium twisted through 360° and again twisted back to its original shape gave almost the same Laue photogram as the original, but the star-like design was not so strongly marked and a polished and etched section showed the presence of twinned crystals along the boundaries of the specimen; annealing at 620° caused complete recrystallisation. From his results, the author expresses the opinion that Pólányi's theory of the deformation of metals by the translation and parallel movement of the crystals does not agree with all the known facts. [Cf. *B.*, 1925, 175.] A. R. P.

Smectic Compounds and *X*-Rays. E. FRIEDEL (*Compt. rend.*, 1925, **180**, 269—271; cf. A., 1923, ii, 223; 1924, ii, 518).—Friedel and de Broglie found that smectic compounds like oleates give diffraction patterns with *X*-rays. McBain asserted that the results were due to crystalline oleates. The typical smectic compounds, ethyl *p*-azoxybenzoate, ethyl *p*-azoxycinnamate, pass from the crystalline to the smectic condition at temperature T_1 and melt to the amorphous condition at T_2. Below T_1, normal *X*-ray spectra are shown, between T_1 and T_2 the results are of a special type characterised by equidistant planes in one direction. Above T_2 no spectra were obtained. For ethyl *p*-azoxybenzoate S=19·9, C=16·2 and for ethyl *p*-azoxycinnamate S=23. A mixture of 15 parts of the former with 1 part of the latter gave

S=20·6, C=16·2 where S and C are the distances between successive planes in the smectic and crystalline states, respectively (C=longest distance). The earlier work on solid soaps and pure oleates gave similar results. The only mesomorphs to show diffraction patterns are the smectic compounds. R. A. M.

Determination of the Molecular Weights of Non-volatile Substances by the Isothermal Distillation of their Solutions. C. Hrywakowski (*J. Chim. physique*, 1924, **21**, 396—399).—The accuracy of the microscopical method of determining molecular weights due to Barger (T., 1904, **85**, 286) has been tested by experiments with aqueous solutions of carbamide and resorcinol. If a thermostat is used, the method gives results correct to 0·005 g.-mol., this degree of accuracy being about the same as that obtained by b. p. or f. p. determinations, but the microscopical method has the advantage of being applicable over a range of temperatures. W. H.-R.

Variation of the Molecular Weights of Sodium, Potassium, and Tellurium with Temperature. A. Jouniaux (*Bull. Soc. chim.*, 1924, [iv], **35**, 1607—1613).—From the previously published observations of other workers it is shown that sodium is monatomic over the temperature range 63·5—1063°; potassium is unimolecular near its m. p., but its complexity increases as the temperature rises. Tellurium is monatomic at 357° and becomes more complex at lower temperatures. It is diatomic at high temperatures (about 1500°). S. K. T.

Optical Constants of Solid Cæsium. J. B. Nathanson (*Physical Rev.*, 1925, [ii], **25**, 75—84).—The optical constants of cæsium with reference to air are, for light of wave-length 4550—6800 Å. (six values are tabulated), as follows: refractive index, 0·362—0·350 (minimum, 0·321 at 5890 Å.); coefficient of absorption, 2·37—4·34; reflecting power, 0·442—0·661; principal angle of incidence, 55° 25′—63° 20′; principal angle of azimuth, 38° 32′—40° 6′. A. A. E.

Thermoelectric Behaviour of Pure Iron at its Transition Points. A. Goetz (*Physikal. Z.*, 1924, **25**, 562—571).—A pure iron wire is heated by the passage of an alternating current. The wire consists of two uniform portions of different diameters, so chosen that when the wire is heated different modifications of iron may exist simultaneously in the two portions. The ratio of the diameters decides the particular modifications which may so exist for a given temperature of the thinner portion. The thermoelectric behaviour of the various modifications may thus be studied right up to the melting point. The results show that there is a big decrease in the thermoelectric power when iron passes from the β modification to the γ modification, and an increase when γ-iron changes to δ-iron, thus showing that the space-centred cube structure is thermoelectrically positive with respect to the surface-centred cube structure. L. F. B.

Molecular Heats of Vaporisation. M. PRUD'HOMME (*J Chim. physique*, 1924, **21**, 461—465).—The molecular heat of vaporisation (L) at any temperature (T) may be expressed by the relation (1), $L=KT(T_c-T)/(T_c-T_1)$ where T_c is the critical temperature and T_1 the boiling point, both on the absolute scale. This relation is tested for methyl alcohol. When plotted against T, the value of L/K rises to a maximum at $T=T_c/2$; the value of K is a minimum at this point, but the minimum is flat so that K is approximately constant at this point, but increases greatly on either side. Empirically L may be expressed by the relation (2), $L=a(T_c-T)^n$, where, for methyl alcohol, log a=0·3381461, and n=0·265; the agreement between observed and calculated results is good to within 100° of the critical temperature. Combination of (1) and (2) shows that K may be expressed in the form $K=(T_c-T)^{n-1}.C/T$, where C is a constant. The values of K at different temperatures are calculated for various substances; for nitrous oxide the value of L calculated for the b. p. indicates that the substance forms unassociated molecules on the basis of Trouton's Law. W. H.-R.

Density of Oxygen. G. P. BAXTER and H. W. STARKWEATHER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 479).—The oxygen was weighed in a globe of about a litre capacity in the usual manner against a counterpoise of similar capacity, but with increased refinements. The balance case was wrapped in felt; it contained radium bromide to dissipate electrostatic charges, the balance room temperature was controlled to 1°, and the barometers were immersed in water at a constant temperature. The average of all the twenty-two experiments gave the density 1·42901 g./litre at 0°, 760 mm. of mercury, and sea level, latitude 45°: the g.-mol. volume is in consequence 22·415 litres. E. B. L.

Properties of Pure Hydrogen Peroxide. V. Vapour Pressure. O. MAASS and P. G. HIEBERT (*J. Amer. Chem. Soc.*, 1924, **46**, 2693—2700).—Direct measurements of the vapour pressure of hydrogen peroxide are summarised by the equation log $p=-(0{\cdot}05223\times48530)/T+8{\cdot}843$. The following constants are deduced: b. p. 152·1°, latent heat of evaporation, 341·5 cal., Trouton's constant, 27·3, critical temperature, 459°. G. M. B.

Hardness of Manganese Steel. C. BENEDICKS (*Nature*, 1925, **115**, 230).—Shavings, obtained by means of quartz or alundum, from a non-magnetic specimen of manganese steel exhibited ferro-magnetism, but no lines due to α-iron could be detected by X-ray analysis. It is nevertheless probable that mechanical stress causes a partial conversion of γ-iron into α-iron. A. A. E.

Property–Composition Curves of Binary Liquid Mixtures. L. FRANK (*Z. physikal. Chem.*, 1924, **114**, 257—274).—The possibility of interpreting property–composition curves in terms of the van der Waals equation is considered. The properties include vapour pressure, boiling point, specific volume, viscosity, surface tension, and partial pressure, and forty-three binary mixtures have

been examined. It has been found that the assumption of compound-formation or association can be frequently dispensed with, although in some cases, *e.g.*, chloroform–ether, carbon disulphide–acetone, mixtures of benzene with methyl alcohol, ethyl alcohol, acetic acid, and carbon disulphide, and nearly all mixtures with water, satisfactory results are not obtained. The mixtures with water are regarded as ternary mixtures, perhaps with $(H_2O)_m$ and $(H_2O)_n$, whilst almost all other mixtures for which calculated and experimental values do not agree contain an associated component. On the other hand, the boiling point–concentration curves show fairly good agreement between calculated and observed values in the case of ether–methyl alcohol and ether–ethyl alcohol, although the alcohols are associated, and the viscosity values also seem to be largely unaffected by association. The vapour pressure–concentration curves for methyl alcohol–ethyl alcohol give good agreement, a fact for which the explanation suggested is that over the temperature range considered (20—100°), both components are associated to the same extent. L. L. B.

Determination of the Structural Composition of Alloys by a Metallographical Planimeter. E. P. POLUSHKIN (*Trans. Amer. Inst. Min. Met. Eng.*, Dec. 1924, 19 pages).—The structural composition of an alloy of two or three constituents may be determined by planimetric measurement of the area occupied by each of the constituents on a few representative photomicrographs. This is accomplished by drawing a series of parallel lines at equal distances apart across the surface of the photograph so as to divide the constituents into a number of trapezoids, the total area of which is found by multiplying the distance between two succeeding lines by the sum of the medians of the trapezoids as measured by a recording planimeter. The volume occupied by a constituent of the alloy is then the same fraction of the total volume of the alloy as the area of the constituent is to the whole area of the photograph. If the density of each constituent is known, the weight of each present can be calculated and thus the composition of the alloy found. The application of the method to the analysis of some bismuth alloys and of cast iron is described; the results obtained agree reasonably closely with those found by chemical analysis. A. R. P.

Equilibrium in Solutions of the Isomorphous Salts, $(NH_4)_2SO_4,MgSO_4,6H_2O$, and $(NH_4)_2SO_4,FeSO_4,6H_2O$. I. ZWEIGLÓWNA (*Roczniki Chemji*, 1924, 4, 331—341).—The solubilities of mixed crystals of these salts between 0° and 6° indicate that the double sulphates are miscible in all proportions and that, in chemical composition, the mixed crystals differ little from the solution, although the two component salts differ in solubility. If c_1 and c_2 indicate respectively the molecular concentrations of the two double sulphates in the solution, and x_1 and x_2 the molecular proportions of the two in the mixed crystals, the values of c_1/x_1 and c_2/x_2 are constant; from this it is inferred that the crystal molecule is identical with the simple chemical molecule. T. H. P.

Relationship between Tensile Strength, Temperature, and Cold-work in some Pure Metals and Single Solid Solutions. D. H. INGALL (*J. Inst. Metals*, 1924, **32**, 41—64).—The tensile strength of any uniform metal or alloy is a linear function of temperature (provided no allotropic or phase change takes place) up to a certain critical inflexion temperature beyond which the function is of a higher order. The critical inflection temperature of an alloy is that of the constituent with the lowest inflexion temperature; it is the limiting temperature at which a metal retains its properties due to cold work and is possibly influenced by the size and distribution of the constituents. [Cf. *B.*, 1924, 836.] S. K. T.

Allotropy of Glass. H. LE CHATELIER (*Compt. rend.*, 1924, **179**, 718—721).—The author claims that his equation representing the viscosity of glass as a function of temperature (*ibid.*, 1924, **179**, 517) and the inference that the substance exists in another allotropic form below 800° are confirmed by the experimental work of English (*J. Soc. Glass Tech.*, 1924, **8**, 205). Calculated values are compared with those obtained experimentally and a diagram indicates the points at which allotropic change occurs for three different types of glass. H. J. E.

Solubility of Chlorine in Carbon Tetrachloride. G.-M. SCHWAB and G. HANKE (*Z. physikal. Chem.*, 1924, **114**, 251—256).—The solubility coefficient, s, has been determined by measuring the decrease in pressure with time of chlorine in an apparatus of known volume connected with a very small flask containing a small quantity of carbon tetrachloride. The value of s is found to be $0{\cdot}031 \pm 0{\cdot}003$ at 19°. The "invasion" coefficient, which is defined as "the number of molecules which pass per second through 1 cm.^{2} of surface with 1 atm. difference between the pressure in the gas phase and the osmotic pressure in the solution," is also determined and is given as $10^5 i = 2{\cdot}2 \pm 0{\cdot}5$ at 19°. L. L. B.

Solubility of Yttrium Salts. M. C. CREW, H. E. STEINERT, and B. S. HOPKINS (*J. Physical Chem.*, 1925, **29**, 34—38).—The solubility of yttrium chloride, bromide, nitrate, and sulphate has been measured over a temperature range of 0—100°. There is no change in the hydration of these salts over this range. M. B. D.

Solubilities of Calcium Soaps. G. A. HARRISON (*Biochem. J.*, 1924, **18**, 1222—1223).—The solubilities of the calcium soaps of oleic, palmitic, and stearic acids in alcohol, ether, chloroform, acetone, benzene, xylene, and light petroleum are given. S. S. Z.

Piezochemical Studies. XXVI. Influence of Pressure on Solubility in the System Naphthalene–Tetrachloroethane. E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **114**, 321—333; cf. A., 1923, ii, 746).—In the course of an earlier investigation (*ibid.*, 1919, **93**, 385) it was found that the solubility could be expressed by means of a parabolic curve, and the existence of a minimum solubility was suggested.

This point has now been further investigated, using the system, naphthalene–tetrachloroethane, in which the solubility is strongly influenced by pressure. The two following equations are used to express the results: (1) $c=\alpha+\beta p+\gamma p^2$ and (2) $\log c=\alpha_1+\beta_1 p+\gamma_1 p^2$, where c is either the weight per cent. with respect to solvent or solution, or the molecular per cent. with respect to solution. In all cases, equation (1) gives better results than (2), especially where c is expressed as percentage by weight of the solvent. It has not been possible, however, to decide with any certainty whether the solubility passes through a minimum or not with rising pressure. The increase of solubility amounts to 10·5% for a pressure increase of 250 atm. Concordant results could only be obtained up to pressures of about 1000 atm., probably on account of the great increase of viscosity of the oil at higher pressures.

L. L. B.

Absorption of Vapours by Charcoal. E. URBAIN (*Compt. rend.*, 1925, **180**, 63—65).—The absorption of chlorine, benzene, and chloropicrin vapours by compressed charcoals has been investigated. If v is the volume of the pores, V the volume actually occupied by the carbon, and Φ the apparent volume of the charcoal, $\Phi=v+V$, and the "compactness" c is defined as $c=V/\Phi$. Increase in the compactness results in increased absorption in the case of chlorine, and diminished absorption with chloropicrin. With benzene, the absorption is a maximum at $c=0{\cdot}300$ and decreases on either side. In the specimens examined c varied from 0·19 to 0·40. W. H.-R.

Adsorption of Vapours by Alumina. L. A. MUNRO and F. M. G. JOHNSON (*Ind. Eng. Chem.*, 1925, **17**, 88).—The adsorptive power of alumina depends on its state of dehydration. When the water content is less than 7·2%, however, the adsorptive power remains constant. The adsorption of gases by alumina can be divided into three classes. Ether, ethyl alcohol, petrol, methyl alcohol, and benzene are never completely adsorbed; water and acetic acid are completely adsorbed until the alumina is within about 40% of saturation; sulphur dioxide and ammonia are completely adsorbed until the alumina has become saturated. Substances such as acetone, esters, and organic compounds containing halogens are catalytically decomposed by the alumina. M. B. D.

Adsorption of Hydrogen and Hydroxyl Ions by Charcoal. C. KROETZ (*Biochem. Z.*, 1924, **153**, 173—184).—Using a series of buffer mixtures of different p_H, and taking the isoelectric point of charcoal to be that of the buffer mixture which does not change in reaction after adding excess of charcoal to it, it is found that blood charcoal has its isoelectric point at p_H 7·58. An appreciable change in the reaction of a medium is brought about only when much charcoal is used and when the medium is only slightly buffered. The effect of therapeutic doses of charcoal on the p_H of the alimentary secretions is negligible. H. D. K.

Adsorption of Nitrogen Peroxide by Silica Gel. R. C. RAY (*J. Physical Chem.*, 1925, **29**, 74—86).—The adsorption iso-

therms for nitrogen peroxide by silica gel have been determined at 15°, 57°, 80°, and 100° at pressures varying from 11 to 490 mm. Gels containing between 5·16 and 4·68% of moisture have the same adsorptive capacity, but below these values the adsorptive power is considerably diminished, probably owing to an incipient fusion of the surface of the gel due to prolonged heating at a fairly high temperature. By repeated adsorption of nitrogen peroxide, the water is replaced by approximately the same volume of nitric acid and the adsorptive capacity of the gel is only slightly diminished.

M. B. D.

Active Charcoal. III. Spacial and Stoicheiometric Relations of Adsorption (Chemical Complex Formation). O. RUFF and E. HOHLFELD (*Kolloid-Z.*, 1925, **36**, 23—39; cf. A., 1923, ii, 411; 1924, ii, 334).—The adsorption curves of gases and dissolved substances by alder-wood charcoal, activated by steam, approximate to a series of intersecting straight lines. In several cases, the adsorption remains constant over a wide range of concentrations up to the saturation of the solution. Mercuric chloride, aniline, phenol, benzoic acid, fumaric acid, and, possibly, oxalic acid give adsorption curves with two marked changes of direction; the curve for thiocarbamide shows three, and those for caffeine and "saccharin" one such change. The adsorption curve of succinic acid consists of two inclined portions separated by a long interval of constant adsorption. With two exceptions, the breaks occur at points within one of the ranges 1·2 to 1·4, 2·25 to 2·6, and 4·0 to 4·6 millimols. per g. of charcoal. The areas of a postulated unimolecular layer of adsorbed substance at the same points are much less concordant. It is inferred that the adsorption depends on the number and valency of the active surface groups in the charcoal, rather than on the size of the adsorbed molecule. The adsorption curve for carbon dioxide near the temperature of condensation shows breaks at 2·6 and 5·3 millimols. per g. of charcoal. It is suggested that the activation of charcoal involves chemical changes at the surface and not a simple increase in surface area. Adsorption is regarded as a special case of molecular complex formation.

E. M. C.

Adsorption by Aluminium Hydroxide Considered as a Solid Solution Phenomenon. L. B. MILLER (*U.S. Pub. Health Repts.*, 1924, **39**, 1502—1516.—The relationship of the Freundlich adsorption isotherm to adsorption by aluminium hydroxide is discussed. Precipitation of aluminium hydroxide was carried out in the presence of varying concentrations of negative ions (sulphate and oxalate), and it was found that varying adsorption of each ion took place dependent on the concentration of each ion present, thereby influencing the character of the floc formed. The total adsorption was practically constant at the same total negative-ion concentration regardless of the relative amounts of each ion present. The p_H is an important factor. Positive-ion concentration may also influence the efficiency of water clarification by alum. Alum floc behaves as a single phase. CHEMICAL ABSTRACTS.

Adsorption from Solution from the Standpoint of Capillarity. I. W. A. PATRICK and D. C. JONES (*J. Physical Chem.*, 1925, 29, 1—10).—The adsorption of formic, acetic, benzoic, and *n*-butyric acids by silica gel containing 6·2% of moisture has been studied in various organic solvents. In general, adsorption of a solute increases as its solubility in the solvent decreases. Although nitrobenzene increases the surface tension, nevertheless it is strongly adsorbed from its solution in kerosene. The adsorption isotherm for acetic acid–carbon disulphide was investigated over the whole available range of concentration. The results are explained by assuming that the adsorbed phase wets the adsorbent and thus presents a highly concave surface to the rest of the solution from the capillaries in the gel. This concave surface decreases the solubility of the solute and hence causes a phase separation.

M. B. D.

Sorption of Toluene and Acetic Acid and their Mixtures by Carbon. A. M. BAKR and J. W. MCBAIN (*J. Amer. Chem. Soc.*, 1924, 46, 2718—2725; cf. T., 1921, 119, 454).—In the sorption of the vapours of toluene and acetic acid by sugar carbon maintained at a higher temperature than the liquid, saturation values are found which are nearly independent of the temperature of the carbon: 1 g. of toluene to 8 g. of carbon and 1 g. of acetic acid to 6 g. of carbon. With acetic acid, however, sorption rapidly diminishes above 180°. The amounts of the two vapours sorbed are in proportion to their molecular weights if the doubled molecules of the acetic acid are taken into account. When solutions of toluene and acetic acid are employed, the results agree with the conception that the two substances can replace each other in the adsorbed film. These absolute determinations of sorption agree with the ordinary relative measurements in which "positive sorption" of acetic acid is shown.

G. M. B.

"Weighting" of Silk with Stannic Chloride. F. FICHTER and F. REICHART (*Helv. Chim. Acta*, 1924, 7, 1078—1082).—Fichter and Müller (*Färber-Ztg.*, 1915, 26, 253, 274, 289) expressed the opinion that in "weighting" silk with stannic chloride the process begins with the formation of an additive compound of the silk and the stannic chloride. Elöd (*Chem.-Ztg.*, 1922, 46, 597; *Koll.-Chem. Beih.*, 1924, 19, 298) doubts this. New experimental data, however, have confirmed the previous conclusions. Silk (Japanese, Chinese, Turkish, and Italian) was treated at 100° with a solution of anhydrous stannic chloride in anhydrous toluene; the increase in weight was 2·91 to 4·81%, according to the provenance of the silk, but in each case the proportion of stannic oxide in the ash agreed fairly with that calculated on the assumption that the increase in weight was due simply to addition of stannic chloride (51·3 to 65·2% found, against 57·85% calculated).

The esters of amino-acids form additive compounds with stannic and titanic chlorides. Ethyl aminoacetate, for example, affords, when treated with stannic chloride in benzene solution, a resinous *compound*, $(C_4H_9O_2N)_2,SnCl_4$, easily decomposed by water.

Titanic and stannic chlorides combine with acetic acid to form *titanium dichloride diacetate*, $TiCl_2Ac_2$, pale yellow crystals, and *tin dichloride diacetate*, $SnCl_2Ac_2$, colourless crystals, respectively. Both compounds are immediately decomposed by water. W. A. S.

Dyeing Processes. IV. Influence of Particle Size on the Process of Dyeing. P. Ruggli and A. Fischli (*Helv. Chim. Acta*, 1924, 7, 1013—1018; cf. A., 1924, ii, 464).—The size of the particles in solutions of various dyes was measured by the rate of diffusion of the dyes into 4% gelatin jelly (cf. Traube and Shikata, A., 1923, ii, 385; Auerbach, A., 1921, ii, 680). The nine (two mono-, three di-, three tri-, and one tetra-) sulphonic acids of benzeneazo-β-naphthol used in the preceding experiments (*loc. cit.*) were compared with crystal-violet, and with six substantive dyes. The acid and basic dyes all diffused at approximately the same rate, viz., 23—31 mm. in 84 hours, but the substantive dyes diffused much more slowly and at varying rates.

Certain " union " dyes give redder shades on wool than on cotton from a neutral bath. Their solutions also become somewhat redder on heating, the original colour returning more or less rapidly on cooling. Comparative experiments made with six dyes are described which show these phenomena. The colours of the dyed cotton and wool, the original dyebath and the exhausted bath (in each case) were all compared with one another by matching the solutions etc. against mixtures of standard solutions of water-blue and naphthol-red O. In general, the exhausted bath was redder than the cotton dyed in it, but bluer than the wool. Conflicting results were obtained in other tests. The conclusion reached, however, is that the redder shades are produced by absorption of the smaller particles, and, indeed, are associated with the passage of the dyestuff into a more highly disperse form, this being also the explanation of the redder solution produced on heating (cf. Haller, *Kolloid-Z.*, 1922, 30, 249). W. A. S.

Theory of Adsorption and Allied Phenomena. J. Frenkel (*Z. Physik*, 1924, 26, 117—138).—Langmuir's qualitative treatment of adsorption (*Physical Rev.*, 1916, 8, 149) is now placed on a quantitative basis and an exponential formula is deduced for the mean time during which a gas atom remains adsorbed at a solid surface. From this, other relations are obtained for the layer density, " critical reflexion temperature," diffusion coefficient, etc. The theory is extended to the sublimation and dissociation of solid substances. S. K. T.

Surface Tension of Sodium and Potassium Amalgams at the Amalgam–Benzene Interface. S. S. Bhatnagar, M. Prasad, and D. M. Mukerji (*J. Indian Chem. Soc.*, 1924, 1, 81—89).—The interfacial tensions between benzene and sodium and potassium amalgams of various concentrations have been determined at 30° by a drop-weight method. Within the range examined the interfacial tension varies in a linear manner with the concentration of the alkali metals, except for two sharp dis-

continuities in the case of each metal (at 0·06 and 0·27% Na and 0·08 and 0·16% K) which are attributed to the formation of definite compounds. (Cf. Hine, A., 1917, ii, 287.) G. M. B.

Structure of Surface Films on Water. N. K. Adams (*J. Physical Chem.*, 1925, **29**, 87—101).—A summary is given of previous work done by the author (cf. A., 1921, ii, 488; 1922, ii, 687; 1923, ii, 539). The forces exerted by unimolecular films of substances on water indicate a strong tendency of long chain molecules to pack closely together, side by side. This lateral adhesion is overcome when a suitable temperature is reached, which is higher, the longer the chains. There is a strong attraction between such groups as OH, CO_2H, CO_2, CH_3, CN, etc., and water. M. B. D.

Molecular Orientation of the Fatty Acids. J. J. Trillat (*Compt. rend.*, 1925, **180**, 280—281; cf. preceding abstract).—Compounds such as the fatty acids orient themselves when melted on a plate of glass and assume the smectic condition in which the molecules are parallel to one another and their extremities parallel to the surface of the glass. Under these conditions excellent *X*-ray reflection can be obtained. Powdered palmitic acid gives rise to large concentric circles corresponding with a microcrystalline structure (distances 3·5—4 Å.). The smectic state gives small circles corresponding with distances of 36 Å. measured both by transmission and reflexion. The latter method also discloses diffuse effects due to larger rings (3·5—4 Å.). As the thickness is increased the influence of orientation grows less and the diffuse rays become more intense. The external layer is thus removed from the oriented part and shows the microcrystalline structure. The photographs resemble those of Friedel for oleates, which should possess not only the smectic structure but also microcrystalline structure in thicker layers. R. A. M.

Phototropism in Solution. II. Optical Activity as an Aid to the Study of Phototrophy. B. K. Singh (*J. Indian Chem. Soc.*, 1924, **1**, 45—50).—A phototropic change in solutions of α-naththylaminocamphor in chloroform (cf. A., 1921, i, 351) has been followed by polarimetric observations during the exposure of the solution to direct sunlight. A large increase of rotation was found to accompany the development of green colour. The reverse change in the dark was much slower. Orange or red light had practically no effect. The change did not occur in any solvent other than chloroform, and it was prevented in chloroform solutions by the addition of a trace of sodium ethoxide. The results are tentatively attributed to the formation of a compound of the keto and enol modifications of the "quinhydrone" type. G. M. B.

Osmotic Pressure of Electrolytes of High Molecular Weight. E. Hammarsten (*Biochem. Z.*, 1924, **151**, 177—180).—The freez-

ing-point depression shown by crystallised egg-albumin chloride prepared by dialysis (*a*) at the isoelectric point, (*b*) in the presence of hydrochloric acid followed by alkali, and (*c*) in the presence of acid at p_H 3, shows that a certain number of the chloride ions are osmotically inactive, a fact which is attributed to the large difference in the ionic volumes of the two constituents of the protein salt (cf. A., 1924, i, 1139). J. P.

Properties of Phosgene [Carbonyl Chloride] Solutions: Vapour Tension Curves of Aluminium Chloride Solution at 0° and 25°. A. F. O. GERMANN and G. H. MCINTYRE (*J. Physical Chem.*, 1925, **29**, 102—105; cf. A., 1924, ii, 674).—The vapour pressure of solutions of aluminium chloride in carbonyl chloride has been determined by a volumetric method (cf. Germann and Gagos, A., 1924, ii, 861) at 0° and 25° over a range of concentration of 0—50% aluminium chloride. M. B. D.

Uric Acid. II. Hydrotropic Action on Uric Acid. R. STERN (*Biochem. Z.*, 1924, **151**, 268—273).—Sodium salicylate and sodium 2-phenylquinoline-4-carboxylate ("Atophan") have a marked hydrotropic action on uric acid, a 0·1% solution of "Atophan" dissolving three times as much uric acid as the same volume of distilled water under parallel conditions. The hydrotropic effect is a permanent one and is not due to a change in p_H. J. P.

Recent Advances in the Field of Colloids. T. SVEDBERG (*Chem. Reviews*, 1924, **1**, 249—275).

Metachemistry and Metachemical Processes (A Nomenclature and System of Colloids). P. D. ZACHARIAS (*Kolloid-Z.*, 1925, **36**, 39—42).—It is suggested that terms such as colloid or dispersoid chemistry should be replaced by "metachemistry," in order to avoid initial assumptions as to the nature of the materials studied. The term "tile" is suggested for all particles between 0·1μ and 1$\mu\mu$. E. M. C.

Dispersoid Synthesis of Gold. II. (Preliminary Communication.) P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 1—12; cf. A., 1923, ii, 645, 869).—Gold sols prepared by the author's modification of the "formol" method with ordinary distilled water have remained stable for many months. Many failures in the formaldehyde method have been due not to the quality of the water, but to impurities in the formaldehyde solutions. The phosphorus, glycerol, tartrate, or citrate methods give stable sols, although moulds may remove the gold. Temperature control and the use of freshly-prepared solutions are necessary to secure reproducible dispersoid synthesis. The factors influencing the size of the colloidal particles are discussed. Increased concentration of the reacting solutions leads to an increase in the mean size of the crystalline aggregates, accompanied by a decrease in the size of the individual crystals. E. M. C.

Influence of Excess of Reagents on the Formation of Dispersoid Solutions of Mercuric Sulphide. N. I. Morosov (*Kolloid-Z.*, 1925, **36**, 21—23).—The addition of sodium sulphide solution to an excess of mercuric chloride gives a white precipitate. With an excess of sodium sulphide, brown stable dispersoid solutions are formed. E. M. C.

Preparation of Colloidal Elements by Photochemical Decomposition of their Gaseous Hydrides. I. Preparation of Colloidal Arsenic. L. Dede and T. Walther (*Ber.*, 1925, **58**, [*B*], 99—102).—Colloidal solutions of arsenic are readily prepared by bubbling purified arsine through water which is exposed to light of short wave-lengths. According to the dilution, these solutions are yellow to bluish-violet in colour. Only the most concentrated solutions show any tendency towards coagulation; more dilute solutions slowly become colourless owing to the gradual oxidation of arsenic to arsenious oxide. They are very insensitive towards electrolytes. The particles are negatively charged. The behaviour of the solutions towards ammoniacal silver solution, mercuric chloride, and alkaline copper solution proves the particles to be arsenic and not solid arsenic hydride. It has been observed incidentally that arsine reacts with antimony sulphide (*e.g.*, of red rubber tube) to yield arsenic sulphide and stibine which decomposes into antimony and hydrogen; the latter unites with the sulphur in the rubber to give hydrogen sulphide. H. W.

Electric Synthesis of Colloids. G. Börjeson (*Diss., Upsala*, 1921).—Although metallic sols produced by electrical spattering consist usually of (*a*) metallic globules of microscopic or sub-microscopic size, and (*b*) a truly colloidal portion, produced by condensation of gaseous metal, it is possible to eliminate the former. Gold alcosols may remain uncoagulated for a year. Most individual particles are secondary particles, *i. e.*, they possess a structure. Increased viscosity of the medium causes the formation of larger particles. Chemical Abstracts.

Metal Sols in Non-dissociating Liquids. II. Composition of the Disperse Phase of Nickel Sols in Benzene and Toluene. E. Hatschek and P. C. L. Thorne (*Kolloid-Z.*, 1925, **36**, 12—16; cf. A., 1923, ii, 390).—The nickel sols in benzene and toluene, previously described, contained both positively and negatively charged particles. The decomposition of nickel carbonyl in boiling toluene in an atmosphere of hydrogen gives sols containing particles with negative charges and a high metallic nickel content. Solutions of nickel carbonyl in benzene or toluene often give a pale green precipitate of a hydrated basic nickel carbonate which is dispersed in the presence of $\frac{1}{6}$% caoutchouc to give a positively charged colloid. It is believed that the nickel sols described previously consist of the oxidation products of nickel carbonyl, held on caoutchouc particles and carrying charges only in the outermost layers, with a corresponding difference of composition which is too small to be detected by analysis. The behaviour of organosols is not neces-

sarily simpler than that of hydrosols. An apparatus is described by means of which it is possible to maintain a steady stream of nickel carbonyl for several hours without attention. E. M. C.

Electrolyte-free, Water-soluble Proteins. III. Salt-Protein Compounds ($ZnCl_2$). I. W. PAULI and M. SCHÖN (*Biochem. Z.*, 1924, **153**, 253—284).—The authors have examined the compounds which are formed when a solution of pure zinc chloride is added to solutions of serum-albumin, gelatin, and ovalbumin freed from alkali- and acid-protein compounds by prolonged electrodialysis. All three proteins form reversible compounds with zinc chloride. In the case of serum-albumin, electrometric determinations of free chloride ions show that about twice as much chlorine is bound to the protein as would be inferred from the conductivity measurements, indicating that complex ions containing bound chlorine assist in carrying the current. Serum-albumin and gelatin behave, on the whole, similarly towards zinc chloride, both in the conductivity changes following the addition of varying quantities of this salt and in the mobility of the ions in the mixed solutions. In such solutions serum-albumin and gelatin migrate chiefly toward the cathode. Over a certain range of zinc chloride concentration, which range increases with the dilution of the serum-albumin, heat coagulation of this protein is prevented. Ovalbumin, in presence of this salt, differs from the other two proteins examined, both in its conductivity relations and in the changes found in the ionic mobility. In an electric field it moves in the opposite direction to serum-albumin, and shows no zone of insusceptibility to heat coagulation. H. D. K.

Quantitative Filtration as a Method for the Analysis of Dispersoids. WO. OSTWALD (*Kolloid-Z.*, 1925, **36**, 46—55).—Curves which show the connexion between the volume of filtrate and the time of filtration under constant pressure, serve to characterise suspensions of clays, soils, precipitates, etc., and to illustrate the changes in the structure of precipitates produced by different methods of preparation, by flocculation and ageing.

E. M. C.

Action of Silver Sol on Arsenious Sulphide Sol. H. FREUNDLICH and F. MOOR (*Kolloid-Z.*, 1925, **36**, 17—21; cf. A., 1921, ii, 494).—A mixture of silver and arsenious sulphide sols undergoes in the dark a change of colour from golden-brown through greenish-brown to lilac, and, with exposure to light, through green to a golden-yellow. Both changes are prevented in the presence of a gelatin gel. The reaction in the dark is regarded as a direct interaction between the particles of the two sols. The secondary change under the action of light is purely chemical and involves oxygen, with the probable formation of a silver thioarsenite.

E. M. C.

Stability of Dispersoid Silver Solutions. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 55; cf. A., 1923, ii, 645; this vol., ii, 196).—Dispersoid silver solutions prepared by the author's modific-

ation of the formaldehyde method have remained stable for a year. E. M. C.

Physical Chemistry of the Globulins. VI. Alteration of Globulin by Heat. M. ADOLF (*Koll.-Chem. Beihefte*, 1925, **20**, 288—318; cf. A., 1923, i, 396; 1924, i, 101; ii, 728, 831).—By heating globulin suspensions in water at 100°, the solubility in alkali was reduced to $\frac{1}{5}$, in hydrochloric acid to $\frac{1}{40}$, and in neutral salt solutions to $\frac{1}{100}$ of that of the unheated globulin. The combination of heated globulin with base increased with the concentration of the latter. The heated globulin combined with 27 times as much acid as the unheated, and observations on cataphoresis showed that the acid was really in molecular combination. The solubility in salt solutions was greatest for salts with tervalent ions. Solutions containing an excess of globulin in acid or alkali showed, after heating, no change in combining power or in solubility. Globulin in neutral salt solutions coagulated on heating, with no essential change in conductivity or hydrogen-ion concentration. Solutions in salts of tervalent ions underwent no change on heating. E. M. C.

Vanadium Pentoxide Sol. I. Streaming Anisotropy. H. FREUNDLICH, F. STAPELFELDT, and H. ZOCHER (*Z. physikal. Chem.*, 1924, **114**, 161—189; cf. A., 1922, ii, 102; 1923, ii, 514).—The double refraction and dichroism (together called streaming anisotropy), which occur on the streaming of vanadium pentoxide sol, have been quantitatively studied, and the influence of age and concentration of sol, of the velocity of flow, and the temperature has been determined. The sol flowed through a tube with rectangular cross-section, and a polarisation spectrometer with a half-shadow apparatus was employed for the measurements. The source of illumination was the green light of the mercury lamp. It was found that the anisotropy is strongly influenced by the age of the sol. In a freshly-prepared sol it is zero; it increases continuously with time, and finally reaches a maximum. The velocity of ageing, at constant streaming velocity and temperature, is given by the equations $d\Delta/dt=k_\Delta(\Delta_\infty-\Delta)^2$ and $d\Gamma/dt=k_\Gamma(\Gamma_\infty-\Gamma)^2$, where Δ is double refraction and Γ dichroism. The magnitude of the velocity of ageing is very sensitive to the presence of impurities, arising from the ammonium vanadate used for the preparation of the sol. The influence of arsenic acid is specially marked. The relation between the velocity coefficients and the temperature is given by the Arrhenius equation $\log_e k=-A/T+B$ in which the constants A have values of over 10,000, and the temperature coefficient for 10° is about 4. If a sol which has reached the limiting value is diluted, the anisotropy at first decreases in proportion to the dilution. The rate of decrease then slowly diminishes, and finally a new limiting value is reached. This behaviour probably depends on the fact that some of the colloid particles, which cause the double refraction, are in a state of true solution. The anisotropy increases with the velocity of flow. With fresh sols, the increase is regular, but with old sols, a limiting value is reached. For the same sol

at different ages, a series of curves is obtained. A similar series is obtained if the ageing is followed at a different temperature and concentration, or with another sample of the starting material (ammonium vanadate), or even with a different method of preparation of the sol. With rising temperature, the anisotropy diminishes, the influence of temperature being practically linear, and greater for fresh sols than for old. It is found that the double refraction of the sol corresponds, within the limits of error, to that of the vanadium pentoxide contained in it. The absolute value of the double refraction is 1·7. L. L. B.

Vanadium Pentoxide Sol. II. The Vortex Cross. H. FREUNDLICH, F. STAPELFELDT, and H. ZOCHER (*Z. physikal. Chem.*, 1924, **114**, 190—207; cf. preceding abstract).—An investigation of the so-called vortex cross of vanadium pentoxide sol, which is formed when the sol is rotated between two cylindrical walls and observed between crossed Nicols. Four minima of brightness are to be seen, giving the appearance of a dark cross, of which the arms form with the direction of polarisation an angle depending on the experimental conditions. The angle has been measured, and found to be independent of the thickness of the liquid layer and the concentration of the sol. It increases rapidly with increasing velocity gradient and increasing age of the sol, and decreases with rise of temperature. The increase of the vortex angle ψ with age has been followed, and it is found that the velocity of ageing is given by the equation $d\psi/dt=k_\psi(\psi_\infty-\psi)^2$. The angle measured in the slowly changing fresh sol has the value 45°, whilst ψ_∞ approximates to 90°. If the increase of ψ_0 with temperature is considered, the influence of temperature on the growth of the angle with age is given by the Arrhenius equation. The temperature coefficient for 10° is about 2·3. The behaviour of the vortex cross is best explained in terms of the elasticity of the sol. The elastic deformation of the sol elements is small in fresh solutions and with small velocity gradient (cf. Schwedoff, *J. Physique*, 1892, [3], **1**, 49). It behaves like that of a rigid body, and the cross angle is 45°. When the velocity gradient is great, and as the sol ages, it approaches 90°. According to this, the cross angle is identical with the angle of maximum deformation; and the direction of maximum deformation corresponds with the direction of the velocity gradient. The colloid particles do not, therefore, arrange themselves along the stream lines, owing to the friction between adjacent liquid layers of different velocities, but place themselves in the direction of maximum deformation. Only in old sols and with high velocity gradients does this direction practically coincide with the direction of flow. L. L. B.

Birefringency in Colloids. A. FREY (*Koll.-Chem. Beih.*, 1925, **20**, 209—243; cf. Wiener, A., 1911, ii, 557).—Lyophilic colloids in which the particles, themselves isotropic, are of elongated shape show positive birefringency, whilst with tabular particles the birefringency is negative, in accordance with Wiener's theory. The same principle applies when elongation or flattening is mechanic-

ally imparted to spherical particles such as those of gelatin. With lyophobic colloids, on the other hand, birefringency is due to orientation of the anisotropic (crystalline) particles, as in vanadium pentoxide sols; here Nägeli's theory satisfactorily accounts for the phenomena. Colloids which form gels but not sols, *e.g.*, animal tissues, starch, and cellulose, stand in an intermediate position: their particles are anisotropic, so that small deformations have little effect on the birefringency. W. A. C.

Birefringency and Dichroism in Dyed Gels. H. NEUBERT (*Koll.-Chem. Beih.*, 1925, **20**, 244—272).—Thin strips of collodion and denitrated collodion and threads of cellulose acetate were dyed, and thereby made dichroic, with (*a*) Congo-red, which increases the birefringency of the colloid, and (*b*) methylene-blue, which decreases it. For a given wave-length the same change in birefringency is brought about by equal amounts of dye, independent of the intrinsic birefringency of the colloid. Exactly the same change is brought about when an equal thickness of the dye itself, *e.g.*, on a glass plate, is rendered dichroic by mechanical stress. Colloids dyed with Prussian-blue show no dichroism and no change in birefringency. W. A. C.

Permeability of the Copper Ferrocyanide Membrane to Acids, and the Action of Protoplasm as an Ultrafilter. R. COLLANDER (*Koll.-Chem. Beih.*, 1925, **20**, 273—287; cf. A., 1924, ii, 154).—The rapidity of diffusion of organic acids through a copper ferrocyanide membrane is approximately inversely proportional to the molecular volume of the acid. The diffusion of strong mineral acids is largely determined by the volume of the anion. Earlier workers (*e.g.*, Walden, A., 1892, ii, 203) confused an exchange of hydrogen ions with rapidly diffusing cations for a true diffusion of acid. Thus a potassium ferrocyanide solution becomes strongly acid when in contact with a copper sulphate solution containing citric acid, but a copper sulphate solution becomes only slightly acid when the citric acid is added to the potassium ferrocyanide. Only traces of citric acid diffuse in both cases, but the potassium ion diffuses through the membrane more rapidly than the copper ion. The high permeability of protoplasm for water and oxygen, the more rapid diffusion of formamide compared with acetamide, and the relative permeability for ions suggest that the permeability of protoplasm for lipoid-insoluble substances is determined by an ultra-filtration process. E. M. C.

Absorbent Power of Agar-Agar. J. EFFRONT (*Compt. rend.*, 1925, **180**, 29—33).—The absorptive power of agar-agar in contact with 0·1*N*-hydrochloric acid depends on the mineral content, and when all mineral matter is removed no absorption of acid takes place. The absorption of alkali is not so greatly affected by the presence of mineral matter; the absorption is due to the formation of a neutral salt which is stable only in the presence of excess of alkali. In the absorption of acid only the hydrogen ion enters the agar pulp. Agar-agar containing mineral matter will absorb copper

sulphate from solution owing to double decomposition between the latter and the alkali metal of the organic acid. Similar absorptive properties are shown by pulps of beetroots, turnips, and apples.
W. H.-R.

Adsorption and Osmotic Phenomena in Gels. T. TOMITA (*Biochem. Z.*, 1924, **153**, 335—357).—The adsorption of various fatty acids and alcohols, of urethane and of diethylamine from their aqueous solutions by certain gels, and the swelling produced by the action of these solutions on such gels were studied. Gelatin, egg-albumin, agar, sodium cholate and silicic acid gels, and mixed gels containing gelatin and lecithin, egg-albumin and egg-yolk, were used. Comparative experiments on these gels, with and without the addition of lecithin, point to the conclusion that substances with a relatively small effect on the surface tension (acetic acid, urethane, or even butyric acid) enter the gels almost entirely through the aqueous phase, whilst substances with greater effect on surface tension (octyl alcohol, *n*-octoic acid) enter mixed gels both by the aqueous and the lipoid phase. If certain colloids, such as peptone, albumin, and acid dyes, are added to the solutions of fatty acids, and the mixed solutions brought into contact with gels, a surface membrane is produced which does not prevent the entry of fatty acids but which interferes markedly with the swelling of the gel. H. D. K.

Density and Hydration in Gelatin Sols and Gels. T. SVEDBERG (*J. Amer. Chem. Soc.*, 1924, **46**, 2673—2676).—The contraction which always accompanies the hydration of gelatin, as measured in a dilatometer, amounts to 54 cub. mm. per gram of dry gelatin in water at 35°. The contraction is diminished considerably in presence of strong acids and alkalis, the first traces of these having relatively the most marked effect. Weak acids and alkalis, and salts or non-electrolytes have no effect. The contraction increases with falling temperature, no discontinuity occurring when the temperature passes into the region of gel formation. G. M. B.

Determination of Distribution of Size of Particles in Emulsions. E. O. KRAEMER and A. J. STAMM (*J. Amer. Chem. Soc.*, 1924, **46**, 2709—2718).—The rate of accumulation of a rising disperse phase in the upper layer of an emulsion is determined by observing the movement of the level of liquid in a slanting capillary side-tube due to the fall of density in the upper layer by which it is balanced (cf. Ostwald and Hahn, A., 1922, ii, 205). Distribution curves are derived from the accumulation curves, and the results with two emulsions prepared under the same conditions are shown to be similar. The positions of the maxima in the distribution curves are little affected by changes in the concentration of the emulsions. Potassium oleate tends to give larger drops in a benzene–water emulsion than does potassium palmitate, in accordance with the wedge theory of emulsification. The effect of a "homogeniser" on the degree of dispersion of benzene-in-water emulsions is described. G. M. B.

Slow Coagulation of Colloids of the First Order. K. JABLCZYŃSKI (*Roczniki Chemji*, 1924, 4, 251—264).—Spectrophotometric investigation of the kinetics of the slow coagulation of colloidal solutions of ferric hydroxide and arsenious sulphide by means of potassium chloride gives results which confirm the accuracy of Smoluchowski's equation, $n=n_0/(1+\epsilon a n_0 t)$ (A., 1917, ii, 297) and of the author's equation, log tan α—log tan $\alpha_0=K$ (this vol., ii, 35). For ferric hydroxide the relation between K and the concentration, c, of the potassium chloride is expressed approximately by the empirical equation, $K=k_1c^{7\cdot5}$; the speed of the coagulation is not influenced by agitation of the liquid. The coefficient of coagulation of arsenious sulphide depends largely on the amount of hydrogen sulphide present in excess; this coagulation may be completely prevented by addition of a stabilising colloid, such as gum arabic.

The author considers that the coagulation of colloids, whether rapid or slow, and whether of the first or of the second order, proceeds according to the two equations mentioned. T. H. P.

Rate of Crystallisation of Undercooled Aqueous Sols. H. FREUNDLICH and F. OPPENHEIMER (*Ber.*, 1925, 58, [*B*], 143—148; cf. Brann, A., 1918, ii, 393).—The rates of crystallisation of water and twenty-two aqueous sols, emulsions, or suspensions have been measured between −3° and −7°. They may be arranged in two groups, in the first of which the particles diminish the rate of crystallisation as dissolved substances invariably do (sols of gold, platinum, arsenic trisulphide, mastic, sulphur, and silicic acid, oil and rubber emulsions, starch and gelatin solutions). In the second group the particles increase the rate of crystallisation (sols of iron oxide, vanadium pentoxide, copper oxide, osmium dioxide, Prussian-blue, benzopurpurin, cotton-yellow, setocyanine, chrysophenin, aniline-blue, soap solution, kaolin suspension). The particles of the substances of the second group are non-spherical (either rodlets or leaflets), whereas those of the first group do not differ greatly from the spherical form. H. W.

Oxydase-like Actions of Colloidal Silicates. H. OTA and M. NODA (*J. Sci. Agr. Soc. Japan*, 1924, No. 258, 287—290).—The activity of the colloidal silicates of silver, copper, cobalt, titanium, aluminium, manganese, zinc, magnesium, and ferrous iron, prepared by adding dilute sodium silicate solution to dilute solutions of the respective salts and examined by the indophenol reaction, decreases in the order given by the above series. Powdered kaolin, talc, and serpentine are inactive. Natural earths obtained from seven different areas in Japan exhibit activity, but the action is very weak compared with that of the above artificial colloidal silicates. K. K.

Ionisation of Proteins. K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 1—29).—It is shown that the theory of Debye and Hückel (A., 1923, ii, 459) leads to similar expressions for the adsorption of hydrogen ions by protein as are obtained from mass law considerations. The equations are applied to

Sørensen's data for the acid-binding power of egg-albumin and lead to the conclusion that the diameter of the protein molecule is $3{\cdot}8\times10^{-7}$ cm., as compared with $2{\cdot}21\times10^{-7}$ cm. from osmotic measurements. The results suggest that the valency varies from 0 to 9 over the range of hydrogen-ion concentration considered. The original paper should be consulted for details. E. M. C.

Measurements of the Mobility of Egg-albumin at Different Acidities. N. D. Scott and T. Svedberg (*J. Amer. Chem. Soc.*, 1924, 46, 2700—2707).—The method previously described (A., 1923, i, 614) has been applied to the study of cataphoresis in sols of egg-albumin. The acidities were varied from p_H 7 down to 2·5 by means of buffer mixtures of sodium acetate with acetic acid and disodium hydrogen phosphate with citric acid. The results with the two buffer mixtures are generally similar, but the acetate–acetic acid mixture gives a broader region of minimum mobility, in which definite indication was obtained of simultaneous movement towards both electrodes. The maximum mobility observed was at p_H 2·93 of $21{\cdot}79\times10^{-5}$ cm./sec. towards the cathode. G. M. B.

Determination of the Mobility of Colloid Particles by the Method of Cataphoresis. A. F. Gerasimov (*J. Russ. Phys. Chem. Soc.*, 1924, 54, 818—828).—The experiments were conducted in a specially designed apparatus, consisting of a U-tube with limbs of unequal diameter to overcome the disturbing effects of the products of electrolysis; the electrode of opposite sign to that of the colloid was placed in the wider limb. "Collargol" was the colloid used, solutions of electrolytes of conductivity equal to that of the colloid being placed above the colloid in each limb. From measurements at small velocities (1 cm. per hour) it is possible to calculate the velocity corresponding with the initial potential gradient in the system and from this the mobility of the particles. It was found that the mobility of the particles in the limb containing the cathode is only affected by cations and in that containing the anode by anions; the mobility appears to increase with concentration. G. A. R. K.

Dissociation Constants of Dibasic Carboxylic Acids and the Normal Potential of the Quinhydrone Electrode in Absolute Methyl Alcohol. L. Ebert.—(See i, 230.)

Relation between the Equilibrium Constants in the Gaseous and Liquid Phases. W. Świętoslawski (*Roczniki Chemji*, 1924, 4, 240—250).—Theoretical. T. H. P.

Studies in the Aluminium-Zinc System. T. Tanabe (*J. Inst. Metals*, 1924, 32, 415—452).—The equilibrium diagram based on measurements of conductivity and thermal expansion agrees with Hanson and Gayler's results, except in the γ-area (cf. *ibid.*, 1922, 27, 267). The eutectoid change, which occurs with all alloys containing 0·5—75% of aluminium, takes place at 270°. A study of the age-hardening of the alloys confirms Hanson and Gayler's

results in the main; the maximum hardness is explained on a colloidal basis. An abnormal change of hardness takes place at 270° with all alloys containing eutectoid; no evidence was found for the existence of Al_2Zn_3. S. K. T.

Equilibrium in the System Gold–Zinc. P. SALDAU (*Z. anorg. Chem.*, 1925, **141**, 325—362).—The system gold–zinc has been investigated by thermal and microscopic analysis, and by measurements of electrical conductivity, the theory of the last-named being developed. Solid phases of variable composition are divided into three classes: (1) those in which the conductivity isotherms show no maximum; these are simple solid solutions; (2) those in which the conductivity isotherms show a maximum which remains well-defined and unchanged in position as the temperature rises; such phases contain a definite compound which is stable at the temperatures concerned; (3) those in which the conductivity isotherms show a maximum which, with rising temperature, becomes flatter and slightly displaced; such phases contain a definite compound which gradually decomposes on heating. In the gold–zinc system, alloys containing less than 30 at.-% of zinc deposit on cooling a solid solution (α) which, if the alloy contains more than 13 at.-% of zinc, undergoes a transformation at about 400°, with the formation of a phase of variable composition (α_1) containing the stable compound Au_3Zn. At about 250°, the α_1 phase is transformed into a second form (α_2), which also contains the compound Au_3Zn, but in this modification the compound is slightly decomposed on heating. Alloys containing more zinc deposit on cooling a solid solution (β), containing the stable compound AuZn, which forms a maximum on the freezing-point curve at 725°, the limits of the β solid solution being between 38 and 58 at.-% of zinc. Alloys containing still more zinc deposit on cooling a γ series of solid solutions, which, on cooling, undergo transformations like those of the α solid solutions; γ_1 and γ_2 phases are formed which contain the compound $AuZn_3$. At the zinc end of the series, a δ phase of very slightly variable composition is formed, the composition corresponding closely with the formula $AuZn_8$, but the existence of a definite compound is not confirmed by the conductivity measurements. Finally, ϵ and ϵ_1 series of zinc-rich solid solutions are formed at the extreme zinc end of the series. It is not possible to detect the changes $\alpha_1 \rightarrow \alpha_2$ or $\gamma_1 \rightarrow \gamma_2$ by thermal means. W. H.-R.

Solidification of Ternary Alloys of Aluminium, Magnesium, and Cadmium. J. VALENTIN and G. CHAUDRON (*Compt. rend.*, 1925, **180**, 61—63).—The ternary system aluminium–magnesium–cadmium has been examined. The triangular equilibrium diagram is characterised by six freezing-point surfaces, three lines corresponding with binary eutectics, and a ternary eutectic at 395°. Aluminium and cadmium are almost completely immiscible in the liquid state, and this region of immiscibility extends for a considerable distance into the ternary alloys. The remaining five surfaces correspond with the primary deposition (on cooling) of

(1) the pure compound MgCd, (2) a solid solution in which the compound Al_2Mg_3 is the chief constituent, and (3) solid solutions rich in aluminium, cadmium, and magnesium, respectively. W. H.-R.

Application of the Ideal Solubility Curve to the Interpretation of Equilibrium Diagrams in Metal Systems. D. H. ANDREWS and J. JOHNSTON (*J. Inst. Metals*, 1924, **32**, 385—404).—The graph of log c against $1000/T$ for metal solutions, where c is the molar concentration of the solution in equilibrium with solid at temperature T, is linear for ideal solutions, the slope being determined by the latent heat of fusion of the solid. Regular divergence from this curve indicates compound formation in the fused mass. The use of the curve in investigating systems not far from ideal is described; in these cases it can be used for interpolation purposes, since it can be plotted for a pure solid phase from a knowledge of the m. p. and the latent heat of fusion. Systems showing limited solid solution give a curve which is linear over a certain range of concentration; outside this range deviation from linearity is found. S. K. T.

Stepwise Dissociation of Magnesium Carbonate. M. CENTNERSZWER and B. BRUŽS (*Z. physikal. Chem.*, 1924, **114**, 237—250).—The method described by Centnerszwer and Andrusow (A., 1924, ii, 655) has been used for the investigation of the dissociation of magnesium carbonate.

For pure, anhydrous magnesium carbonate, the following dissociation steps have been established: (*a*) $2MgCO_3 \rightleftharpoons MgO,MgCO_3+CO_2$; (*b*) $2[MgO,MgCO_3] \rightleftharpoons 3MgO,MgCO_3+CO_2$; (*c*) $3MgO,MgCO_3 \rightleftharpoons 4MgO+CO_2$; control experiments have been performed with natural rhombic magnesite, which is found to decompose by the following stages: (*a*) $4MgCO_3 \rightleftharpoons MgO,3MgCO_3+CO_2$; (*b*) $MgO,3MgCO_3 \rightleftharpoons 2[MgO,MgCO_3]+CO_2$, or $2MgCO_3 \rightleftharpoons MgO,MgCO_3+CO_2$; (*c*) $MgO,MgCO_3 \rightleftharpoons 2MgO+CO_2$. The first of the dissociation products of magnesite, the monoxytricarbonate, is metastable, and passes into the monoxymonocarbonate. L. L. B.

Action of Sulphuric Acid on Calcium Oxalate. E. CARRIÈRE and E. VILON (*Compt. rend.*, 1924, **179**, 1402—1404).—A definite equilibrium is established in the reaction $CaC_2O_4+H_2SO_4 \rightleftharpoons CaSO_4+H_2C_2O_4$. Increase of the concentration of the reagents results in a displacement of the equilibrium to the left. Excess of sulphuric acid leads to an almost proportional increase in the oxalic acid formed. With rise in temperature the yield of oxalic acid at first increases, is maximal at 30° and minimal at 35°, and afterwards increases. This minimum is connected with the maximum solubility of calcium sulphate at this temperature. H. T.

Double Decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftharpoons Na_2B_4O_7+(NH_4)_2SO_4$, in Aqueous Solution. V. U. SBORGI and E. BOVALINI (*Gazzetta*, 1924, **54**, 919—933; cf. A., 1924, ii, 477, 478).—Solubility data are recorded for temperatures between the

eutectic point and the temperature at which double salt is formed. T. H. P.

Double Decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftarrows Na_2B_4O_7+(NH_4)_2SO_4$, in Aqueous Solution. VI. U. Sborgi, E. Bovalini, and M. Medici (*Gazzetta*, 1924, **54**, 934—945).—Solubility data are recorded for temperatures between −11·02° and 38·7°; over this range double salt formation occurs. T. H. P.

Double Decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftarrows Na_2B_4O_7+(NH_4)_2SO_4$, in Aqueous Solution. VII. U. Sborgi and E. Burichetti. **VIII.** U. Sborgi (*Gazzetta*, 1924, **54**, 946—964).—Solubility data are recorded for the region 38·7—55·7° in which the salts Na_2SO_4 and $(NH_4)_2B_4O_7$ are stable; at higher temperatures, loss of ammonia creates complications.

These and previous results are shown in diagrams which serve to indicate a method for the preparation of borax from ammonium borate and sodium sulphate, which exhibits certain advantages over the method using sodium chloride (cf. A., 1921, ii, 580).

The diagram given by Meyerhoffer and Saunders (A., 1899, ii, 410; 1900, ii, 198) is confirmed and extended, but it remains undecided whether, in a double decomposition complicated by the formation of a double sat, such a diagram is the only one possible. T. H. P.

Influence of Salts on Solubility. H. von Euler and K. Rudberg (*Z. physiol. Chem.*, 1924, **140**, 113—127).—According to Bjerrum (A., 1923, i, 445), the solubility of amino-acids should be greater in salt solutions than in water. This is shown not to be invariably the case. The decreases which occur may be due to a salting-out action on the undissociated molecule, the solubility of which possibly determines the total solubility of the amino-acid. In comparing the solubilities of ampholytes in different salt solutions the p_H of the solution should be defined. The solubilities of amino-acids are usually greater in mixtures than when alone; the reverse is found with mixtures of leucine and tyrosine. E. S.

Heats of Fusion of Trinitrotoluene, "Tetryl," and Picric Acid. W. H. Rinkenbach and R. E. Hall (*J. Amer. Chem. Soc.*, 1924, **46**, 2637—2639).—From data obtained in the study of the binary systems trinitrotoluene–"tetryl," trinitrotoluene–picric acid, and "tetryl"–picric acid (*e.g.*, A., 1923, i, 909, 1193) the following mean values of the heats of fusion are calculated: trinitrotoluene 20·2, picric acid 20·4, "tetryl" 22·2 g.-cal./g. G. M. B.

Heats of Dissociation of the Oxygen and Nitrogen Molecules. A. Eucken (*Annalen*, 1924, **440**, 111—121).—The heats of dissociation of oxygen and nitrogen are shown to be much larger than the values usually accepted, viz. 150 Cal. (cf. A., 1920, ii, 210; *Z. Physik*, 1921, **5**, 440). A simple thermochemical calculation, which assumes Kohn's value for the heat of vaporisation of carbon (cf. this vol., ii, 100), gives 352 Cal. as the lower limit in

the case of oxygen; calculation of the work of separation of the atoms in the molecule gives an upper limit of 440 Cal. for nitrogen and 425 Cal. for oxygen. The value of this quantity for other di- and tri-atomic gases is also calculated; it is approximately proportional to the number of pairs of electrons concerned in the union of the atoms, each pair corresponding with a work of separation of approximately 80 Cal. The results agree fairly well with those calculated from thermochemical data. S. K. T.

Re-determination of the Heats of Oxidation of Certain Metals. J. E. Moose and S. W. Parr (*J. Amer. Chem. Soc.*, 1924, **46**, 2656—2661).—The heats of oxidation of a number of pure metals have been determined by direct measurement in a bomb calorimeter, the completeness of oxidation being 99% in all cases except that of beryllium. The mean values obtained are as follows: aluminium 6970, beryllium 14,879, cadmium 580, cerium 1661, lanthanum 1641, magnesium 5996, molybdenum 1829, tantalum 1373, tin 1164, tungsten 1059, and zinc 1298 cals./g. G. M. B.

Thermochemical Studies on the Oximes. III. Stereoisomeric Dioximes. A. Dorabialska (*Roczniki Chemji*, 1924, **4**, 265—286).—The heats of formation of the sodium salts of glyoxime and methylglyoxime suggest the possibility of stereoisomerisation, three stereoisomeric forms being distinguished for glyoxime and four for methylglyoxime. In aqueous solution each of these two oximes forms a mixture of stereoisomerides. Electronic formulæ are suggested for the stereoisomeric oximes. T. H. P.

Conductivity of Salt Vapours in the Chlorhydrogen Flame. S. Kalandyk (*J. Phys. Radium*, 1924, [vi], **5**, 345—352).—Alkali halides diluted with sand to varying concentrations are introduced in finely powdered condition into the oxy- and chlorhydrogen flames, and the electrical conductivity measured, using a hot cathode and a hot anode alternately. In general, the conductivity increases with concentration to a maximum, which is very pronounced with a hot cathode in the oxyhydrogen flame. With the chlorhydrogen flame, the conductivity is greater with a hot anode than with a hot cathode for the same concentration of salt. This may be due to greater mobility of the positive ions, but may result from the thermionic emission of positive ions from the anode, and experimental evidence is adduced in favour of the latter view. C. H. D. C.

Electrical Conductivity Measurements in Dilute Methyl- and Ethyl-alcoholic Solution at 0°, 25°, and 56°. P. Walden, H. Ulich, and F. Laun (*Z. physikal. Chem.*, 1924, **114**, 275—296; cf. A., 1923, ii, 723).—The conductivities of tetraethylammonium picrate, tetramethylammonium chloride, diethylamine hydrochloride, *iso*butylamine hydrochloride, and the tetraethylammonium salt of trinitroresorcinol have been measured at 0°, 25°, and 56° in methyl- and ethyl-alcoholic solutions, down to

very great dilutions—in one case, to 60,000 litres per mol. The authors describe a new form of conductivity cell, and methods for the purification of the alcohols, for which the values of κ_{25} were found to be 0·15 and 0·22 . 10^{-6} respectively. Tables are given of the conductivities at round dilutions, the values of Λ_∞ being obtained graphically by the square-root law. L. L. B.

Conductivity Determinations in Non-aqueous Salt Solutions. P. WALDEN and H. ULICH (*Z. physikal. Chem.*, 1924, **114**, 297—319; cf. preceding abstract).—Conductivity data for solutions of neutral uni-univalent salts in methyl and ethyl alcohol, aqueous ammonia, nitromethane, and acetophenone, are considered with reference to (1) the relation between conductivity and concentration, (2) the change of limiting conductivity with temperature, and (3) the mobilities of the ions (in the case of methyl- and ethyl-alcoholic solutions). The conclusion is reached that in non-aqueous salt solutions, as in aqueous, the region of dilute solutions is characterised by the validity of the cube-root formula at medium dilutions, and of the square-root formula at high dilutions, but that, as with aqueous solutions, the law of mass action is not applicable. The region of dilute solutions in the solvents here considered begins at some hundred litres per mol., whereas with water it begins at from 20 to 50 litres per mol.

It is shown that the numerous earlier measurements giving evidence for the validity of Ostwald's dilution law in non-aqueous solutions cannot be regarded as trustworthy. It is pointed out that the Hertz theory of ionic mobility, although it does not appear to agree with that developed by Debye and Hückel (cf. A., 1923, ii, 724), nevertheless gives almost identical values of Λ_∞. It does not appear possible to decide experimentally between these two theories at the present time, and further theoretical investigation is necessary. New experimental data are advanced in support of the law $\Lambda_\infty . \eta =$ constant.

Ionic mobilities in methyl and ethyl alcohol are calculated for temperatures between 0° and 56°. It is found that although the simple ions, *e.g.*, Cl^- and Na^+, have a much higher speed in water than the polyatomic picric acid and tetraethylammonium ions, in organic media the mobility of these simple ions rapidly falls off, ultimately becoming smaller than that of the complex ions. This effect can probably be explained by increasing solvation with decreasing dissociation constant of the medium. It is also shown that isomeric organic cations do not move with equal speeds, and that the number, nature, and symmetry of the substituents in the ammonium radical exercise a marked influence. L. L. B.

Cobalt Chloride Solutions. I. C. MAZZETTI (*Gazzetta*, 1924, **54**, 891—907).—The mobility of the cobalt ion at various temperatures shows that the ratio of the mobility to the fluidity of water at the same temperature increases with the temperature from 10° to about 30° and then diminishes regularly with further rise of temperature. This divergence from the behaviour observed by Johnston (A., 1909, ii, 854) with all ions except calcium and

lanthanum probably depends on an independent increase in the value of Λ owing to dehydration of the cobalt ion.

The curves which show the relation between the equivalent conductivity (corrected for viscosity) and the concentration of cobalt chloride solutions exhibit, at all temperatures, a point of inflexion, suggesting that two distinct curves are involved. This behaviour is also explainable in terms of a change in the degree of hydration.

The values of $C^{-1/3}$. log $1/\alpha$ (cf. Ghosh, T., 1918, **113**, 449, 627, 707, 790) differ but little from the theoretical values at high, but considerably at low, concentrations; as the temperature is raised, the agreement becomes perfect at the higher concentrations. The deviations are attributed to diminution of the hydration of the ions with increase in the concentration; hence the equivalent conductivity falls less rapidly than would be expected from the diminution in α. It seems probable that complex ions are partly responsible for the observed effects, increase of the transport numbers of the anion with increase of the concentration being thus explained. T. H. P.

Cobalt Chloride Solutions. II. Solutions of Barium Chloride and of Barium and Cobalt Chlorides. C. MAZZETTI (*Gazzetta*, 1924, **54**, 908—918; cf. preceding abstract).—Contrary to what was found for cobalt chloride solutions, the values of $C^{-1/3}$. log $1/\alpha$ for barium chloride solutions at 20° and 50° are in all cases less than the theoretical values. The observations point to hydration of the ions, the extent of which diminishes as the concentration increases.

Data obtained for the conductivity and viscosity of solutions containing both cobalt and barium chlorides afford evidence of the formation of complex ions. T. H. P.

The Electron in the Chemistry of Solutions and in Electrochemistry. V. Ionic Reactions, the Ionisation of Metals, and the Osmotic Theory of the Galvanic Current. VI. Electrical Nature of Catalytic Phenomena. L. PISARSHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 777—797, 798—804).—V.—The processes of electrolysis and osmosis are discussed in the light of the author's views (A., 1923, ii, 729, 730). The atoms in a metal are ionised to a certain extent, depending on the more or less pronounced electropositive character of the metal. When the latter is immersed in water or an aqueous solution, an equilibrium is established between the ions which pass into solution, the electrons liberated in the process, and the "undissociated" atoms. The electrolytic solution pressure therefore depends on two factors: the internal ionisation of the metal, and the electrostatic attraction between the ions so produced and the solvent. The laws of osmosis are also readily interpreted on the basis of these considerations. The electrolytic potential of non-metals in contact with solutions containing their ions depends not only on their chemical nature, that is the tendency of the atoms to

acquire electrons, but also on the degree of ionisation of the electrode immersed in the solution.

VI.—The accelerating action of ferric ions on the oxidation of hydrogen iodide by chlorates is explained by the fact that the ferric ion is positive and therefore comes more readily into contact with both the negative ions taking part in the reaction, thus facilitating the transference of an electron which constitutes the process of oxidation (cf. A., 1923, ii, 730). Hydrogen ions act in a somewhat similar manner in accelerating the interaction between ferric and stannous ions on account of their great mobility (due to absence of solvate formation). The catalytic action of platinum on the union of hydrogen and oxygen is also discussed and it is suggested that the activity of the metal depends on its capacity to adsorb the gases on the one hand and to ionise on the other; the electrons formed act on the adsorbed gases and cause combination. Oxidation of the surface in such metals as zinc prevents their activity. G. A. R. K.

Significance of the Electrode Potential. J. HEYROVSKÝ (*Chem. News*, 1924, **129**, 379—380).—It is contended that Butler (*ibid.*, **128**, 357), in criticising the author's thermodynamic treatment of electrode potentials, wrongly identifies the pressure of the metallic ions over the dry metal with the concentration of ions in the vapour over the moist interface, and that this leads to an erroneous step in the cycle. C. H. D. C.

Commutator Measurements on Polarised Electrodes. M. KNOBEL (*J. Amer. Chem. Soc.*, 1924, **46**, 2613—2621).—Overvoltage–time curves have been obtained both for increasing and decreasing overvoltage, using a special form of commutator. It is shown that the usual commutator method of measuring overvoltage (cf. Newbery, T., 1914, **105**, 2419) is incorrect owing to the fact that the overvoltage falls in a few thousandths of a second when the polarising current is cut off. With platinised platinum electrodes the hydrogen is, however, retained on the surface and maintains the overvoltage. By a graphical method approximate values for the gas concentrations on the polarised electrodes have been deduced. On smooth electrodes, the adsorbed hydrogen is present as about 0·01 of a molecular layer at low polarisations, approaching a molecular layer at high polarisations. G. M. B.

Two Types of Overvoltage and the Temperature Effect. J. L. BIRCHER, W. D. HARKINS, and G. DIETRICHSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2622—2631).—Two types of overvoltage are distinguished which have hitherto been confused. That of type *A* has a negative temperature coefficient which has the same value for several metals, thus indicating that this is not a property of the cathode material, but rather of the electrolyte. Overvoltage of type *B*, on the other hand, is more stable, tends to appear at low current densities, and is peculiar to active metals. It has a positive temperature coefficient and corresponds closely with the single potential of the metal. The effect of stirring the

electrolyte, of the solubility of the cathode, and of the roughness of its surface are discussed, and it is pointed out that variations in the latter make the values of true current density impossible to determine. G. M. B.

Effect of Pressure on Overvoltage. M. KNOBEL (*J. Amer. Chem. Soc.*, 1924, 46, 2751—2753).—Measurements of the influence of pressure on the hydrogen overvoltage on platinum, lead, copper, and nickel confirm the results of Bircher and Harkins (A., 1924, ii, 88) even when the stirring is violent owing to larger current density and low pressure. G. M. B.

Behaviour of Silver Iodide in the Photo-voltaic Cell. II. New Type of Silver Iodide Photo-voltaic Cell. A. GARRISON (*J. Physical Chem.*, 1925, 29, 58—67; cf. A., 1924, ii, 401).—A thin, transparent film of silver iodide is allowed to solidify on a gold plate and is immersed in a 0·1*N*-ammonium nitrate solution. The rate of rise of photo-potential is proportional to the light intensity at the beginning of the illumination. For a fixed intensity of light, the rate of chemical change decreases as the light is made more nearly monochromatic for any part of the visible spectrum. A freshly-prepared electrode is more sensitive in the blue region, but after exposure in this region it becomes much more sensitive to red light. The author assumes that the greater the degree of polarity of silver iodide, the longer the wave-length of the light which the valency electrons absorb. A molecule having absorbed a quantum of energy and become polar may return to a less polar state by giving up part of its energy to other molecules. The absorption of a quantum of blue light thus increases the number of molecules capable of absorbing green or red light and accounts for the fact that previous illumination intensifies the effect of long wave-lengths and that the parts of the spectrum taken separately are not additive in their chemical effect. M. B. D.

Nitric Acid. I. Behaviour as a Nitrating Agent. A. KLEMENC and R. SCHÖLLER (*Z. anorg. Chem.*, 1924, 141, 231—283).—The nitration of organic substances in solution in water and ether by nitric acid in presence of nitrous acid has been further examined. Nitration proceeds only in presence of oxides of nitrogen in which the nitrogen has a valency lower than five, and is accompanied by oxidation, being therefore autocatalytic. The experimental results indicate that the velocity of nitration varies with the 2·5 power of nitric acid concentration; a tentative assumption of an intermediate compound, *E*-acid, $H_2N_3O_8$ [$2HNO_3 + NO_2 \rightleftharpoons H_2N_3O_8$] leads to the equation

$$-d[HNO_3]/dt = Kk_1[HNO_3]^{5/2}[HNO_2]^{\frac{1}{2}}[RH]^2/k_2k''^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}$$

for the nitration velocity, RH being the material nitrated. The oxidising action under the same conditions is also examined on the basis of the formation and decomposition of *E*-acid; the oxidation of arsenious acid is represented by the cycle $H_3AsO_3 + H_2N_3O_8 \rightleftharpoons H_3AsO_4 + H_2N_3O_7$; $H_2N_3O_7 + HNO_3 \rightleftharpoons H_2N_3O_8 + HNO_2$, the latter reaction being strongly catalysed by mercury ions. The

velocity equations deduced from these assumptions are tested by observations on the nitration of methyl *p*-hydroxybenzoate in ether solution and of phenol in water; the values obtained for the constants are not uniform, but are held to indicate the general truth of the assumptions. Nitrosophenol is not an intermediate product in the nitration of phenol in water. Experiments on the partition of nitric and nitrous acids between ether and water, and on the conductivity of solutions of nitric acid containing nitrous acid, undertaken to obtain evidence of the existence of *E*-acid, gave no definite results.

Nitration in presence of sulphuric acid, using 2 : 4-dinitro-*m*-xylene, *p*-chloronitrobenzene, and 4 : 6-*m*-xylenedisulphonic acid, gave excellent constants for bimolecular reactions, the constants not being appreciably altered by the presence of nitrous acid and lower oxides of nitrogen. In this solvent, therefore, there is no formation of the intermediate *E*-acid. Nitric anhydride, N_2O_5, reacts as $N_2O_5/2$, giving the same constants as nitric acid. S. I. L.

Oxidation of Acetaldehyde. II. L. Reiner (*Z. anorg. Chem.*, 1925, **141**, 363—374; cf. A., 1923, i, 1176).—When solutions of acetaldehyde and hydrogen peroxide are mixed, heat is evolved owing to the formation of diacetaldehyde hydroperoxide: $2CH_3{\cdot}CHO+H_2O_2 \rightleftharpoons (CH_3{\cdot}CHO)_2,H_2O_2$ (1). At 0° this compound is fairly stable, but dissociates rapidly on heating the solution. The velocity of oxidation of acetaldehyde by hydrogen peroxide increases with increasing concentration of aldehyde, but is little affected by the amount of hydrogen peroxide, provided that the ratio hydrogen peroxide/aldehyde is greater than 0·25 : 1; a large excess of hydrogen peroxide slightly retards the oxidation. The amount of acetic acid produced is usually greater than that corresponding with the hydrogen peroxide used up, and the amount of this excess increases with the absolute concentration, but is unaffected by the ratio hydrogen peroxide/aldehyde. These results are accounted for if the diacetaldehyde hydroperoxide produced in (1) combines with aldehyde according to the reaction

$$(CH_3{\cdot}CHO)_2,H_2O_2+CH_3{\cdot}CHO \rightleftharpoons (CH_3{\cdot}CHO)_3,H_2O_2 \quad (2).$$

This second additive product is then oxidised directly by molecular oxygen to acetic acid: $(CH_3{\cdot}CHO)_3,H_2O_2+O_2 \longrightarrow 3CH_3{\cdot}CO_2H+H_2O$ (3). The molecular oxygen required in (3) may be obtained either from decomposition of the hydrogen peroxide or from the air, and the excess of acetic acid referred to above is greatly reduced if oxygen is excluded from the reaction vessel. The retarding effect of a large excess of hydrogen peroxide is due to its reducing the concentration of free aldehyde owing to the mass-action effect in equation (1). The oxidation may be regarded as an autoxidation of diacetaldehyde hydroperoxide, acetaldehyde being the acceptor; on the basis of the theory of Goard (A., 1924, ii, 161), the oxidation potentials are in the order $(CH_3{\cdot}CHO)_3,H_2O_2 > CH_3{\cdot}CHO > (CH_3{\cdot}CHO)_2,H_2O_2$. The autocatalytic effect of acetic acid previously reported (Reiner, *loc. cit.*) is incorrect.

W. H.-R.

Molecular Attraction and Velocity of Reactions at Low Temperatures of Unsaturated Hydrocarbons. O. MAASS and C. H. WRIGHT (*J. Amer. Chem. Soc.*, 1924, **46**, 2664—2673; cf. A., 1921, i, 761).—The freezing-point diagrams of the systems ethylene–hydrogen bromide and propylene–hydrogen bromide show that propylene molecules have a greater attraction for hydrogen bromide than have ethylene molecules, there being definite indication of compound formation in the case of propylene only. The fact that propylene combines in the liquid state with hydrogen bromide, whilst ethylene does not, is attributed to this difference in the respective attractions of the molecules. The velocity and the course of the reaction between propylene and hydrogen bromide have been determined at −78·2° and at 0°, *iso*propyl bromide being the main product together with a small amount of a secondary hexyl bromide. G. M. B.

Activation of Atoms and Molecules and Mechanism of Chemical Change. N. R. DHAR (*Z. anorg. Chem.*, 1924, **141**, 1—22).—The well-known fundamental concepts of the activation of molecules and the radiation theory of chemical change are reviewed. Stress is laid on the fact that ionic reactions are very rapid compared with non-ionic. The similarity in mechanism between rise of temperature, light absorption, and catalysis is emphasised. Experimental observations support the view that if a sufficient quantity of catalyst could be added to change a large number of molecules from the inactive to the active form, or conversely, then the temperature coefficient would be smaller (in the case of positive catalysis), or greater (for negative catalysis), than for the uncatalysed reaction. The opinion is expressed that active nitrogen, ozone, active hydrogen, active chlorine, etc. are activated by light or electric discharge, and can be charged to a certain potential. Their activity is conditioned by the ease with which they can give up their charge as energy. The luminescence of active gases, such as nitrogen, hydrogen, oxygen, etc., and the appearance of radioactive excited phosphorescence, can probably be traced to the conversion of the active form of these substances into the inactive form by loss of energy.

All slow oxidations seem to yield ions and electrons, which could activate the oxygen molecule. This active oxygen would show all the characteristics of ozone. A part would revert spontaneously to the inactive form, with production of luminescence. This is the probable cause of the luminescence caused by the slow oxidation of phosphorus, the organic sulphur compounds, etc.

L. L. B.

Perchlorate Ion as Catalyst in the Electrolytic Preparation of Persulphuric Acid. A. MAZZUCCHELLI (*Gazzetta*, 1924, **54**, 1010—1013).—The yields of persulphuric acid prepared by the anodic oxidation of sulphuric acid are markedly improved by addition to the solution used of a small proportion of perchloric acid or its ammonium or potassium salt. No hydrochloric acid is formed under these conditions. T. H. P.

Autocatalytic Reaction: Ferric Chloride–Sodium Thiosulphate. J. HOLLUTA and A. MARTINI (*Z. anorg. Chem.*, 1924, **141**, 23—37; cf. *ibid.*, 1924, **140**, 206).—An unsuccessful attempt has been made to trace the initial acceleration of the reaction ferric chloride–sodium thiosulphate to the autocatalytic action of the end products, *i.e.*, the ferrous or tetrathionate ion. Addition of both ferrous and tetrathionate salts retards the reaction. The influence of the ferrous ion on the reaction velocity may be represented by the equation,

$$dx/dt=[k_2-k'_2\sqrt{x}\,.\,(1301-21563x)]\,.\,(a-x)(b-x).$$

It was thought that the phenomenon might be due to the catalytic action of sulphur formed by the reaction between hydrogen ions and sodium thiosulphate, or to the means adopted to stop the reaction at the required point. Both these explanations were, however, found to be incorrect. Investigations with the addition of foreign, complex anions (phosphate), and with a higher acidity, showed that the acceleration is probably due to a negative catalyst which is removed during the reaction; it is assumed to be the reacting ferrithiosulphate complex. L. L. B.

Method of Producing Chemical Reactions. M. BRUTZKUS (*Compt. rend.*, 1925, **180**, 199—201; cf. Brit. Pat. 155776, 217747).—A chemical reaction may be directed or accelerated by means of continuous and simultaneous variations of pressure, temperature, and concentration opposite to those resulting from the desired reaction, whereby a series of impulses is given to the reaction. Metals and metal oxides which catalyse gaseous reactions probably alter the conditions of pressure and concentration by differential absorption of the reacting gases, and temperature by rapid conduction of the heat liberated, thus preventing the reversible reaction from setting in. Internal-combustion engines provide the best means of studying chemical reactions under such conditions. J. W. B.

Synthesis of Ammonia at High Pressures. II. W. MOLDENHAUER (*Chem.-Ztg.*, 1925, **49**, 65—66; cf. A., 1924, ii, 404).—The author compares the results obtained by Larson and Dodge (A., 1924, ii, 104) and by Larson (A., 1924, ii, 331) on the ammonia equilibrium at high pressures with those of Claude and with Haber's equation. M. B. D.

Mechanism of the Inhibition of the Catalytic Action of Platinum Black and Partly Reduced Nickel Oxide by Chlorine. M. C. BOSWELL and C. H. BAYLEY (*J. Physical Chem.*, 1925, **29**, 11—19).—Nickel oxide on asbestos is reduced by hydrogen at 275° to a constant oxygen content (cf. A., 1923, ii, 231). After chlorine has been introduced, the oxide content can be decreased by passing more hydrogen over the catalyst. When hydrogen and oxygen are passed alternately over platinum black at 150°, an equilibrium is reached when the amounts of the two gases converted into water each time remain constant (cf. *Proc. Roy.*

Soc. Canada, 1923, **17**, 1). After poisoning the catalyst with chlorine, hydrogen accumulates after each successive gas treatment until it is suddenly evolved in a large amount as water. The poisoning is accomplished by the destruction of the surface film of the catalyst, thus rendering the interior oxygen accessible to free hydrogen. This interior oxygen is vital to the maintenance of the active surface film and hence of the catalytic action of the normal catalyst. M. B. D.

Theory of Catalytic Hydrogenation by Means of Platinum. M. BODENSTEIN (*Annalen*, 1924, **440**, 177—185).—The hydrogen layer formed on platinum immersed in a mixture of hydrogen and oxygen is found by electro-potential measurements to be replaced by a layer of oxygen when the ratio of oxygen to hydrogen in the gas is 3·6 : 2 by volume, or greater. Other evidence supports this conclusion. A theory of heterogeneous catalysis is proposed in which the valency force emerging from the surface of a catalyst is supposed to deform the gaseous molecules adsorbed by a surface in such a way that they are in a specially active state. Thus, hydrogen may become atomic on platinum surfaces, the nucleus of the atom adhering to the surface of the catalyst by virtue of its electron, which is held between two slightly vibrating electrons in the metal. It is very improbable that a peroxide of platinum is formed in the catalysis of electrolytic gas (cf. A., 1921, ii, 185; 1924, ii, 724). S. K. T.

Catalytic Action of Alumina containing Other Substances. A. CHARRIOU (*Compt. rend.*, 1925, **180**, 213—215).—The effect of foreign substances on the activity of alumina used as catalyst in the decomposition of ethyl ether (cf. Sabatier and Mailhe, A., 1910, i, 606) has been investigated. The least active sample of alumina contained 15% of calcium oxide. A sample containing 4·5% of the same impurity was slightly more active, and samples containing 2·5% of cobaltous oxide, 7·7% of cupric oxide, or 15% of phosphoric oxide were still more active. Other catalysts submitted to examination contained 6·5% WO_3, 8% SO_3, and 1% SO_3, whilst a fourth was prepared by the oxidation of aluminium in presence of mercury. The activity of these was found to increase in the order given. When pure alumina is heated at a red heat for ½ hour the activity falls to less than half its original value. The only admixture having a beneficial effect is that of blue tungsten oxide, W_2O_5; a sample, prepared by treating alumina containing the trioxide with hydrogen at 250°, was considerably more active than the pure alumina. W. A. S.

Reduction of Nickelous and Ferric Oxides by Hydrogen. A. F. BENTON and P. H. EMMETT (*J. Amer. Chem. Soc.*, 1924, **46**, 2728—2737).—The kinetics of the reduction by hydrogen of various specimens of nickel and ferric oxides have been examined. Reduction of nickel oxide is auto-catalytic, proceeding mainly at the interface between the solid phases, whilst no autocatalysis is

observed in the reduction of ferric to ferro-ferric oxide, the reaction velocity being greatest at the start and diminishing continuously. These results are in agreement with Langmuir's theory that heterogeneous reactions involving a solid substance on each side of the equation should be "interfacial" when the solids remain separate, but "non-interfacial" when solid solution occurs. Reduction of the nickel oxide is less rapid the higher the temperature of preparation of the sample. At higher reduction temperatures, the maximum rate of reduction is greater and occurs earlier in the process. Water vapour retards the reaction, as does oxygen in the hydrogen used. The mechanism of the hydrogen–oxygen catalysis over nickelous oxide appears to be that of activation of the oxygen by adsorption or by superficial conversion into a higher oxide of nickel. G. M. B.

Behaviour as Salts of Alkali Alkyls Dissolved in Metal Alkyls. F. HEIN [with E. PETZCHNER, K. WAGLER, and F. A. SEGITZ] (*Z. anorg. Chem.*, 1924, **141**, 161—227).—The alkali alkyls, LiEt, NaEt, KEt, LiMe, LiPh, and $LiCH_2Ph$, dissolve in zinc ethyl to form solutions which conduct electricity; with increasing electro-positive character of the alkali metal, the molecular conductivity and m. p. of the alkyl compound rise, and its miscibility with the solvent falls. Since lithium ethyl does not act as a conductor either in the fused state or in solution in benzene, and since the molar conductivities fall sharply with dilution in some cases, it appears that association with the solvent and formation of complex ions are necessary conditions, absence of which may cause the solution to remain non-conducting. Thus lithium phenyl conducts very little, sodium phenyl not at all, whilst *lithium benzyl*, $LiCH_2Ph$, a yellow, amorphous precipitate obtained by the reaction between lithium ethyl and mercury dibenzyl in benzene solution, has the highest conductivity of the lithium alkyls examined. Aluminium ethyl and zinc propyl are also solvents giving conducting solvates; the associated compounds of the alkali alkyls with the former have higher m. p. and conductivities, with the latter lower, than the compounds with zinc ethyl. Dilute solutions of the alkali methyls in zinc methyl and aluminium methyl, and concentrated solutions of sodium and lithium ethyl in cadmium ethyl, do not conduct.

Electrolysis of sodium ethyl dissolved in zinc ethyl gives at the anode a mixture of gases containing about 40% of ethylene, about 40% of ethane, and the remainder butane, propane, and methane, justifying the assumption that the ethyl radical is liberated by the electrode. Zinc is deposited quantitatively at the cathode, Faraday's law being strictly obeyed. The conductivity temperature coefficient is positive. The potential required is less than 0·1 volt. With a lead anode, lead tetraethyl is obtained quantitatively; after passing a current of 0·02 amp. for 7 hours, the lead electrode had lost almost the theoretical weight, and the tetraethyl compound separated as an oil at the bottom of the electrolyte. S. I. L.

[Corrosion of Copper, Brass, and Zinc in Sea-water.] Seventh Report to the Corrosion Research Committee of the Institute of Metals. G. D. BENGOUGH and R. MAY (*J. Inst. Metals*, 1924, 32, 81—256).—The chief initial corrosion product of copper in chloride solutions is cuprous chloride which, in both distilled and sea-water at the ordinary temperature, is oxidised to cupric chloride and cuprous oxide; in presence of sufficient oxygen, these are further oxidised to a basic chloride, $Cu_4(OH)_6Cl_2,H_2O$. Cupric chloride does not accumulate in the water; it may attack the copper, causing an electrolytic corrosion in which metal is transferred from one part of the copper to another. The scales on copper exposed to sea-water were found to consist of calcium sulphate, cupric hydroxide (both probably forming protective layers), cupric oxychloride, and a basic copper carbonate. The scales have a much lower protective value in rapidly moving than in stagnant water. The corrosion of zinc in sea-water results mainly in the formation of carbonate, hydroxide, and oxychloride; the two last form protective layers, which, however, are greatly impaired by the presence of carbon dioxide. When brass corrodes in cupric chloride solution, zinc chloride and copper are first produced; the latter then redissolves to form cuprous chloride, which is then oxidised, in presence of sufficient oxygen, to the above-mentioned basic chloride. If the reaction is stopped at the first stage, no further corrosion takes place and copper is deposited on the zinc beneath the scales ("dezincification"); 0·02% of arsenic in the brass prevents this, but iron and manganese accelerate it. Brass in still water is cathodic with respect to a similar specimen in unaërated moving water and is anodic to one in slowly moving aërated water, but it becomes cathodic again in rapidly moving aërated water. The corrosion of brass condenser tubes is also investigated; it is very sensitive to the presence of "entangled" air in the water. [Cf. *B.*, 1924, 833.] S. K. T.

Anodic Oxidation of Gold. II. Properties of Auric Sulphate. F. JIRSA and H. JELINEK (*Chem. Listy*, 1924, **18**, 251—252; see A., 1924, ii, 692). W. A. S.

Photochemical Formation of Hydrogen Bromide and Velocity of Formation of the Bromine Molecule from the Atoms. M. BODENSTEIN and H. LÜTKEMEYER (*Z. physikal. Chem.*, 1924, **114**, 208—236).—The velocity of combination of hydrogen and bromine in moderately intense light has been investigated. The views which have been put forward to explain the phenomena of the reaction are recapitulated, and a method is described which allows a decision to be made between the various possibilities. The method consists of subjecting bromine vapour and hydrogen, contained in suitable concentration in a silica vessel with plane parallel walls, to illumination from a tungsten arc lamp. The vessel is kept at a constant temperature over the range 160—218°. After each illumination, the absorption of bromine is measured with a spectrophotometer, from which the reaction velocity can be determined. The energy absorbed from the light is measured in

the cold vessel by means of a thermopile. It is shown that the measurement of the absorbed radiation (of wave-length 525, 516, and 504 $\mu\mu$) is not affected by temperature over the range investigated. It is found that the combination of hydrogen and bromine takes place with a velocity which is about three hundred times as great as that of the reaction in the dark at the same temperature, and according to a law which follows from that of the dark reaction. By this, the velocity is determined by that of the combination of hydrogen with bromine atoms, existing according to the equilibrium $Br_2 \rightleftharpoons 2Br$. In light, there is in place of the velocity of spontaneous decomposition, that of the decomposition of the bromine molecule by absorbed light quanta. The equation for the light reaction therefore has the form

$$+d[HBr]/dt = k\sqrt{\text{light absorbed}} \,.\, [H_2]/(1+[HBr]/10[Br_2])$$

This is derived in all particulars from the theory of the reaction in the dark. A measurement of the absorbed light quanta allows the velocity with which bromine atoms are formed and recombine to be ascertained. A comparison of the velocities in light and in the dark is supplied by associating the known dissociation equilibrium of bromine vapour with the concentration of bromine atoms. From this, the number of collisions can be calculated, and a comparison of this with the number of combinations to form molecules leads to the conclusion that only 1·25% of the collisions result in combination, independent of the total pressure of the gas, and of the temperature (within the narrow range investigated). This result contradicts that expected from theoretical considerations.

L. L. B.

Photochemical Studies. IV. Properties of the Silver Gelatino-halides. A. Reychler (*Bull. Soc. chim. Belg.*, 1924, **33**, 550—558).—Aqueous colloidal solutions of silver chloride or bromide are rapidly reduced by "metol"-quinol developer in daylight. Colloidal solutions of these salts in 1% gelatin solution prepared in the dark slowly become rose-coloured, then grey, and finally black and flocculent on exposure to daylight. The developer has no action in the dark, but after a short period of incubation rapidly reduces the solutions on exposure to daylight. If the gelatin solution is prepared in the light, the reducing action of the developer is more rapid the greater the age of the solution, bromide solutions in all cases being more slowly reduced. Colloidal silver iodide solutions are practically unaffected by light and only very slowly and incompletely reduced by the developer, yielding yellow to brown translucent liquids. It is suggested that the action of the light in promoting the reducing action of the developer may be explained by assuming that the reduction is due to electrochemical action; the light reduces photochemically part of the silver halide to metal and this metal then becomes an anode and the unchanged halide a cathode, the anode being constantly depolarised by the developer and the cathode progressively reduced to metallic silver by the hydrogen ions discharged on its surface.

A. R. P.

Photochemical Decomposition of Chromium Salts in the Presence of Organic Matter. A. POPOVICKI (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 1—6).—It is suggested that the substance obtained when gelatin treated with a dichromate is exposed to sunlight is the compound, $4Cr_2O_3,3CrO_3$; the tanning action on gelatin is attributed to this compound. G. A. R. K.

Alleged Influence of Light on Electrophoresis. K. SCHAUM and P. FRIEDERICH (*Z. wiss. Phot.*, 1924, 23, 98—101).—Sols of metals in water and organic media, prepared according to the methods of Bredig and of Svedberg, and of sulphur and arsenious sulphide in water, and suspensions of anthracene in pure hexane were investigated. Practically all the sols and suspensions examined showed no difference in the migration velocity in ultra-violet light and in light of long wave-length. Zinc hydrosol alone showed a small decrease in the velocity on exposure to ultra-violet radiation. The effect was not observed with zinc sols in alcohol, and is probably due to some chemical action. Electrophoresis of hydrosols of the silver halides is appreciably affected by light, which can bring about reversal of the direction of migration. The presence of silver oxide particles in a silver sol in water prepared by Bredig's method can be investigated by adding gelatin and observing a thin preparation in the microscope with dark-ground illumination. If acetic acid is allowed to diffuse in, any silver oxide particles are rapidly dissolved. The influence of positive particles of silver oxide on the direction of migration in a negative silver sol is briefly discussed. W. C.

Photochlorination of Aliphatic Compounds in Carbon Tetrachloride. J. PLOTNIKOV (*Z. wiss. Phot.*, 1924, 23, 79—80).—Some of the results obtained by Benrath and Hertel (A., 1924, i, 821) indicate a tendency for periodicity in the photochlorination, an effect which would undoubtedly be more pronounced if longer times of exposure were employed. The results, however, are of little value, since monochromatic light was not used, and the source of light was not specified. W. C.

Internally Complex Beryllates. A. ROSENHEIM and F. LEHMANN (*Annalen*, 1924, 440, 153—166).—The following crystalline metallic *salts* of internally complex beryllates of some organic acids were prepared by dissolving beryllium carbonate or freshly-precipitated hydroxide in boiling solutions of alkali salts of the acid: salicylic acid, $M_2[Be(C_6H_4O,CO_2)_2],xH_2O$, where M=K, Na, or 0·5Ba and $x=3$, M=NH_4 and $x=2$; glycollic acid, $M_2[Be_3(C_2H_2O_3)_4],xH_2O$, where M=K and $x=8·5$, M=Na and $x=4·5$, and the ammonium salt, $(NH_4)_4H_2[Be_5(C_2H_2O_3)_8],3H_2O$. With *o*-hydroxytoluic acid, two series of compounds were obtained, one, $M_2[Be(C_8H_6O_3)_2],xH_2O$, where M=Na and $x=0$, M=NH_4 and $x=1$, when freshly-precipitated hydroxide was used, and the other, $M_2[Be_2O(C_8H_6O_3)_2],H_2O$, where M=$NH_4$ or K, when the hydroxide was stale. Boiling, strongly alkaline solutions of pyrocatechol dissolved beryllium

hydroxide and gave a series of normal salts, $M_2[Be(C_6H_4O_6)_2],xH_2O$, where M=$NH_4$, Na, K, 0·5Ba, and x=1, 5, 2, 1·5, respectively. By warming together known amounts of pyrocatechol with excess of hydroxide and gradually adding alkali the following polyberyllates were obtained: $(NH_4)_2[Be_2O(C_6H_4O_2)_2],5H_2O$; $(NH_4)_4[Be_3(C_6H_4O_2)_5],2H_2O$; $(NH_4)_4[(Be_2O)_3(C_6H_4O_2)_5],13H_2O$; $M_8[Be_6O(C_6H_4O_2)_9],xH_2O$, where M=Na and x=20, M=K and x=9. A crystalline salt, $(NH_4)_6[Be_3(C_6H_3O_2,SO_3)_4],8H_2O$, and an amorphous product, probably a mixture, corresponding with $Ba[Be_2(C_6H_3O_2,SO_3)_2]$, were also prepared. Vitreous metallic salts of internally complex beryllates of citric acid were obtained, but are not described. Similar compounds are formed with polyphenols, but not with polyalcohols. Boiling ethyl salicylate dissolves beryllium carbonate to form a complex beryllium compound.

The beryllium in the compounds derived from salicylic and *o*-hydroxytoluic acids is scarcely precipitated at all by ammonia or alkali hydroxide, showing that it is present in an exceedingly complex state. This is probably not caused by adsorption of beryllium hydroxide by the salt, since the compounds are reproducible. The glycollic acid compounds are readily, and the pyrocatechol compounds partly, decomposed by ammonia. The complex beryllium tartrate and the basic acetate are considered to be internally complex salts of the sexavalent radical, Be_4O.

S. K. T.

Silicate Compounds of Cadmium. A. Dubon (*Compt. rend.*, 1924, **179**, 769—771; cf. A., 1921, ii, 403, and previous papers).—Addition of silica, followed by cadmium oxide, to fused potassium fluoride yields a semi-crystalline product which, when heated with excess of potassium chloride, yields a mixture of well-crystallised compounds. The latter, on separation by flotation methods, proved to contain (*a*) long prismatic *crystals*, $K_2O,CdO,4SiO_2$; (*b*) *crystals* of $2CdO,SiO_2$ containing potassium, probably as impurity, and (*c*) yellow flattened prismatic *crystals* of $3CdO,SiO_2$. H. J. E.

Absorption of Halogens by Mercurous Salts. I. Formation and Properties of some Complex Compounds of Mercury. K. G. Naik and M. D. Avasare (*J. Indian Chem. Soc.*, 1924, **1**, 75—80; cf. A., 1924, ii, 48).—Mercurous chloride, sulphate, and nitrate combine with bromine and iodine in alcoholic solution to yield crystalline substances which are not double salts, but complex compounds. *Mercuric chloroiodide*, HgClI, red crystals becoming yellow at 125°, m. p. 153°. *Mercuric chlorobromide*, HgClBr, white crystals, subliming without melting. *Di-iodomercuric sulphate*, $SO_4(HgI)_2$, red crystals turning yellow at 143°, m. p. 248°. *Tetrabromodimercuric sulphate*, $[SO_4(HgBr)_2]Br_2$, white crystals, decomp. 125°, and m. p. 235° (decomp.). *Dichlorodimercuric sulphate*, $SO_4(HgCl)_2$, m. p. 270°. *Tetraiododimercuric nitrate*, $(HgNO_3I)_2I_2$, red crystals turning yellow at 145—146°, m. p. 250°. *Tetrabromodimercuric nitrate*, $(HgNO_3Br)_2Br_2$ (decomp.). *Tetrachlorodimercuric nitrate*, $(HgNO_3Cl)_2Cl_2$, decomp. 100°.

G. M. B.

Direct Formation of Mercuric Oxychlorides. H. PÉLABON (*Compt. rend.*, 1925, **180**, 143—145; cf. A., 1924, ii, 762).—Determinations of the concentrations of mercuric chloride in solution in equilibrium with the solid phases obtained from mercuric chloride and red mercuric oxide demonstrate the existence of three oxychlorides, $HgO,2HgCl_2$, $2HgO,HgCl_2$, and $4HgO,HgCl_2$. The same products are obtained more rapidly in presence of ethyl alcohol. The compound $HgO,2HgCl_2$ is a white solid which is not produced if the temperature is above 30°, but once formed it is stable at 100°. G. M. B.

Double Sulphates of Rare Earth and Alkali Metals. I. Lanthanum and Potassium. F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 301—308; cf. A., 1911, ii, 42).—The equilibrium between an aqueous lanthanum sulphate solution and solid potassium sulphate at 25° has been studied, and the results are represented graphically by plotting the values of K_2SO_4/H_2O in the liquid phase as abscissæ against those of $La_2(SO_4)_3/K_2SO_4$ in the solid phase. Interpreted according to the phase rule (cf. A., 1903, ii, 473), this diagram indicates the formation of the following new (microcrystalline) double *salts*: $2La_2(SO_4)_3,3K_2SO_4,8H_2O$ (monoclinic); $La_2(SO_4)_3,4K_2SO_4,H_2O$ (spherical); $La_2(SO_4)_3,4{\cdot}5K_2SO_4,2H_2O$ (globular); $La_2(SO_4)_3,5K_2SO_4,2H_2O$ (globular). W. E. E.

Double Sulphates of Rare Earth and Alkali Metals. II. Neodymium and Potassium. F. ZAMBONINI and V. CAGLIOTI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 308—313).—An examination of the system neodymium sulphate–potassium sulphate–water (cf. preceding abstract) shows that, at 25°, the following double *salts* are formed: $Nd_2(SO_4)_3,K_2SO_4,2H_2O$; $Nd_2(SO_4)_3,3K_2SO_4,2H_2O$; $Nd_2(SO_4)_3,4K_2SO_4,H_2O$; $Nd_2(SO_4)_3,4K_2SO_4,2H_2O$; $Nd_2(SO_4)_3,5K_2SO_4,2H_2O$; $2Nd_2(SO_4)_3,3K_2SO_4,8H_2O$ (microcrystalline: rosettes of pink monoclinic tablets, d^{15} 3·026). W. E. E.

Silicic Acids. II. R. SCHWARZ and E. MENNER (*Ber.*, 1925, **58**, [*B*], 73—77; cf. A., 1924, ii, 753).—The silicic acids described previously (*loc. cit.*) have been subjected to desiccation by means of acetone (cf. Willstätter and Kraut, A., 1924, ii, 615). Metasilicic acid loses combined water at 15°, but can be freed from adsorbed water by acetone at 0°. Granatic acid, $H_4Si_3O_8$, which has now been prepared from the corresponding sodium salt, is also unstable at the atmospheric temperature. Di- and tri-silicic acids are easily desiccated by means of acetone under widely varied conditions. The dehydration curves of granatic acid and of metasilicic acid at 0° are given; the existence of two further hydrates, $12SiO_2,10H_2O$ and $12SiO_2,9H_2O$, is rendered probable. H. W.

Double Nitrates of Metals of the Cerium Group with Copper and Cadmium. G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 322—326; cf. this vol., ii, 145).—The following new *compounds* are described: $2Nd(NO_3)_3,3Cu(NO_3)_2,24H_2O$, lilac crystals,

d^{15} 2·248; of the same form and obtained in the same way as the corresponding cerium compound; $2Pr(NO_3)_3,3Cu(NO_3)_2,24H_2O$, minute, green crystals, and $2Sm(NO_3)_3,3Cu(NO_3)_2,24H_2O$, both of the same type as the preceding, were obtained similarly. The double nitrates of cadmium with cerium, lanthanum, and neodymium were prepared by evaporating the mixed solutions of the nitrates over sulphuric acid, at reduced pressure, below 12°. The following were obtained: $2La(NO_3)_3,3Cd(NO_3)_2,24H_2O$, colourless tablets like those of the copper compounds, d^{12} 2·226;

$$2Ce(NO_3)_3,3Cd(NO_3)_2,24H_2O,$$

d^{12} 2·294; $2Nd(NO_3)_3,3Cd(NO_3)_2,24H_2O$, minute rose-coloured crystals of the same crystalline form as that of the lanthanum salt. Jantsch has observed a parallelism among the molecular volume curves of the double salts obtained from elements of the cerium group and certain members of the magnesium series of isomorphous elements; this is now shown to be shared by the curves of the double nitrates of copper and cadmium with elements of the cerium group. When the double salts given by the elements of the magnesium family with any other single metal are placed in order of decreasing molecular volumes, the succession, which has always been observed previously, is: cadmium, manganese, iron, copper, cobalt, magnesium, zinc, nickel. The double salts given by the members of this family with any one metal of the cerium group, however, fall into the following sequence: cadmium, manganese, magnesium, cobalt, zinc, nickel, copper. The copper double nitrates afford an excellent means of separating lanthanum from praseodymium. W. E. E.

Reduction of Azoimide. F. Raschig (*Schwefel- u. Stickstoffstudien*, 1924, 213—220; from *Chem. Zentr.*, 1924, ii, 602—603).—Acid reducing agents such as stannous chloride and hydriodic acid reduce azoimide to ammonia and nitrogen. The reaction of azoimide with sodium hydrogen sulphite may be represented thus: $NaHSO_3+NaN_3+H_2O=NH_2\cdot SO_3Na+N_2+NaOH$, together with a subsidiary reaction: $2NaHSO_3+NaN_3+H_2O=Na_2S_2O_6+NH_3+NaOH$. In the reduction of azoimide by aluminium in alkaline solution, hydrazine and ammonia are formed: (i) $N_3H+H_2=N_2+NH_3$; (ii) $N_3H+3H_2=NH_3+N_2H_4$. G. W. R.

Oxidation of Azoimide. F. Raschig (*Schwefel- u. Stickstoffstudien*, 1924, ii, 602; from *Chem. Zentr.*, 1924, ii, 602; cf. A., 1906, ii, 98).—Azoimide is unattacked by potassium permanganate in neutral or alkaline solution. In sulphuric acid solution, a slow oxidation takes place: $HN_3+O=N_3OH$. In addition, a portion of the azoimide appears to be oxidised to triatomic nitrogen, which then decomposes, yielding ordinary nitrogen molecules. Hydrogen hypoazide, N_3OH, resembles hypochlorous acid in its properties. It decomposes, yielding oxygen and, probably, azoimide. By oxidation of azoimide in sulphuric acid or boric acid solution in the presence of sodium nitride, nitric acid is produced, the first stage being the compound $\overset{N}{\underset{N}{\|}}>N\lessdot\overset{OH}{O}$, which then takes up more

oxygen, yielding the compound, $\begin{matrix}N\\ \|\\ N\end{matrix}>N(OH)<\begin{matrix}O\\ O\end{matrix}$, which by loss of nitrogen yields nitric acid. G. W. R.

Combustion of Ammonia to Hydrazine and Di-imide. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 221—224; from *Chem. Zentr.*, 1924, 95, ii, 1068).—The primary reaction in the combustion of ammonia in oxygen is: $2NH_3+O_2=N_2H_2+2H_2O$, the di-imide at once decomposing into its elements. A small part of the ammonia is oxidised to hydrazine, which can be detected with benzaldehyde. R. B.

Oxidation of Hydrazine and its Sulphonic Acids. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 188—200; from *Chem. Zentr.*, 1924, ii, 601—602).—Hydrazine may be used for standardisation in acidimetry and iodometry. When a standard solution of hydrazine sulphate is titrated with sodium hydroxide solution, the following reaction occurs: $2N_2H_4,H_2SO_4+2NaOH=(N_2H_4)_2,H_2SO_4+Na_2SO_4+2H_2O$. After addition of sodium hydrogen carbonate and starch solution, 0·1*N*-iodine solution is added. The blue coloration is obtained when four times as much 0·1*N*-iodine solution has been added as 0·1*N*-sodium hydroxide required for the first reaction. In the oxidation of hydrazine by iodine and by most other oxidising agents nitrogen is set free. Oxidation with potassium permanganate in hot sulphuric acid solution yields ammonium sulphate. The oxidation of hydrazinemonosulphonic acid and of hydrazinedisulphonic acid is also discussed. G. W. R.

Oxidation of Hydroxylamine. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 163—187; from *Chem. Zentr.*, 1924, ii, 600—601).—When hydroxylamine is oxidised by adding it together with dilute sulphuric acid to potassium permanganate solution, the successive stages of oxidation are dihydroxyhydrazine, OH·HN·NH·OH; dihydroxydi-imide, OH·N:N·OH; nitric oxide, O:N·N:O, and a nitrogen tetroxide having the constitution $\begin{matrix}O\\ |\\ O\end{matrix}>N\cdot N<\begin{matrix}O\\ |\\ O\end{matrix}$, called by the author ortho-nitrogen tetroxide. The last compound yields nitric acid and nitrogen: $5N_2O_4+4H_2O=8HNO_3+N_2$. Some nitrous oxide is also formed. Complete oxidation to nitric acid cannot be effected with permanganate. Hypochlorous acid can oxidise hydroxylamine completely to nitric acid. The oxidation of hydroxylamine by iodine and other oxidising agents is also discussed. The views of Kurtenacker and Neusser (A., 1924, ii, 249) are criticised. G. W. R.

Oxidation of Hydroxylamine. II. A. KURTENACKER and F. WENGEFELD (*Z. anorg. Chem.*, 1924, **141**, 119—130; cf. A., 1924, ii, 249).—The results of a number of studies of the oxidation of hydroxylamine by different investigators are reviewed. The authors' hypothesis is preferred to that of Angeli and of Raschig, since the intermediate compound postulated by both these in-

vestigators is not known to exist. Experiments are described on the oxidation of hydroxylamine by potassium dichromate in both acid and alkaline solution. In weak acid solution, half the hydroxylamine is oxidised to nitric acid, the percentage of nitric oxide increasing, and of nitrous oxide decreasing, with decreasing acidity of the solution. In strong acid solution, the percentage of hydroxylamine oxidised to nitric acid sinks to about 25, the gas produced at the same time being pure nitrous oxide. In alkaline solution, the formation of nitric acid is still further reduced, the gaseous products being nitrous oxide and nitrogen. The oxidation of the hydroxylamine is complete only in weak acid solution; in alkaline solution it varied from 47 to 64%, and in strong acid solution was about 78%. Oxidation experiments were also made with mercuric chloride in alkaline solution. L. L. B.

Hydroxylaminemonosulphonic Acid. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 154—162; from *Chem. Zentr.*, 1924, ii, 448—449).—Hydroxylaminemonosulphonic acid, formed according to the following reactions:

(i) $NaNO_2+NaHSO_3+SO_2=HO\cdot N(SO_3Na)_2$,

(ii) $HO\cdot N(SO_3Na)_2+H_2O=HO\cdot NH\cdot SO_3Na+NaHSO_4$,

is in some respects similar to, but is more readily oxidised than, the disulphonic acid. Its reducing properties are associated with the hydrogen atom which is directly linked with the nitrogen and not with the hydroxyl hydrogen. It can be determined titrimetrically by the reaction $2HO\cdot NH\cdot SO_3Na+4I+H_2O=N_2O+4HI+2NaHSO_4$. The primary product of alkaline oxidation is the residue $-(OH)N\cdot SO_3K$, which associates, yielding potassium dihydroxyhydrazinedisulphonate. This yields by loss of 1 mol. of water an azoxy compound, $O<\begin{matrix}N-SO_3K\\ |\\ N-SO_3K\end{matrix}$, which, being unstable, decomposes, giving half of its sulphur as a sulphite and the remainder as the compound $K_2N_2O_2\cdot SO_3$ (potassium dinitrosulphonate). G. W. R.

Hydroxylaminedisulphonic Acid. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 147—153; from *Chem. Zentr.*, 1924, ii, 448; cf. preceding abstracts).—Hydroxylaminedisulphonic acid yields in the cold in acid solution hydroxylaminemonosulphonic acid. The sodium disulphonate gives, on oxidation with alkaline permanganate, sodium sulphazalinate, $O:N:(SO_3K)_2$, a compound of quadrivalent nitrogen, which by hydrolysis with potassium hydroxide yields potassium hydroxylaminetrisulphonate and potassium hydroxylaminedisulphonate according to the equation $4ON(SO_3K)_2+KOH=HON(SO_3K)_2+2ON(SO_3K)_3+KNO_2$. The mechanism of this reaction is discussed. G. W. R.

Hydroxylamine*iso*disulphonic Acid. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 132—146; from *Chem. Zentr.*, 1924, ii, 447; cf. preceding abstracts and A., 1906, ii, 159).—Directions are given for the preparation of potassium hydroxylamine*iso*disulphonate from the corresponding trisulphonate by hydrolysis with

a weak acid. It has the constitution $NH(SO_3K)\cdot O\cdot SO_3K$. In the presence of hydrochloric acid, the $-SO_3K$ group attached to the nitrogen atom may be eliminated, whereby hydroxylamine-*iso*monosulphonic acid, $NH_2\cdot O\cdot SO_3H$, is produced. The oxidation of hydroxylamine*iso*disulphonic acid by sodium hypochlorite is discussed. G. W. R.

Hydroxylaminetrisulphonic Acid. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 128—131; from *Chem. Zentr.*, 1924, ii, 446—447; cf. preceding abstracts).—Potassium hydroxylaminetrisulphonate has the constitution $(KSO_3)_2{:}N\cdot O\cdot SO_3K$ (cf. Haga, T., 1904, **85**, 78), which corresponds with its formation from potassium sulphite and potassium nitrosodisulphonate (obtained from the oxidation of potassium hydroxylaminedisulphonate) according to the equation $2O{:}N(SO_3K)_2+H\cdot SO_3K=OH\cdot N(SO_3K)_2+KSO_3\cdot O\cdot N(SO_3K)_2$. Directions are given for its preparation, starting from sodium nitrite and sodium hydrogen sulphite, using lead peroxide as an oxidising reagent in the preparation of the intermediate nitrosodisulphonate. G. W. R.

Action of Sulphite, Hydrogen Sulphite, and Sulphurous Acid on Hydroxylamine. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 225—240; from *Chem. Zentr.*, 1924, ii, 1069).—The author regards the reaction, $NH_2\cdot OH,HCl+H\cdot SO_2\cdot ONa=NH_2\cdot SO_2\cdot ONa+H_2O+HCl$, as proof of the asymmetrical constitution of sodium hydrogen sulphite. In the presence of sulphurous acid, the reaction with hydroxylamine gives, besides amidosulphonic acid, a considerable amount of ammonium sulphate, and nitrogen is evolved. It is assumed that the sulphurous acid is mainly present in the tautomeric form, $H_2{:}SO_2{:}O$, which by replacement of the hydrogen atoms may yield the diamide of a persulphuric acid, $(NH_2)_2SO_2{:}O$, and this oxidises a further 2 mols. of hydroxylamine, yielding nitrogen and sulphamide, $(NH_2)_2SO_2{:}O+2NH_2\cdot OH=(NH_2)_2SO_2+N_2+3H_2O$; the latter substance in aqueous solution decomposes into ammonia and amidosulphonic acid. It is calculated that in aqueous solution two-thirds of the sulphurous acid is present in the normal asymmetric form and one-third in the tautomeric form. The difference in constitution between hydrogen sulphites and monosulphites is also shown in the reaction with chloroamide, which in the former case yields sodium chlorosulphonate, whilst in the latter case amidosulphonic acid is formed. (Cf. also Schäfer and Köhler, A., 1919, ii, 38.) R. B.

Potassium "Nitrososulphite" [Dinitrososulphonate]. F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 108—127; from *Chem. Zentr.*, 1924, ii, 445—446).—The preparation of potassium nitrososulphite, $K_2N_2SO_5$, by the action of nitric oxide on 40% potassium sulphite solution is described. Its properties agree with the constitutional formula of Hantzsch (A., 1895, ii, 75). It is unattacked by potassium permanganate in acid solution. It is oxidised by sodium hypochlorite in the presence of small amounts of water. The usual products of decomposition are nitrous oxide and potassium

sulphate. Nitric oxide and potassium sulphite may be obtained from it by boiling with potassium hydroxide solution or by fusion. Hydrazinesulphonic acid may be obtained from it by alkaline reduction. The formation of potassium nitrososulphite can be explained by assuming, with Hantzsch, that nitric oxide before combination forms double molecules and also that both potassium atoms in potassium sulphite are joined to the sulphur atom. When nitric oxide reacts with potassium hydrogen sulphite the first product probably has the constitution $NO{\cdot}N(OK)SO_3K$, which then undergoes rearrangement. When nitric oxide is passed into potassium hydrogen sulphite solution, potassium nitrilosulphonate, $N(SO_3K)_3,2H_2O$, is formed, which decomposes on boiling, yielding potassium hydrogen sulphate and potassium amidosulphonate. The reaction between nitric oxide and potassium hydrogen sulphite may be explained by assuming the formation of potassium nitroxylsulphonate, $OH{\cdot}N{\cdot}SO_3K$, which combines further with nitric oxide, yielding potassium nitrosohydroxylaminesulphonate, $ON{\cdot}N(OH)SO_3K$, from which the potassium nitrososulphite, $ON{\cdot}N(OK)SO_3K$, is formed in alkaline solution. In the absence of alkali, potassium nitrosoaminedisulphonate is formed. In the decomposition of potassium nitroxylsulphonate, $OH{\cdot}N{\cdot}SO_3K$, hyponitrous acid and the residue, $-SO_3K$, are first formed. From the latter by simple association potassium dithionate is formed.

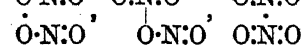
G. W. R.

Reduction of Oxides of Nitrogen in Presence of Sulphuric and Sulphurous Acids. A. Graire (*Compt. rend.*, 1925, **180**, 292—294).—A quantitative investigation of the reduction of oxides of nitrogen with a view to elucidate the mechanism of loss of nitrogen in the "lead chamber" process. Impure nitrosulphuric acid under normal conditions is not reduced further than nitric oxide by agitation over mercury, so that ferrous sulphate can effect a complete recovery of the nitrogen products. Addition of sulphur dioxide and other changed conditions result in loss of nitrogen through reduction to nitrous oxide in the liquid phase. Mixtures of nitric and sulphuric acids in presence of ferrous sulphate and sodium sulphite have been studied. Nitrous oxide is formed by the slow interaction of sulphur dioxide and nitric oxide (as $FeSO_4,NO$) in the liquid phase. Dilution increases the reduction; it is feeble in 35% sulphuric acid, but takes place readily at 25%. The product of the reaction is always nitrous oxide, nitrogen having been observed only in traces.

R. A. M.

Nitrogen Peroxide. A. Schaarschmidt (*Z. angew. Chem.*, 1924, **37**, 933—938).—Saturated aliphatic hydrocarbons are but slowly attacked by nitrogen peroxide, fatty acids being first formed and then further oxidised to oxalic acid and carbon dioxide, whilst the peroxide is reduced to nitric and nitrous oxides and ultimately to nitrogen. Branched-chain paraffins are less resistant than straight-chain paraffins. An apparatus is described for conveniently observing the reaction in a closed glass tube (which ultimately bursts) at temperatures up to 150°; there was no spontaneous

evolution of heat, but, even after the appearance of nitrogen trioxide in the tube, the mixture cooled as soon as the source of external heat was removed. With olefinic hydrocarbons (*e.g.*, amylene, *cyclo*hexene), there is immediate formation of extremely unstable isomeric nitrosates and ψ-nitrosites, accompanied, in some cases, by polymerisation products. Nitrogen peroxide, in the cold, converts benzene very slowly into picric acid, and toluene more readily into trinitrotoluene (cf. this vol., i, 123). At the same time, nitro–nitrite compounds are formed, which are decomposed by alkalis (*e.g.*, to dinitrocresol). The various ways in which nitrogen peroxide reacts lead to the assumption that it occurs as an equilibrium mixture of three forms, viz.,



W. T. K. B.

Action of Nitrogen Peroxide on Metallic Copper and its Adsorption by Cuprous Oxide. A. KLEMENC and A. SCHROTH (*Ber.*, 1925, 58, [*B*], 168—175; cf. Sabatier and Senderens, A., 1893, ii, 374; Tartar and Semon, A., 1921, ii, 336; Park and Partington, A., 1924, ii, 183).—The action of nitrogen peroxide on specially prepared copper at the atmospheric or somewhat reduced pressure gives a product in which the value of the atomic ratio O : N is about 3. If the gas is used under increased pressure, an entirely different product is obtained in which the ratio O : N is 6·5. If nitrogen peroxide is passed several times over the same specimen of copper from which the adsorbed gas is removed after each passage, the quantity of adsorbed gas diminishes at the second passage and subsequently becomes approximately constant. It is therefore suggested that two actions occur simultaneously consisting in the adsorption of nitrogen peroxide by metallic copper and the oxidation of copper to cuprous oxide which also adsorbs nitrogen peroxide. The adsorptive capacity of the element for nitrogen peroxide appears to be greater than that of its oxide. "Nitro-copper" as postulated by Sabatier and Senderens (*loc. cit.*) does not appear to exist and the other "nitrometals" cannot be regarded as chemical individuals. The adsorption isotherm of the system Cu_2O–NO_2, passes through a maximum at about 1·6 atm.

H. W.

Hydrogen Persulphide. O. VON DIENES (*Annalen*, 1924, 440, 213—214).—Hypophosphorous acid solution reduces sulphur dioxide, both as a gas and in aqueous solution, to a product from which hydrogen persulphide may be extracted with ether, a solution of large quantities of sulphur in the persulphide remaining undissolved. Before the persulphide separates from the ether solution, crystals of monoclinic monosymmetric β-sulphur form as small, transparent, nacreous plates, which rapidly form tufts of monoclinic needles and change to pseudomonoclinic rhombic sulphur. The sulphur henceforth separates in rhombic form on the edges of these crystals (cf. A., 1885, 1037).

S. K. T.

Formation and Decomposition of Polythionates. F. FOERSTER (*Z. anorg. Chem.*, 1924, **141**, 228—230; cf. *ibid.*, 1924, **139**, 246; Foerster and Hornig, A., 1923, ii, 23).—Besides the course indicated by the equation $2SO+H_2O \rightleftharpoons S_2O_3'' + 2H^{\cdot}$, *i.e.*, by the formation of thiosulphuric acid, the intermediate product SO may lead to the production of polythionic acids by other changes, *e.g.*, $SO+2S_2O_3'' + 2H^{\cdot} \rightarrow S_5O_6'' + H_2O$, and $SO+2HSO_3 \rightarrow S_3O_6'' + H_2O$, analogous to those known in the case of selenium oxide, SeO.

S. I. L.

Formation and Decomposition of Polythionates. E. H. RIESENFELD (*Z. anorg. Chem.*, 1924, **141**, 109—110).—A reply to Foerster's criticism (this vol., ii, 148) of Josephy's paper (A., 1924, ii, 470). The constitution of the intermediate compounds in the formation and decomposition of polythionates is discussed.

L. L. B.

Preparation and Properties of Polythionic Acids. F. RASCHIG (*Schwefel- u. Stickstoff-studien*, 1924, 273—304; from *Chem. Zentr.*, 1924, ii, 1065—1068).—Pentathionic acid is prepared by the action of hydrochloric acid on cooled aqueous sodium thiosulphate in the presence of sodium arsenite; sodium pentathionate gradually separates on concentration of the filtrate at 35°. The filtrate, which still contains 12% of the sodium salt, contains 60% of pentathionic acid, $H_2S_5O_6$, free from tetrathionic or trithionic acids, and is practically unchanged after 2 months. The *potassium* salt has been obtained. Pentathionic acid is oxidised to sulphuric acid, quantitatively by potassium chlorate and hydrochloric acid, slowly by acidified potassium permanganate. With sodium carbonate, the pentathionate slowly deposits sulphur; under suitable conditions, the reaction, $K_2S_5O_6 \rightarrow K_2S_4O_6+S$, is quantitative. Antimony and tin, like arsenic, prevent the separation of sulphur on acidifying sodium thiosulphate solutions. In the presence of sodium dihydrogen arsenite, the decomposition $Na_2S_2O_3+2HCl \rightarrow 2NaCl+SO_2+S$ was reduced from 88·8 to 13% of the reaction, pentathionic acid being formed to the extent of 85—90%. The intermediate formation of a dipentathionic acid, $H_4S_{10}O_{12}$, is assumed. The author represents the formation of pentathionic acid in Wackenroder's solution as being due to the condensation of five SO groups (cf. following abstract) arising from the reaction: $SO_2+H_2S=SO+S+H_2O$, addition of water yielding pentathionic acid of the structure

$$\begin{array}{c} \text{S}\!:\!\text{S}\!:\!\text{S} \\ \| \quad\quad \| \\ \text{OH}\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{OH} \end{array}$$

The alternative reaction, $2SO_2+H_2S=3SO+H_2O$, is excluded, whilst with excess of hydrogen sulphide the reaction proceeds smoothly according to the equation, $2H_2S+SO_2=3S+2H_2O$. Hyposulphurous acid is not formed, and the author accounts for the formation of pentathionic acid from sodium thiosulphate by suggesting decomposition to the group $S{:}SO_2$, which polymerises to $S_{10}O_{10}$.

Potassium tetrathionate is obtained by the oxidation of sodium thiosulphate with cupric sulphate: $3Na_2S_2O_3+2CuSO_4=Cu_2S_2O_3+2Na_2SO_4+Na_2S_4O_6$, and treatment of the concentrated filtrate with potassium acetate. The potassium tetrathionate which separates is washed with alcohol. With sodium carbonate, the first reaction is: $4Na_2S_4O_6+4Na_2CO_3=6Na_2S_2O_3+Na_2S_3O_6+Na_2SO_4+4CO_2$. Tetrathionate is the first stage in the preparation of sodium trithionate by Willstätter's method (A., 1903, i, 543). Better yields are, however, obtained by the reaction $Na_2S_2O_3+2NaHSO_3+2SO_2=2Na_2S_3O_6+H_2O$ in the presence of sodium arsenite. Acid potassium permanganate oxidises two-thirds of the trithionate sulphur to sulphate, the remainder forming dithionic acid. Alkaline permanganate oxidises thiosulphate to sulphate, whilst sodium hypochlorite in acid solution gives partly sulphate and partly tetrathionate. The action of sodium sulphide on sodium hydrogen sulphite is in accordance with the equation $6NaHSO_3+2Na_2S=2Na_2SO_3+3Na_2S_2O_3+3H_2O$. R. B.

Constitution of Polythionic Acids. F. Raschig (*Schwefel- u. Stickstoffstudien*, 1924, 305—310; from *Chem. Zentr.*, 1924, ii, 1068).—The following structural formulæ are proposed for sodium tetra-, $NaO\cdot\overset{\overset{S}{\|}}{SO_2}\cdot\overset{\overset{S}{\|}}{SO_2}\cdot Na$, tri-, $NaO\cdot\overset{\overset{S}{\|}}{SO_2}\cdot SO_2\cdot Na$, and penta-thionate, $NaO\cdot\overset{\overset{S:S:S}{\|}}{SO_2}\cdot\overset{\overset{\|}{}}{SO_2}\cdot ONa$, and dithionic acid, $HO\cdot SO_2\cdot SO_2\cdot OH$. R. B.

Complex Chromium Ammonium Compounds. P. Rây and P. B. Sarkar (*J. Indian Chem. Soc.*, 1924, 1, 91—99).—By the action of ammonium thiosulphate and ammonia on chromium hydroxide, two compounds have been prepared which are the first examples to be described of trinuclear chromium ammonium compounds: *Decamminemonoaquotrihydroxydioltrichromium thiosulphate*, $[Cr(OH)_3,2CrOH(NH_3)_5,H_2O](S_2O_3)_2,xH_2O$, reddish-violet crystals and *enneamminediaquotrihydroxydioltrichromium thiosulphate*, $[Cr(OH)_3,CrOH(NH_3)_5,CrOH(NH_3)_4H_2O,H_2O](S_2O_3)_2,2H_2O$, pinkish-violet crystals. The behaviour of these substances with a number of reagents is described and the arguments for the constitutions proposed are discussed. G. M. B.

Sulphates of Quadrivalent Uranium. R. J. Meyer and H. Nachod (*Annalen*, 1924, 440, 186—199).—Uranous sulphate octahydrate, $U(SO_4)_2,8H_2O$, is obtained by reducing a saturated solution of uranyl sulphate containing 2 mols. of concentrated sulphuric acid per mol. of crystalline salt, by Rosenheim and Lobel's electrolytic method (A., 1908, ii, 294) and either precipitating the solution with alcohol or evaporating at 75° or over sulphuric acid. Evaporation at 93—95° gives the tetrahydrate, which is also obtained by gradually adding concentrated sulphuric acid to the reduced solution between 0° and 70° until precipitation ceases. The precipitation of the two salts from solution depends only on the acidity of the latter.

The octahydrate is converted irreversibly into the tetrahydrate

at 68° (cf. A., 1905, ii, 827). It is less soluble in 0·1*N*-sulphuric acid than in water; the tetrahydrate below 55° is more soluble, indicating the presence of complex ions. The solubility curves for the two salts in sulphuric acid solution intersect at 26°, but this is not a transition point. Both hydrates are stable in solution between 15° and 92°. Freezing-point depression measurements show that the tetrahydrate has twice the molecular weight of the octahydrate in *N*/8—*N*/32-solutions in 0·1*N*-sulphuric acid.

S. K. T.

Iron Carbonyls. H. FREUNDLICH and W. MALCHOW (*Z. anorg. Chem.*, 1924, **141**, 317—324).—All three carbonyl compounds, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe(CO)_4$, when treated with sodium ethoxide in alcoholic solution, give red compounds soluble in water, and apparently hydrates; that from iron pentacarbonyl is thought to have the composition $Fe(CO)_5,2H_2O$. The tetracarbonyl is the most stable, and is readily prepared from the red compounds. No other derivatives of the carbonyls could be obtained. Resemblances between the carbonyls and the chlorides of bivalent molybdenum and ruthenium are pointed out. S. I. L.

Reaction between Potassamide and Salts of Cobalt and Iron in Liquid Ammonia. F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1924, **46**, 2631—2636).—Potassamide acts on cobaltous thiocyanate in liquid ammonia to give *cobaltous amide*, $Co(NH_2)_2$, which loses ammonia when heated above 120° to yield *cobaltous nitride*, Co_3N_2, a black solid almost unaffected by water. *Ferrous tetramminethiocyanate*, $Fe(SCN)_2,4NH_3$, is obtained by the action of iron wire on mercuric thiocyanate in liquid ammonia solution. Potassamide converts this salt into a slightly impure *ferrous nitride*, Fe_3N_2, which is also obtainable by treating ferrous bromide with potassamide and then with a solution of ammonium thiocyanate. The action of potassamide on a number of other salts of cobalt and iron has been examined, but no definite products were isolated.

G. M. B.

Solubility of Nickel in Water containing Carbon Dioxide. R. ROBL (*Z. angew. Chem.*, 1924, **37**, 938—939).—Commercially pure nickel (Fe 0·8%, Cu 0·4%) is appreciably attacked by water containing carbon dioxide, nickel carbonate being formed.

W. T. K. B.

Isomeric Potassium Pentachlororuthenites. A. GUTBIER and W. NIEMANN (*Z. anorg. Chem.*, 1924, **141**, 312—316; cf. Aoyama, A., 1924, ii, 771).—There is no ground for supposing the existence of a new γ-form; material prepared by the method of Howe (A., 1902, ii, 86) is found to have the properties ascribed by Aoyama to the γ-form, though Howe's product was named by Aoyama the β-form. S. I. L.

Osmium Tetroxide. H. VON WARTENBERG (*Annalen*, 1924, **440**, 97—110).—Osmium may be obtained from alkaline solutions containing the tetroxide by heating with alcohol, mixing the pre-

cipitated hydrated osmium dioxide with sodium chloride (to prevent explosions) and vaporising at 150°, finally reducing in hydrogen for ½ hour at red heat. The latter operation is then repeated after washing. By burning hydrogen in oxygen containing osmium tetroxide, the dioxide is formed and may then be reduced to the metal.

One hundred g. of water dissolve 6·47 g. of osmium tetroxide at 18°; 100 g. of carbon tetrachloride dissolve about 250 g. at 20°. Hence the oxide may be extracted from slightly acid solutions by shaking with carbon tetrachloride; it may be completely removed from the latter solution by shaking with sodium hydroxide. Osmium is precipitated from the alkaline solution, which probably contains $HOsO_5$ ions, by platinum saturated with adsorbed hydrogen. The yellow colour given with alkali solution will detect 0·001% of the tetroxide in aqueous solution. Water does not wet the oxide.

The vapour-pressure curves of the solid and liquid oxide, which are given by $\log p(\text{atm.}) = -13500/4{\cdot}57T + 7{\cdot}83$ and $\log p(\text{atm.}) = -10100/4{\cdot}57T + 5{\cdot}49$, respectively, run parallel with the corresponding curves for water up to the critical temperature. The interpolated m. p. is 40·1° and b. p. 129°. The critical data are: $t_c = 404{\cdot}8°$ (surface tension data, assuming linear dependence on the temperature, gave 390°); $v_c = 0{\cdot}007$ and p_c, calculated from van der Waals' vapour-pressure equation by assuming the constant for water (an associated liquid) to hold for osmium tetroxide, 170 atm. Application of the Eötvös rule shows the fused oxide to be non-associated.

The molecular latent heat of fusion, determined by Schottky's method (*Physikal. Z.*, 1909, **10**, 634), is 3·41 (±2%) Cals. in agreement with the vapour-pressure measurements. The characteristic odour of the oxide first becomes apparent when its concentration is 2×10^{-5} mg. per c.c. Other physical constants are: n^{45} 1·56; κ(specific conductivity) for liquid $< 1 \times 10^{-11}$ rec.-ohms; d^{42} 4·44 and d^{22} 4·91; coefficient of expansion 0·00102. The heat of formation from the elements is 93·37 (±1·5%) Cal.; the vapour is quite stable up to 1500°. S. K. T.

Compounds of Carbon Monoxide with Osmium Chloride. W. Manchot and J. König (*Ber.*, 1925, **58**, [*B*], 229—232).—Osmium trichloride reacts with moist or dry carbon monoxide at 270°, giving a crystalline sublimate which is separated by boiling carbon tetrachloride into a *compound*, (?) $Os(CO)_3Cl_2$, m. p. 269—273°, and a more soluble substance, m. p. 252°, which has not been fully investigated. The main product, $Os(CO)_2Cl_2$, is characterised by unusual stability. H. W.

Metal-Carbon Monoxide Salts. IX. Compound of Carbon Monoxide with Iridium Chloride. W. Manchot and H. Gall (*Ber.*, 1925, **58**, [*B*], 232—234).—Iridium trichloride is converted by carbon monoxide at 150° into the *compound*, $IrCl_2(CO)_2$, m. p. 140°, which differs from the other compounds of the metals of the platinum group (cf. this vol., ii, 149 and preceding abstract) in its instability particularly towards moisture, by which it is hydrolysed

to iridium oxide or hydrate, hydrochloric acid, and carbon monoxide. H. W.

Preparation of Pure Hydrogen. V. BAYERLE and M. TAMELE (*Chem. Listy*, 1924, **18**, 389—390).—Amalgamated zinc does not dissolve in dilute acids owing to the high overvoltage of the hydrogen; contact with a platinum sheet, however, immediately induces a rapid evolution of hydrogen from the platinum. An apparatus is described and illustrated which allows a continuous supply of pure hydrogen under considerable pressure to be obtained by making use of this reaction. A. R. P.

Displacement of Alkali Metals by Iron. L. HACKSPILL and R. GRANDADAM (*Compt. rend.*, 1925, **180**, 68—70).—When heated in a vacuum, iron can displace the alkali metals from their salts or hydroxide. With the chlorides, bromides, and iodides of sodium or potassium, the reaction is slight owing to the volatility of the halides, but, with the less volatile fluorides, a copious yield of alkali metal can be obtained. The sulphates are attacked by iron at 1000°, the first reaction being according to the scheme $M_2SO_4+Fe=FeSO_4+2M$, followed by the decomposition of the ferrous sulphate to give ferric oxide. Potassium carbonate reacts with iron at 800—900° according to the equation $2K_2CO_3+2Fe=Fe_2O_3+CO+CO_2+4K$, whilst, with the hydroxide, a yield of 70—80% of the theoretical can be obtained at 600—650°. W. H.-R.

Hafnium Oxide in Tungsten Filaments. J. A. M. VAN LIEMPT (*Nature*, 1925, **115**, 194).—A mixture of tungstic oxide with a solution of hafnium nitrate, when dried, heated, and reduced with hydrogen, yields tungsten powder of definite hafnium oxide content. On sintering in hydrogen, a portion of the hafnium oxide is reduced; the hafnium combines with the tungsten and influences recrystallisation. A. A. E.

Ultra-centrifuge. T. SVEDBERG and H. RINDE (*J. Amer. Chem. Soc.*, 1924, **46**, 2677—2693; cf. A., 1924, ii, 97).—The "ultra-centrifuge" here described is an apparatus designed for the study of the changes taking place in fine-grained sols during centrifuging. By direct or photographic observation of the changes of concentration of the sol, or of the boundary between clear dispersion medium and sol, with time, data are obtained from which, by means of a modified Stokes' law, the size and distribution of size of particles can be calculated. The results of measurements with a fine-grained gold sol are given, the radius values obtained being from 11 to 38% higher than those arrived at by means of Zsigmondy's nuclear method. The ultra-centrifuge has also been used to study the protective action of gelatin on a gold sol, and maximum and minimum values for the thickness of the adsorbed gelatin layer are calculated. G. M. B.

Method of Determining the Solubility of Gases in Liquids. W. MANCHOT (*Z. anorg. Chem.*, 1924, **141**, 38—44).—An apparatus is described for the determination of gas solubilities in salt solutions,

which consists of a modification of Ostwald's arrangement. A device is introduced to avoid the error arising from the difference of vapour pressure in the apparatus before and after the experiment.

L. L. B.

Experimental Technique of Photochemistry. I. The Quartz Mercury Lamp as a Photo-chemical Light Source. L. REEVE (*J. Physical Chem.*, 1925, 29, 39—57).—The total radiation of a quartz mercury lamp grows rapidly with increase of voltage and depends greatly on the degree of cooling of the lamp. The intensities of various portions of the spectrum do not grow with wattage at the same rate, and, on the whole, the infra-red and extreme ultra-violet grow the fastest. The radiation is affected by adsorption by the luminous mercury vapour inside the lamp and therefore the dimensions of a lamp will affect its energy characteristics. The falling off in efficiency with age, due to devitrification and discoloration of the quartz, is most marked in the extreme ultra-violet.

M. B. D.

Extraction Apparatus for Solid Substances at a Raised Temperature. H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1924, [ii], **108**, 355—357).—A simple apparatus is described in which a solid is extracted by circulation of a small amount of solvent. As this acts at its b. p., it is claimed that the extractor is more efficient than that of Soxhlet. [Cf. *B.*, 1925, 115.]

F. M. H.

Mineralogical Chemistry.

Radial Distribution of certain Elements in the Earth. H. S. WASHINGTON (*J. Washington Acad. Sci.*, 1924, **14**, 435—442).—The central core of the earth is composed of nickel-iron which gradually merges into a shell of silicates. Orthosilicates lie nearest the centre, but silication increases towards the surface so that metasilicates, alkali polysilicates, and pure silica are obtained. Progressions in other constituents may also be observed. Iron and magnesium as silicates increase at first from the border of the nickel-iron core until they reach a maximum in the metal-free shell composed chiefly of olivine and pyroxene. Above this, they decrease steadily until they are almost negligible in the granitic upper part of the crust. As regards the relative progression of calcium, sodium, and potassium, calcium begins to appear near the core with very little sodium and no potassium. It reaches a maximum and then falls off towards the surface, whilst sodium becomes more important, and potassium finally appears about the middle of the crustal shell and gradually becomes more abundant than sodium. The elements in the order of abundance which make up 98·6% of the earth's crust are: oxygen, silicon, aluminium,

iron, calcium, sodium, potassium, and magnesium. The earth as a whole is composed chiefly of seven elements. These are in order of abundance iron, oxygen, silicon, magnesium, nickel, calcium, and aluminium. M. S. B.

Radioactivity of Gases Emitted from Vesuvius and the Solfataras of Campania and their Influence on the Development of Bacteria and Higher Plants. J. STOKLASA and J. PENKAVA (*Compt. rend.*, 1924, 179, 819—822).—The conductivity of the atmosphere varies from point to point, reaching a maximum in volcanic districts; this maximum is nearly equalled by the values given by air taken from the neighbourhood of potash mines. The β- and γ-rays derived from radioactive substances of volcanic origin and also from potassium accelerate photosynthesis in cells containing chlorophyll. The mechanism is based on the decomposition of potassium hydrogen carbonate, under the influence of light and radioactivity, into formic acid, oxygen, and potassium carbonate with subsequent decomposition of the formic acid into formaldehyde and oxygen. Radioactivity in soil or atmosphere favours development of *Leguminosæ* and of nitrogen-fixing bacteria. H. J. E.

New Mineral: Dussertite. J. BARTHOUX (*Compt. rend.*, 1925, 180, 299—301).—Dussertite, an arsenical mineral from Djebel Debar mountain (Algeria), exists as minute rhombohedral or hexagonal green crystals, *d* 3·75, hardness 3·5. A typical analysis is: As_2O_3, 31·90%; Fe_2O_3, 31·24%; CaO, 22·03%; H_2O, 10·61%, with smaller quantities of ferrous iron, magnesia, alumina, and sulphate; the mineral is regarded as similar to arseniosiderite, $[AsO_4]_2(Fe\mathit{Al})_3(Ca\mathit{Mg})_3[OH]_9$. The other properties with the exception of birefringence (0·012) confirm this view. R. A. M.

Crystal Structure, Chemical Analysis, and Dehydration of Becquerelite and Schoepite. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, 33, 578—587).—The axial ratios of becquerelite are $a : b : c = 0·5537 : 1 : 0·5938$; characteristic faces are (101), (102), (021), (110), (001), (305); the cleavage is perfect parallel to (001) and nearly perfect parallel to (101). Characteristic faces of schoepite are (001), (100), (111), (124), (122), (110), (021). Both minerals contain uranium trioxide, lead oxide, and water, together with small amounts of tellurium trioxide, sulphur trioxide, ferric oxide, and silica; becquerelite contains more than 5% of lead oxide, whilst schoepite rarely contains as much as 1%. The former mineral loses half its water at 150° and the remainder at 500°, whilst the latter loses half at 110° and the remainder at 325°. Neglecting impurities, the composition of each mineral agrees with the formula $UO_3,2H_2O$; the minerals therefore represent dimorphous forms of the dihydrate of uranium trioxide. A. R. P.

Sklodowskite, a New Uranium Mineral and its Relation to Uranotile. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, 33, 562—570).—The fibrous radiated nodules of sklodowskite previously described (A., 1924, ii, 868) have *d* 3·54 and contain 13·33% H_2O, 13·49% SiO_2, 67·25% UO_3, 1·91% MgO, 2·57% CaO, and 1·27%

CoO. The compact form of the mineral is of a pale yellow colour, opaque and hard; it has no cleavage; in thin splinters it has n 1·64 and d 3·74. This form contains nearly 4% MgO and 2·64% TeO_3 but no calcium or cobalt. A citron-yellow, translucent, crystalline variety has also been found; the crystals are long, slender, orthorhombic prisms terminated by pyramids and contain 3·74% MgO, 1·08% TeO_3, and 1·97% of alkali oxides together with a little nickel. The mineral loses about half its water at 110°, but the remainder is not expelled completely below 500°. Its composition agrees most closely with the formula $MgO,2UO_3,2SiO_2,7H_2O$, and it is, therefore, the magnesium analogue of uranotile. A. R. P.

Chemical Composition of Fourmarierite. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, **33**, 558—562).—Fourmarierite is a reddish-brown mineral found associated with other uranium minerals in the Belgian Congo. It crystallises in the orthorhombic system, exhibits dichroism, and has a perfect cleavage perpendicular to the inclined axis. Its chemical constitution is most nearly represented by the formula $PbO,4UO_3,5H_2O$, but, as the proportion of lead varies somewhat, the author prefers to formulate it as $(Pb,UO_2)O,H_2O$. No water is lost at 100°, but all the water and some oxygen are expelled at 350°. Some specimens contain as much as 0·67% of tellurium trioxide, and there is always a small quantity of ferric oxide present. A. R. P.

Analytical Chemistry.

Universal Commutator for Potentiometric Measurements by the Compensation Method. A. ERNEST (*Chem. Listy*, 1924, **18**, 250—251). W. A. S.

Hydrogen Electrode Technique. J. P. BAUMBERGER (*J. Lab. Clin. Med.*, 1924, **9**, 720—722).—As the hydrogen electrode, a platinum wire spiral flattened while hot is recommended. Potassium chloride agar (2%) solution is preferred to saturated potassium chloride solution as a contact liquid. A device for rocking a Clark hydrogen electrode is described. CHEMICAL ABSTRACTS.

Scrubber for Ammonia Distillates. A. G. MURRAY (*J. Amer. Pharm. Assoc.*, 1924, **13**, 423).—The apparatus is designed to fit in the neck of a Kjeldahl flask. The steam enters the scrubber through an opening near the top, passes down to the bottom and up through the neck to the condenser. The pocket of water is maintained by an outlet tube a short distance from the bottom, which ends in a fish-hook-shaped bend below. CHEMICAL ABSTRACTS.

Apparatus for the Precipitation of Barium Sulphate. A. G. MURRAY (*J. Amer. Pharm. Assoc.*, 1924, **13**, 424).—The apparatus consists of a cup drawn to a capillary tube at the lower

end to permit a discharge of 2—3 drops per sec. The cup has a broad rim to rest in the neck of a capacious Erlenmeyer flask. The sulphate solution is boiled and the dilute barium chloride solution placed in the cup from which it is delivered hot.

CHEMICAL ABSTRACTS.

Apparatus for the Determination of Urea by the Urease Method. A. A. HORVATH (*J. Lab. Clin. Med.*, 1924, 9, 722—723).—The modification consists of a device for regulating the pressure.

CHEMICAL ABSTRACTS.

Röntgen Spectroscopic Method of Quantitative Analysis. P. GÜNTHER and G. WILCKE (*Annalen*, 1924, 440, 203—212).—A simple *X*-ray spectroscopic method of quantitative analysis is described in which a small induction coil is used as the generator of energy. The spectrum lines are photographed and their relative intensities measured by counting the silver particles per unit area. The results agree to about 2% with those obtained gravimetrically.

S. K. T.

Possibility of Determining Spectrophotometrically Substances Oxidisable by Permanganate. H. GOMBOS (*Biochem. Z.*, 1924, 151, 1—6).—A spectrophotometric examination of solutions of potassium permanganate with the view of utilising the method as a quantitative measure of oxidisable substances. J. P.

Influence of Alcohol, Salts, and Temperature on the Change Point of some Indicators and Means of Avoiding Errors in Acidimetric Titrations. A. RICHTER (*Z. anal. Chem.*, 1924, 65, 209—245).—The dissociation constant of dimethyl-yellow in pure water is $1{\cdot}22 \times 10^{-11}$ and is increased by the addition of sodium chloride to $2{\cdot}61 \times 10^{-11}$ in *N*-solution. The temperature factor is considerable, the dissociation constant increasing to $12{\cdot}0 \times 10^{-11}$ at 75° in water and to $24{\cdot}9 \times 10^{-11}$ in *N*-sodium chloride. With 0·1*N*-hydrochloric acid, the correction to be applied for the indicator increases from 0·15 c.c. at 20° to 0·34 c.c. at 80°; in the presence of sodium sulphate the correction increases from 0·23 c.c. to 2·0 c.c. in 0·1*N*-solution and to 4·8 c.c. in 0·5*N*-solution. Carbon dioxide has very little influence on the transition range of this indicator, the effect rarely amounting to the equivalent of 0·1 c.c. of 0·1*N*-acid. The dissociation constant of bromophenol-blue rises from $0{\cdot}85 \times 10^{-4}$ in pure water to $1{\cdot}9 \times 10^{-4}$ in *N*-sodium chloride and these figures are altered only slightly by increase of temperature or by the presence of alcohol. The smallest indicator correction is required when the solution contains half its volume of alcohol. The sensitivity of phenolphthalein to alkalis falls with increase of temperature, but this effect may be appreciably diminished by addition of sodium sulphate and increased by the presence of excessive amounts of alcohol. A theoretical discussion of the results is given together with tables of corrections for the three indicators examined.

A. R. P.

Sodium Arsenite as a Reagent for Loosely-combined Halogen. A. GUTMANN (*Z. anal. Chem.*, 1924, 65, 246—254).—Sodium arsenite in alkaline solution reacts with many organic compounds containing loosely-combined halogen atoms and with some non-metallic halides to form sodium arsenate, sodium halide, and derivatives of the compounds used containing less halogen. This reaction may be utilised as a test for the presence of loosely-combined halogen atoms and in some cases serves as a means of determining the compound tested. The following examples are described showing the action of alkaline arsenite: Iodoform is converted into methylene iodide, showing that only one of its iodine atoms is present in the labile, tervalent form. Similarly, di-iodophenol iodide is converted into di-iodophenol, but the isomeric tri-iodophenol is unattacked. Phenyl iododichloride is reduced to iodobenzene, dibromourethane to ethyl alcohol, ammonia, and carbon dioxide, and *p*-toluenesulphochloroamide to ammonia and the corresponding amine. Nitrogen halides are converted into ammonia, whilst halogen azides and cyanides yield salts of the corresponding acids. Sulphur monochloride converts sodium arsenite into sulphoxyarsenate with the simultaneous formation of sulphite and chloride. A. R. P.

Universal Indicator for the Colorimetric Determination of p_H Values in Soil Experiments. H. NIKLAS and A. HOCK.—(See i, 348.)

Occurrence of Iodine in Nature. II. Determination of Minute Quantities of Iodine. T. VON FELLENBERG.—(See i, 329.) **III. Iodine Determinations on Foodstuffs, Manures, and Swiss Mineral Waters.** T. VON FELLENBERG.—(See i, 347.)

Mohr's Method for Determination of Silver and Halogens in other than Neutral Solutions. H. W. DOUGHTY (*J. Amer. Chem. Soc.*, 1924, 46, 2707—2709).—Chlorides may be titrated accurately with silver nitrate in any acid solution using potassium chromate as indicator provided that the p_H value is first reduced to between 5 and 7 by addition of a sodium acetate–acetic acid (2 mol. : 1) buffer mixture. G. M. B.

Absorbent for Oxygen in Gas Analysis. L. F. FIESER (*J. Amer. Chem. Soc.*, 1924, 46, 2639—2647).—The completeness and the rapidity of the action of an alkaline solution of sodium hyposulphite for absorbing oxygen are increased by the addition of 2% of sodium anthraquinone-2-sulphonate. G. M. B.

Sensitive, Qualitative Method for the Detection of Oxygen with Pyrogallol and Potassium Hydroxide. H. SCHMALFUSS and H. WERNER (*Ber.*, 1925, 58, [*B*], 71—73; cf. Schmalfuss, A., 1923, ii, 783).—The gas under investigation is placed in a sealed glass bulb inside a bottle containing a few drops of water and a piece of filter-paper moistened with potassium hydroxide solution. The bottle is closed by a rubber stopper which holds an inverted glass

"mushroom," on the top of which a few grains of moistened pyrogallol are placed. The apparatus is evacuated at 20° until the air has been replaced completely by water vapour. It is then quickly shaken so that the pyrogallol falls on to the filter-paper, after which the bulb is broken. In the presence of 0·008% of oxygen, the paper acquires a pale pink tint within 2 minutes; with higher concentrations it becomes bluish-violet, pale brown, and dark brown. Accurate results are obtained in the presence of nitrogen, hydrogen, acetylene, carbon monoxide, nitrous oxide, nitric oxide, and ammonia, but not of carbon dioxide, sulphur dioxide, hydrogen sulphide, hydrogen cyanide, cyanogen, chlorine, or bromine.

H. W.

Iodometric Analysis of a Mixture of Sulphide, Sulphite, and Thiosulphate. A. KURTENACKER and K. BITTNER (*Z. anorg. Chem.*, 1924, **141**, 297—303).—A measured volume of the solution is allowed to flow into an excess of iodine solution in presence of acid, and the excess determined with thiosulphate. A second fraction is treated with zinc acetate and, without filtration, formaldehyde, and then added to excess of iodine solution; the back titration gives the iodine required by the sulphide and thiosulphate. If the zinc sulphide precipitate be filtered off, formaldehyde added to the filtrate, and the determination repeated, only the thiosulphate reacts.

S. I. L.

Electrometric Titration of Hydrazine and its Salts. E. C. GILBERT (*J. Amer. Chem. Soc.*, 1924, **46**, 2648—2655).—From the absence of any second point of inflexion in the titration curves of hydrazine in various concentrations with acids the conclusion is reached that the second dissociation constant of hydrazine hydrate is less than 1×10^{-12}, as compared with the value $2{\cdot}8 \times 10^{-13}$ calculated by Kolthoff (A., 1924, ii, 871). Curves for the titration of hydrazine salts with bases are very similar to that obtained with ammonium hydrogen sulphate. Curves were also obtained for the titration of hydrazine with iodine and with potassium bromate, and the incidental discovery is recorded that hydroxylamine is completely oxidised by bromate either to nitrate or to nitrous oxide, depending solely on the order of mixing of the reagents.

G. M. B.

Volumetric Determination of Sulphate in Minute Amounts. K. KLINKE (*Biochem. Z.*, 1924, **154**, 171—175).—Andrews' volumetric method for determining sulphate (A., 1890, 414) is modified and an attempt made to calculate the amount of sulphate with the help of the mass law. This failed and an empirical method is adopted. The author claims the limit of 0·01 mg. of sulphur.

P. W. C.

Determination of Blood Urea-Nitrogen. W. G. KARR.—(See i, 323.)

Ammonia Content and Ammonia Formation of Blood. J. K. PARNAS and J. HELLER.—(See i, 323.)

Determination of Nitrates. P. L. HIBBARD (*Ind. Eng. Chem.*, 1925, **17**, 58).—Satisfactory results can be obtained with Scales' method only if any sodium carbonate present in the magnesium oxide is neutralised; Devarda's method is more trustworthy. [Cf. *B.*, 1925, 154.] C. I.

Detection of Nitrates and Perchlorates. C. S. MARVEL and V. DU VIGNEAUD (*J. Amer. Chem. Soc.*, 1924, **46**, 2661—2663).—α-Phenyl-β-diethylaminoethyl *p*-nitrobenzoate may be used in the form of its hydrochloride for detecting nitrates in 0·005*N*-solution and perchlorates in 0·0025*N*-solution. The only other common anions which interfere are iodides, oxalates, thiocyanates, and dichromates. The solubilities of the *perchlorate*, m. p. 144°, and of the nitrate are too great for their use in an accurate gravimetric determination. G. M. B.

Determination of Arsenic in "Salvarsan" and its Congeners. A. KIRCHER and F. VON RUPPERT (*Arch. Pharm.*, 1924, **262**, 613—614).—The earlier method (A., 1921, ii, 130) is improved by using potassium bromate instead of iodine in titrating the arsenious acid produced when the substance is decomposed by boiling with sulphuric acid and potassium sulphate. [Cf. *B.*, 1925, 188.] W. A. S.

Chromic Acid Method for Determining Organic Carbon J. W. WHITE and F. J. HOLBEN (*Ind. Eng. Chem.*, 1925, **17**, 83—85).—Organic carbon either in the dry state or in solution can be accurately determined by chromic acid oxidation, provided that the acid mixture is boiled. The sulphur trioxide fumes produced are absorbed in a U-tube placed at the beginning of the absorption train and containing glass wool moistened with 98·3% sulphuric acid. The oxidation is carried out in a Knorr's apparatus with 10 c.c. of 34% chromium trioxide solution and 50 c.c. of sulphuric acid (*d* 1·84). The method is especially suitable for the analysis of soils and soil extracts which need not be evaporated. [Cf. *B.*, 1925, 156.] C. I.

[Analysis of Coal.] Three Point Method with Rapid Cooling. D. J. W. KREULEN (*Chem. Weekblad*, 1925, **22**, 28—29).—The method of determining volatile matter in coal by fixing three points on the curve showing loss of weight plotted against time under specified conditions (Delmarcel and Mertens, *Bull. Féd. Ind. Chim. Belg.*, Oct. and Nov., 1921) is modified by cooling the crucible in water, when fixing the first point, to arrest the decomposition suddenly. S. I. L.

Polarimetric Determination of Inactive Substances: Potassium. A. WRÓBEL (*Roczniki Chemji*, 1924, **4**, 287—294).—When a solution containing sodium hydrogen tartrate and ammonium molybdate is treated with a potassium salt, the reaction of the latter with the tartrate results in depression of the optical rotation of the liquid, the extent of this depression serving as a means of determining the amount of potassium used. [Cf. *B.*, 1925, 192.] T. H. P.

Determination of Sodium in Aluminium. D. M. FAIRLIE and G. B. BROOK (*J. Inst. Metals*, 1924, **32**, 283—289).—The aluminium is removed as crystals of nitrate from a strong nitric acid solution of the metal containing mercuric chloride; the sodium in the mother-liquor is converted into impure sulphate by ignition with sulphuric acid, the amounts of impurities present being determined by a separate analysis and deducted from the weight of the sodium salt. Ninety % of the sodium is extracted by this method; a further 5% is extracted by repeating the process on the aluminium nitrate crystals. The percentage error is large when the sodium content is very low. S. K. T.

Simple Clinical Micro-method for Determining Sodium in Blood-serum. F. LEBERMANN.—(See i, 324.)

Determination of Radium in Uranium Minerals Containing Tantalum, Niobium, and Titanium. (MME.) P. CURIE (*Compt. rend.*, 1925, **180**, 208—211.—Generally the extraction of radium with the barium sulphate is the most certain of action. A mixture of the mineral with barium sulphate is fused with potassium hydrogen sulphate, the mass is extracted with water, and the residue treated with dilute hydrofluoric acid which leaves the barium sulphate containing the radium, the small portion of the latter which passes into solution being precipitated by the addition of sulphuric acid and barium chloride. The barium sulphate is converted into chloride by way of the carbonate, and its radium content is determined by transferring the emanation produced in a given time to an ionisation chamber by means of a current of air (cf. A., 1910, ii, 476). The accuracy of the method is 1% for radium contents of 10^{-6}—10^{-8} g. per g. of mineral, and slightly less for those of 10^{-8}—10^{-9} g. The residue obtained by the evaporation of the hydrofluoric acid solution may contain protoactinium accounting for 1% of the radioactivity of the mineral. J. W. B.

Electrolytic Determination of Zinc [in the Presence of Copper]. J. W. SPRINGER (*Z. anal. Chem.*, 1924, **65**, 315—317).—The nitric acid solution of the two metals is neutralised with ammonia, sulphuric acid is added, and the copper deposited on a rotating cathode from the boiling solution. The electrolyte, freed from copper, is then neutralised with sodium hydroxide, treated with a further 10 g. of the alkali, and electrolysed for 20 minutes, using a rotating cathode of amalgamated brass gauze. [Cf. *B.*, 1925, 175.] A. R. P.

Determination of Copper by Rapid Electrolysis in the Presence of Tin, Antimony, and Lead. J. LUKAS and A. JILEK (*Chem. Listy*, 1924, **18**, 378—383).—For the separation of copper from tin by rapid electrolysis, the sample is dissolved in a mixture of nitric and tartaric acids and the solution electrolysed in a platinum dish, which serves as cathode, using a rotating anode. If antimony is present hydrofluoric and phosphoric acids must also be added; in neither case does the presence of lead affect the

results. The first copper deposit should be redissolved in nitric acid and the solution filtered and electrolysed again in order to remove traces of carbon and antimony. [Cf. *B.*, 1925, 192.]
A. R. P.

Detection of Copper in Distilled Water. G. POIROT (*J. Pharm. Chim.*, 1924, [vii], **30**, 393—399).—When a solution of alcohol-soluble guaiacum resin in pyridine is added to a mixture of alcohol and the water to be tested in the presence of a few drops of dilute hydrogen peroxide solution, a characteristic blue coloration is produced if copper is present, the limit of sensitiveness being 1 in 10^8. The colour is soluble in alcohol, chloroform, and ethyl acetate, sparingly soluble in ether, benzene, and toluene, and insoluble in xylene, carbon disulphide, and light petroleum. It is destroyed by acids and by ammonia. The presence of pyridine, however, intensifies the colour and stabilises the resin solution, which is unchanged in activity after 50 days if kept in a yellow bottle with a ground-in stopper. W. T. K. B.

Systematic Detection of the Rarer Chemical Elements. A. A. NOYES and W. C. BRAY (*Chem. Reviews*, 1924, **1**, 277—291).

Qualitative Separation of Cobalt, Nickel, Zinc, and Manganese. LEMARCHANDS (*Bull. Soc. chim.*, 1924, [iv], **35**, 1666—1668).—Potassium hydroxide is added to the solution containing the chlorides of the metals; the lower oxides of nickel, cobalt, and manganese are precipitated and are converted into higher oxides by addition of sodium perborate. The precipitate is collected and treated with warm dilute nitric acid; the cobalt and nickel oxides dissolve and are recognised in the solution by the potassium cobalti-nitrite and dimethylglyoxime tests, respectively. Manganese dioxide is insoluble and its presence may be confirmed by conversion into potassium manganate. Zinc is detected by passing hydrogen sulphide into the first filtrate. S. K. T.

Detection of Cobalt, Alone or in Presence of Nickel and Other Salts, in Neutral Solution. S. J. TINDAL (*Chem. News*, 1925, **130**, 34—35).—Neutral solutions of cobalt salts yield a blue precipitate with solutions of sodium silicate soluble in excess of the precipitant; nickel salts under the same conditions give a pale green precipitate insoluble in excess of sodium silicate. The bright blue sodium cobalto-silicate solution is decolorised by mineral acids, rendered greenish-yellow by addition of bromine water in the cold, and black on boiling, owing to separation of cobaltic hydroxide, and turned a greenish-yellow colour both at the ordinary and elevated temperatures by addition of hydrogen peroxide. Nickel and the alkaline-earth metals do not interfere with the test, which will detect 0·00004 g. of cobalt in 5 c.c. of solution. A. R. P.

Rapid Separation of Tin and Tungsten by Electroanalysis. A. JILEK and J. LUKAS (*Chem. Listy*, 1924, **18**, 205—210).—To a solution containing tin and tungsten with an excess of an alkali

sulphide, Rochelle-salt and potassium hydroxide are added, followed by hydrogen peroxide. The solution is boiled, potassium phosphate added, and the electrolysis carried out at 60—70°. The method is superior to that of Treadwell, jun. ("Elektroanalytische Methoden"). It is not applicable to mixtures of tin and molybdenum or vanadium. [cf. *B.*, 1925, 155.] W. A. S.

Electrometric Titration of Antimony and Tin by Potassium Dichromate. M. H. FLEYSHER (*J. Amer. Chem. Soc.*, 1924, **46**, 2725—2727).—Stannous and antimonious chlorides may be titrated by potassium dichromate in hydrochloric acid solutions, using the oxidation-reduction electrode to indicate the end-point. For the analysis of mixtures of the two, both are titrated together, and the antimony is then titrated separately, after addition of mercuric chloride in excess. G. M. B.

Use of Titanous Chloride in Potentiometric Titrations. O. TOMÍČEK (*Chem. Listy*, 1924, **18**, 210—220; 233—241).—The reducing power of titanous chloride is the greater the lower the hydrogen-ion concentration of the solution, so much so that when Rochelle-salt is present, copper, bismuth, and lead salts are reduced to the metallic state. If titanous chloride titrations are followed potentiometrically, the method can be applied to determining vanadium, antimony, uranium, molybdenum, selenium, and copper. In the last three cases, the usefulness of the reagent has been questioned and in the others it has hitherto not been used. By similar means, chromates and vanadates may be determined in presence of ferric salts, chromates in presence of ferric salts and vanadates, and ferric in presence of cupric or uranyl salts. W. A. S.

Separation of Zirconium and Hafnium by Crystallisation of the Double Ammonium Fluorides. J. H. DE BOER and A. E. VAN ARKEL (*Z. anorg. Chem.*, 1924, **141**, 284—288; cf. Hevesy and Jantzen, A., 1924, ii, 53).—The action of fused sodium hydrogen sulphate on alvite and zirkite effects some separation, the soluble sulphates having a higher hafnium : zirconium ratio than the original mineral. The double fluorides, $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$, are less suitable for the separation than the compounds $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$. Two methods of fractionation were followed; the first fractions of the second series in each case were free from hafnium; about 150 crystallisations in 23 series gave end fractions containing 50% of hafnium, calculated on the zirconium present. S. I. L.

Separation of Zirconium from other Metals, including Hafnium, by Fractional Distillation. A. E. VAN ARKEL and J. H. DE BOER (*Z. anorg. Chem.*, 1924, **141**, 289—296).—The existence of the compound $2ZrCl_4,PCl_5$ (Paykull, *Ber.*, 1879, **12**, 1719) has been confirmed; it is a white, crystalline solid, m. p. 164·5°, b. p. 416°. Traces of moisture hydrolyse it to the *compound*

$2ZrCl_4,POCl_3$, a vitreous solid, b. p. 363—364°, readily converted into the first by the action of phosphorus pentachloride. Titanium and silicon if present distil readily in the form of the chlorides or additive compounds of these; iron and aluminium form much less readily volatile additive compounds, and remain in the residue. Hafnium forms compounds analogous to but slightly more volatile than those of zirconium, and can be concentrated by repeated distillation of the earlier fractions. S. I. L.

Determination of Antimony in Stibnite and in Antimony Pentasulphide. E. RUPP, G. SIEBLER, and W. BRACHMANN (*Pharm. Zentr.*, 1925, 66, 33—36).—Digestion of finely-divided stibnite with 15% sodium hydroxide solution at 100° results in complete dissolution of the antimony sulphide and its separation from iron sulphide and silicious impurities. The solution after being boiled with sufficient hydrochloric acid to convert the antimony into trichloride may be titrated directly with bromate or "chloramine," or after oxidation with hydrogen peroxide, the amount of pentachloride present may be determined iodometrically. For the determination of antimony in the pentasulphide, the sample may be dissolved directly to trichloride by heating with concentrated hydrochloric acid and the antimony determined as indicated above. A. R. P.

Micro-method for Determining Organic Substances. M. BALINT and P. RUSZCZYNSKI.—(See i, 323.)

Analysis of Mixtures of Sugars. E. HILDT (*Ann. Chim. anal.*, 1925, [ii], 7, 4—8).—The applications of fractional inversion methods are discussed and it is shown that at 75° 1% solutions of lactose remain practically unaltered. The source of some strobopolarimetric errors due to mutarotation, particularly in connexion with lævulose, are detailed, and a comparative table is given showing the differences of coefficients of inversion of sucrose for a series of times, measured polarimetrically and by the copper method. [Cf. *B.*, 1925, 142.] D. G. H.

Micro-determination of Blood Sugar. E. DINGEMANSE.—(See i, 323.)

Reducing Power of Organic Compounds in Alkaline Solution and the Determination of Sugar by Analysis in Stages and with Separation of Colloidal Cuprous Oxide. H. RUOSS (*Biochem. Z.*, 1924, 151, 337—356).—An investigation of the reduction by sugars of copper salts and dyes (orange II and fast red C) in alkaline solutions. A simple method of analysis in stages is described. The general conclusions reached are, that if 100 c.c. of the alkaline solution are reduced by z c.c. of the solution of reducing substance, the latter contains $(A/z + B + Cz)\%$. Or, if 100 c.c. of the alkaline solution are diluted until the alkalinity is n-N, they require for complete reduction $D + E/n + F/n^2$ mg. of the reducing substance. A, B, C, D, E, and F are constants. J. P.

Determination of Invert Sugar. C. J. DE WOLFF (*Chem. Weekblad*, 1925, 22, 78—79).—The work of van den Hout, Neeteson, and van Scherpenberg (this vol., ii, 74) is criticised. No effect could be observed as a result of washing out the vessels with sodium hydroxide, neither does distilled water cause any measurable inversion. The quantity of starch used does not influence the result. The diminution of the extent of the reduction of Fehling's solution by sucrose with increasing quantities of the latter is confirmed. S. I. L.

Determination of Free Phenol and Cresol in Small Amounts of Blood. G. HAAS and E. F. SCHLESINGER.—(See i, 334.)

Colorimetric Picric Acid Method for Determining Lactose. H. R. BIERMAN and F. J. DOAN (*J. Dairy Sci.*, 1924, 7, 381—392).—A modification of the method of Folin and Denis for the removal of fat and protein. CHEMICAL ABSTRACTS.

Determination of the Reducing Power of Cellulose Products. K. HESS [with W. WELTZIEN and H. NAKAMURA] (*Annalen*, 1924, 440, 290—304).—"Copper numbers" obtained from alkali-soluble celluloses by Schwalbe's method ("Die Chemie der Cellulose," 1911, 625) are not comparable with data similarly obtained from alkali-insoluble celluloses, on account of the sensitiveness of the alkali-soluble materials to the action of hot alkali. This is circumvented by precipitating the cellulose from its solution in alkali as the insoluble copper–cellulose compound by means of cold Fehling's solution (cf. A., 1924, i, 142) prior to completing the reaction at the boiling point of the solution. Consistent results are obtained if temperature and duration of reaction, as well as concentrations of all reactants, are standardised, and optimum conditions are described in detail. Reaction is complete after 5 minutes' boiling (cf. Bang, *Biochem. Z.*, 1907, 2, 284). The copper number yielded by a given sample is lower the higher the concentration of cellulose, alkali, or copper in the reaction mixture, variation of alkali content having the greatest effect. The effect is ascribed to the variation of solubility, in accordance with the law of mass action, of the copper–cellulose–alkali compound, the production of which is formulated $2[C_6H_9O_5]^- + [CuC_4H_3O_6]^- + 2Na^+ \rightleftharpoons [CuC_{12}H_{16}O_{10}]Na_2 \downarrow + [C_4H_5O_6]^-$. The reduction takes place at the surface of the precipitate, and not in the solution. Its completion in one operation indicates absence of attack on the cellulose molecule, whilst with Schwalbe's method, complete oxidation requires several treatments, a fraction of the cellulose, depending on its original purity, being attacked each time. The decrease in copper number with increasing copper content of the reagent emphasises the difference between cellulose and sugar with respect to this reaction, the effect being reversed in the case of the latter. Comparison of copper numbers obtained in this way with the specific rotations of the respective samples in cuprammonium solutions indicates that the copper number provides an exact criterion of purity. [Cf. *B.*, 1925, 94.] F. G. W.

Determination of Acetone in Presence of Alcohol by a Vapour Pressure Method. E. A. VUILLEUMIER (*Ind. Eng. Chem.*, 1925, **17**, 174).—Since the difference is vapour pressure between an aqueous alcohol and an alcohol containing acetone of the same specific gravity is very marked, increasing with rise of temperature, this denaturant can be conveniently determined by comparing at the same temperature the vapour pressure of the unknown sample with that of a sample containing a known proportion of acetone and diluted to the same specific gravity.

D. G. H.

Detection of Citric Acid. RODILLON (*Répert. Pharm.*, 1924, **35**, 233—234).—The solution to be tested is boiled with a little potassium dichromate solution, and a mixture of acetic acid and sodium nitroprusside is added after cooling. Ammonium hydroxide solution free from acetone is added without mixing, when acetone produced from the citric acid generates a violet-red colour at the surface of contact. Alternatively, the acetone may be detected by the iodoform reaction. CHEMICAL ABSTRACTS.

[Determination of Citric Acid.] A. F. CAMP (*Ann. Missouri Bot. Garden*, 1923, **10**, 213—298).—A dilute aqueous solution of citric and sulphuric acids is distilled, the first distillate being discarded, and that obtained after addition of potassium permanganate is collected and redistilled after addition of sodium hydroxide and hydrogen peroxide. The distillate so obtained, after being shaken with iodine and sodium hydroxide solutions, is acidified and the mixture titrated with standard thiosulphate solution. A percentage correction, depending on the amount of citric acid found, is applied. In certain circumstances, it is necessary first to separate the citric acid as the calcium or barium salt.

CHEMICAL ABSTRACTS.

Determination of Phenolsulphonephthalein in the Urine of Jaundice. H. A. ABRAMSON.—(See i, 329.)

Winkler's Method for Determining the Iodine-Bromine Number without Potassium Bromide. O. KÖPKE (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 364—370; cf. A., 1922, ii, 534).—In the revised method, standard potassium bromate solution, dilute hydrochloric acid, and a small quantity of powdered potassium bromide are added to a solution of the oil or fat in carbon tetrachloride solution. After keeping for some hours in a dark place, an excess of standard sodium arsenite solution is added, the liquid is acidified with hydrochloric acid, and titrated with standard potassium bromate solution. In unsuitable illumination, indigo-carmine may be used as an indicator. G. S. W.

Detection of Nitroaminophenols in Urine. L. DESVERGNES.—(See i, 328.)

Urea Oxalates and their Determination as Secondary Oxalate in Fertilisers. T. SABALITSCHKA and G. KUBISCH.—(See i, 347.)

Indicator Method for the Determination of Urea and Arginase. A. HUNTER and J. A. DAUPHINEE (*Proc. Physiol. Soc.*; *J. Physiol.*, 1924, 59, xxxiv).—Urea in concentrations up to 0·15% can be determined by decomposing it with urease in the presence of 0·05*M*-phosphate at a p_H of 6·9 and determining colorimetrically the resulting change in p_H. For the detection and determination of arginase the extract is allowed to act under specified conditions of temperature and p_H on a standard solution of arginine, and the urea produced in a given time is determined as above.

CHEMICAL ABSTRACTS.

Determination of Small Amounts of Glycogen in Solution. S. E. DE JONGH and J. PLANELLES.—(See i, 325.)

Titration of Alkaloids. H. B. RASMUSSEN and S. A. SCHOU (*Pharm. Zentr.*, 1924, 65, 729—730).—A solution of the alkaloid in dilute hydrochloric acid was titrated with 0·1*N*-sodium hydroxide. The potential, relative to a quinhydrone electrode (cf. Veibel, T., 1923, 123, 2203), and hence the p_H, was determined after each addition of alkali. The results are represented in graphs, which show a point of inversion, and the corresponding values for p_H, as found directly and as interpolated from the titrimetric curves, are given. The values found by interpolation are as follows: strychnine, 4·96—5·09; brucine, 4·65—4·83; morphine, 4·77—4·90; codeine, 4·93—4·94; narcotine, 4·29—4·32; nicotine, 6·41—6·58; hydrastine, 4·92—5·01; cinchonine, 5·93—5·96; quinine, 6·39—6·42; atropine, 4·75—4·90. Methyl-red is recommended as indicator for all the above (for cinchonine with buffer solution of p_H 5·9), except narcotine (methyl-orange, buffer solution of p_H 4·2), and quinine (*p*-nitrophenol, buffer solution of p_H 6·2).

W. T. K. B.

Colorimetric Determination of Solutions of Novocaine. [illegible]RAMY (*J. Pharm. Chim.*, 1924, 30, 408—411).—The colour [illegible] on mixing solutions of novocaine, sodium nitrite, hydrochloric acid, and sodium carbonate containing 0·5% of potassium diacolsulphonate varies from red to yellow, according to dilution, and is suitable for colorimetric comparison with a standard novocaine solution at a dilution of 1 : 20,000 of novocaine. The colour reaction is unaffected by the presence of methyl *m*-amino-*p*-hydroxybenzoate, *p*-aminobenzoic acid, cocaine, stovaine, or of small amounts of adrenaline, although more concentrated solutions of the last-named also give a red coloration due to oxidation. Sodium hydrogen sulphite, however, exerts a markedly depressant action on the colour formation, and should be removed, before diazotising, by addition of 1 drop of 0·1*N*-iodine solution. Solutions of novocaine may be sterilised, without change, in slightly alkaline glass vessels at 100°, but at 120° the alkali causes appreciable change and sterilisation should be effected in vessels of superior glass or in the presence of a solution of benzoic acid. W. T. K. B.

Colour Reactions of Eserine. L. EKKERT (*Pharm. Zentr.*, 1925, 66, 53).—Eserine and its salts, when left in the air, are trans-

formed into rubreserine (Ehrenberg, A., 1895, i, 436) which, when warmed with sodium hydroxide solution, yields various colour changes, and finally an emerald-green solution (*A*) is obtained. When acidified with mineral acids, this solution becomes ruby-red and, on the addition of dilute sodium thiosulphate solution, carmine-red with a blue fluorescence, or of ammonium sulphide, green. On acidification of solution *A* with acetic acid, an indigo-blue or, if more dilute, a garnet colour is produced which is extractable with chloroform. If a salt of eserine be dissolved in chloroform and heated to the b. p. with sodium hydroxide, these colour reactions are not obtained, but the aqueous layer becomes gradually golden-yellow, whilst the chloroform assumes a pale rose tint. This is cited as further evidence of the presence in eserine of an hydroxyl group. L. F. H.

Analysis of Adrenaline. D. Echave (*Anal. Asoc. Quím., Argentina*, 1924, **12**, 234—257).—A discussion from the analytical point of view of the physical and chemical properties of different samples of commercial adrenaline. G. W. R.

Application of the Denigès-Grimbert-Leclère Reaction to the Characterisation and Determination of Adrenaline in Suprarenal Powders. O. Bailly (*J. Pharm. Chim.*, 1924, [vii], **30**, 404—405).—When an aqueous sulphuric acid maceration extract of suprarenal powder is filtered and mixed with solutions of sodium acetate and mercuric chloride, the presence of adrenaline produces a red coloration, which attains its maximum intensity after 3 minutes and can serve for the determination by colorimetric comparison with a standard solution of adrenaline. W. T. K. B.

Bitter Principles in Hops and Beer. L. Klein (*Chem. J.*, 1924, **18**, 221—226; 242—244).—Siller's method (A., 1909, [illegible]ne for determining humulone in hops is improved by substi[illegible] potassium iodide for potassium sulphide in detecting the exc[illegible] lead salt used as the precipitating agent.

The "iodine-number" of the resinous extract from beer or wo[illegible] made from fresh hops is about 200, but that of the extract from bee[illegible] made from old hops is only 150 to 170. The longer the wort is boiled with the hops, the higher is the "iodine-number" of the resin extracted from it. W. A. S.

Extraction of Proteins. G. Pinkss, H. Miller, and G. A. Alles.—(See i, 331.)

Determination of Colloid Material in Soils. G. J. Bouyoucos.—(See i, 348.)

General, Physical, and Inorganic Chemistry.

Apparent Tripling of certain Lines in Arc Spectra. T. ROYDS (*Proc. Roy. Soc.*, 1925, **A**, **107**, 360—367).—As many spectra as possible have been searched through the visible region for instances of lines becoming complex when the amount of material in the arc is increased. Only seven such lines have been found, these being lithium 6708, 6103; thallium 5350; strontium 4876·2, 4872, 4832; manganese pair 4235. The thallium line 5350 has been specially studied; it is shown that it is essentially a doublet and that the different phases can be simply explained as different stages in the self-reversal of the two lines of the doublet. The resolution by interatomic fields suggested by King is considered unnecessary to the explanation. N. H. H.

Fine Structure of the Helium Line 5876 Å. R. BRUNETTI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 413—415).—The D_3 helium line appears to be undecomposable and endowed with only a single satellite. Both retain their separate structures in even intense magnetic fields and are, therefore, not lines of a multiple series in the ordinary sense of the term. The origin of the structure of the helium line 5876 Å. is thus still unexplained. T. H. P.

Comet Tail Spectrum and Deslandres' First Negative Group. H. B. LEMON (*Proc. Nat. Acad. Sci.*, 1925, **11**, 41—43).—A long vacuum tube of the Wood type filled with helium pumped by circulation through activated carbon furnishes an extremely brilliant comet tail spectrum provided the partial pressure of the carbon compounds is of the order 10^{-4} mm. The composition of the residual carbon compounds is quantitatively unknown, although carbon dioxide and certain hydrocarbons are present. The helium plays only a secondary *rôle* in the excitation of these spectra, but nevertheless is necessary for their production with great intensity. J. S. C.

Auroral Green Line. J. C. MCLENNAN (*Nature*, 1925, **115**, 382).—Under conditions which indicate its identity with the auroral green line, a line at 5577·35 ± 0·15 Å. has been observed in the spectrum of a mixture of air with excess of helium. A. A. E.

"Dashed" and Displaced Spectral Terms. A. LANDÉ (*Z. Physik*, 1924, 27, 149—156).—An alternative allocation of quantum numbers to certain terms in the spectra of the alkaline-earth metals is suggested. S. B.

Spark-spectra of Indium and Gallium in the Extreme Ultra-violet Region. M. WEINBERG (*Proc. Roy. Soc.*, 1925, **A**, **107**, 138—156).—By means of the quartz spectrograph 80 gallium lines between 1855 and 2364 Å. have been examined and

107 indium lines between 1855 and 2337 Å. Using a vacuum grating spectrograph, 828 lines which could be attributed to gallium were found and measured between 157 and 2059 Å., and 464 indium lines in the range 161—2082 Å. For the examination of the quartz region, the spark chamber was filled with hydrogen. M. S. B.

Structure of the Line Spectra of Ionised Oxygen. F. CROZE (*Compt. rend.*, 1925, **180**, 432—433; cf. this vol., ii, 166).—In addition to the six multiplets in the spectra of ionised oxygen, resulting from combinations between two systems of quadruple terms, there are also combinations between double terms, the more important of which are given. J. S. C.

Structure of Spectrum of Ionised Nitrogen. A. FOWLER (*Proc. Roy. Soc.*, 1925, **A**, **107**, 31—42).—The second line spectrum of nitrogen, between λ 6650 and 2200, due to singly-ionised nitrogen, has been examined in vacuum tubes with gas at various pressures, and under varying conditions of electrical discharge. The terms identified belong to singlet and triplet systems, and combine with each other in agreement with the selection rules applicable to other spectra in which p' and d' terms appear. The value 70,000 has been provisionally assigned to $2p$. The series electron in singly-ionised nitrogen, N^+, probably occupies, normally, a 2_2 orbit, so that it has two electrons in 1_1 orbits, two in 2_1, and two in 2_2. From the spectroscopic displacement law it may be inferred that this is also the probable arrangement of orbits in the neutral atom of carbon. Three groups of lines involving one of the p terms show large displacements (>0·5 Å.) to the red in vacuum tubes at relatively high pressures. M. S. B.

Scattered Radiation due to *X*-Rays from Molybdenum and Tungsten. S. K. ALLISON and W. DUANE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 25—27).—Using an improved form of the apparatus previously described (*ibid.*, 1924, **10**, 381) and employing a modified technique, previous work has been repeated and it is found that the equation of Compton, deduced from his theory of single electron scattering, represents the wave-lengths of a large part of the secondary radiation due to primary rays in the *K*-series spectra of molybdenum and tungsten. J. S. C.

Short Wave *X*-Ray Spectrograph and some *K*-Series Emission Wave-lengths. J. M. CORK (*Physical Rev.*, 1925, [ii], **25**, 197—200).—A transmission type of spectrograph for short *X*-rays is described. The results of measurements of wave-lengths (in *X*-units) of *K*-series lines α', α, β, and γ, respectively, are as follows:—barium, 389·45, 384·83, 340·66, 332·62; lanthanum, 375·18, 370·29, 327·99, 319·57; cerium, 361·24, 356·73, 315·75, 307·32; praseodymium, 348·66, 343·84, 304·12, 296·55; neodymium, 336·40, 331·51, 293·33, 286·15; samarium, 313·46, 308·75, 273·55, 265·72; gadolinium, 293·01, 287·71, 254·28, 248·01; dysprosium, 274·14, 269·28, 238·08, 231·53; erbium, 256·95, 251·90, 222·74, 216·93; tungsten, 213·69, 208·84, 184·56, 179·07.

A. A. E.

Complex Structure of Röntgen-spark Spectra. G. WENTZEL (*Z. Physik*, 1925, **31**, 445—452; cf. A., 1924, ii, 638).—A provisional attempt to predict complex spark spectra from the theories of Röntgen-arc and optical spectra. R. A. M.

Influence of Velocity-Dependence of Electron Mass on the Zeeman Effect. W. PAULI, jun. (*Z. Physik*, 1925, **31**, 373—385). —Mathematical. The Zeeman effect in a homologous series of elements, especially the alkali metals, would depend on the atomic number if the relativity mass change exerted any influence. This would imply a contribution by the electrons of the *K*-shell to the impulse moment and to the magnetic moment. The absence of such effects supports other arguments against the participation of the inner closed shell in the form of core-impulses in the origin of complex optical spectra and Zeeman effects. R. A. M.

Atomic Rays. G. C. SCHMIDT (*Ann. Physik*, 1924, [iv], **75**, 337—368; cf. A., 1924, ii, 727).—The nature of the charged particles emitted on heating a series of salts has been examined. The halogen salts of iron, magnesium, zinc, ammonium, etc. emit positively charged particles which e/m measurements prove to be charged atoms of the metals. The chlorides of lead and barium emit both positively and negatively charged particles. The nitrates of barium etc. decompose, and the residual oxides emit electrons (by the Wehnelt effects). It is suggested that fused or solid salts which conduct electrolytically emit their more mobile ionic constituents in the form of these charged particles. The emission of electrons is taken to indicate "metallic" conduction. S. B.

Positive Rays produced by Ultra-violet Light. L. A. DU BRIDGE (*Physical Rev.*, 1925, [ii], **25**, 201—207).—When precautions are taken against scattered light effects, no positive current can be observed from gold, copper or aluminium surfaces exposed to ultra-violet light (cf. Dember, *Ann. Physik*, 1909, **30**, 137). A. A. E.

Cathode Rays. A. BECKER (*Ann. Physik*, 1924, [iv], **75**, 435—447).—The advantages of the hot electrode tube over the older methods for the production of moderately fast cathode rays are discussed. S. B.

Intensities of Multiplet-lines. L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1925, **31**, 355).—The view advanced by Burger and Dorgelo (A., 1924, ii, 361) that the sum of the intensities of the components of multiple spectral lines with common end or initial levels was proportional to the statistical weight of these levels, is regarded as inadequate and a new theoretical treatment based on the work of Sommerfeld and Heisenberg (*Z. Physik*, 1922, **11**, 131) is advanced. The measurement of intensities is troublesome, but preliminary work on a *d f* multiplet of iron discloses three weak lines the intensities of which are in excellent agreement with the newer theoretical considerations. A discussion of the summation rule follows. R. A. M.

Series Spectra of Two-valency-electron Systems and of Three-valency-electron Systems. I. S. BOWEN and R. A. MILLIKAN (*Nature*, 1925, **115**, 422—423).—Tabulated data are given for the comparison of term-values of series of atoms constituting a two-electron system (Mg I, Al II, Si III, P IV, S V) and a three-electron system (Al I, Si II, P III, S IV). A. A. E.

Harmonic Analysis of Electron Orbits. F. C. HOYT (*Physical Rev.*, 1925, [ii], **25**, 174—186).

Momentum Imparted to Electrons by Radiation. E. O. HULBURT and G. BREIT (*Physical Rev.*, 1925, [ii], **25**, 193—196).—Theoretical. Only experiments of the " fish track " type are likely to permit of the observation of the deflexion of a part of a beam of electrons by electromagnetic radiation. A. A. E.

Magnetic Field of a Moving Electron. F. GUÉRY (*Compt. rend.*, 1924, **179**, 895—897).—The application of Maxwell's theory leads to a value for the magnetic field of a moving electron which is not in accordance with the first law of Laplace. There results from this expression an action between elements of current which is half that observed, but it is not an admissible hypothesis to attribute half the action to modifications of the electric field due to the movement. The conclusion is reached that the magnetic field of an electron is a mathematical expression without physical reality. H. J. E.

Photographic and Ionisation Effect of X-Rays of Different Wave-lengths. R. BERTHOLD (*Ann. Physik*, 1925, [iv], **76**, 409—438).—The relation between the darkening of a photographic plate and the amount of ionisation produced by a homogeneous beam of *X*-rays was determined for a range of four octaves, using *K*-radiation from selected anti-cathodes. Both effects diminish with increasing frequency, the relation being linear, *viz.* $S/I = m(47{\cdot}5-\nu)$, where S is the darkening, I the ionisation, and ν the frequency $\times 10^{18}$; m is a constant which can have any value. E. B. L.

Number of Free Electrons with a Metal. E. H. HALL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 36—38).—The relations existing between the atoms, the free electrons, and the positive ions within a metal are essentially those of dissociation equilibrium, there being certain essential mechanical differences between the condition of the ions within a solid metal and those in a liquid solution which render the third law of thermodynamics inapplicable. The number of free electrons may be as great as 2 or 3% of the number of atoms at the ordinary temperature and the alteration of the number of free electrons with rise of temperature need not be in accord with the reaction isochore equation. The "ionising potential" of metals varies from 0·125 volt in cobalt to 0·33 volt in iron at 0°, a much smaller quantity than the ionising potential of the corresponding metal vapour. J. S. C.

Heat of Evaporation of Electrons. J. J. WEIGLE (*Physical Rev.*, 1925, [ii], **25**, 187—192).—Values (volts/electron) equivalent to the heat of evaporation of 1 g.-mol. of electrons at 0° Abs. are calculated on the assumption that the electrons form a space lattice, and compared with values measured experimentally by thermionic emission or by the photoelectric effect. The respective results, preceded by the heat of evaporation (in kg.-cal./mol.), are: sodium, 42·3, 1·83, 1·82; potassium, 35·3, 1·53, 1·55; rubidium, 35·6, 1·54, 1·45; cæsium, 30·6, 1·34, 1·36. The assumption of electronic space lattices is thus supported. A. A. E.

Diffusion of Electrons against an Electric Field in the Non-oscillatory Abnormal Low-voltage Arc. K. T. COMPTON and C. ECKART (*Physical Rev.*, 1925, [ii], **25**, 139—146).

Atomic Fields of Helium and Neon. J. E. JONES (*Proc. Roy. Soc.*, 1925, **A**, **107**, 157—170).—Theoretical. Experimental data on the viscosity and the equation of state of helium indicate that the atomic field can be represented by a repulsive force equal to $5{\cdot}74 \,.\, 10^{-113}\, r^{-14}$, where r is the distance between the centres of the atoms and an attractive force $1{\cdot}930 \,.\, 10^{-45}\, r^{-5}$. The atomic field of neon has been calculated from thermal conductivity and viscosity data, and also from X-ray measurements of the interatomic distances in crystals of sodium fluoride and magnesium oxide, the ions of which are assumed to have the same outer field as neon, plus that due to their electrostatic charges. The repulsive force is $3{\cdot}892 \,.\, 10^{-165}\, r^{-21}$. The value of the attractive force has not been determined, but is shown to be very small. M. S. B.

Influence of Ionic Diffusion on Almost Saturated Currents. G. JAFFÉ (*Ann. Physik*, 1924, [iv], **75**, 391—402).—A theoretical discussion of the effect of the diffusion of gaseous ions upon the current–voltage curves of condensers, near the saturation point. Expressions are developed for the characteristics of plate, cylindrical, and spherical condensers. S. B.

Determination of Elementary Charge E from Measurements of Shot-effect. A. W. HULL and N. H. WILLIAMS (*Physical Rev.*, 1925, [ii], **25**, 147—173).

Precise Measurement of the Critical Potentials of Gases. E. G. DYMOND (*Proc. Roy. Soc.*, 1925, **A**, **107**, 291—309; cf. this vol., ii, 6).—The author describes the application of an apparatus giving automatic differentiation of the characteristic current–voltage curves with a view to increase the sharpness of the bends. The reasons for the divergence of the value found for the first excitation potential of helium, 20·9 volts, from that calculated from the optical data are discussed. The problem of interpretation of the characteristic curves taking into account the variation in the probability of effective collision and the velocity distribution of the electrons is attacked. N. H. H.

Abnormal Low-voltage Arcs in Mercury Vapour, Argon, and Helium. R. Bär (*Z. Physik*, 1925, **31**, 430—438; cf. Eckart and Compton, *Physical Rev.*, 1924, [ii], **24**, 97; Bär, Laue, and Meyer, *Z. Physik*, 1923, **20**, 83).—The low-voltage arcs obtained by a potential difference of a few volts in neon, argon, and mercury vapour are not caused merely by oscillations, but correspond with true abnormal arcs. In helium such an oscillation-free, low-voltage arc can only be obtained after the strongest heating of a filament, and a potential difference of 16·5 volts (which is not far from the excitation potential of helium) is required. The average voltage required for a helium arc caused by oscillations is 8. R. A. M.

Influence of Radiation on Ionisation Equilibrium. M. Saha and R. K. Swe (*Nature*, 1925, **115**, 377—378).

Thermionic Effects Caused by Vapours of Alkali Metals. I. Langmuir and K. H. Kingdon (*Proc. Roy. Soc.*, 1925, **A**, **107**, 61—79; cf. A., 1923, ii, 367).—When a tungsten filament is heated at 1200° Abs., or above, in saturated cæsium vapour, and surrounded by a negatively charged cylinder, a positive ion current flows from the filament, because all the cæsium atoms striking the filament are converted into ions. Since at high filament temperatures and low pressures of alkali metal vapour the electron emission is the same as in the absence of vapour, the positive ion emission can be determined and the thermal ionisation of cæsium vapour calculated. These experimental results are in good agreement with Saha's equation (Fowler and Milne, *Mon. Not. Roy. Astr. Soc.*, 1923, **83**, 403). At high filament temperatures, for example, 1500° Abs., at which all the atoms striking the filament are converted into ions, the vapour pressure may be calculated from the positive ion current. The pressure p (in bars) of cæsium vapour is given accurately by the equation $\log_{10} p = 10{\cdot}65 - 3992/T$, where T is the absolute temperature.

If the tungsten filament be covered with a monatomic layer of thorium, the electron emission is greatly increased, but the positive ion emission becomes practically negligible.

At lower filament temperatures, the pure tungsten surface is covered by a layer of adsorbed ions, which share electrons with the tungsten, and electron emission is increased, whilst positive ion emission is decreased. There is qualitative evidence of the existence of two phases in the adsorbed films, since the positive ion emission increases discontinuously with rise of temperature. From a consideration of dilute adsorbed films the equation of state for the film is found to correspond to the ideal gas laws. The heat of evaporation of adsorbed cæsium from tungsten, in the form of ions, corresponds with 4·0 volts for dilute and 4·3 volts for concentrated films, and 5·1 volts for an oxygenated filament. Curves have been drawn showing the variation of electron emission with temperature for different pressures of cæsium vapour, both from pure tungsten and from a filament covered with a film of oxygen from which the electron emission is greatly increased. M. S. B.

Halogen Isotopes and Infra-red Reflexion Spectra. A. H. PFUND (*Proc. Nat. Acad. Sci.*, 1925, **11**, 53—55).—On the assumption that the resonating mechanism responsible for bands of selective reflexion is localised in the negative ion, each halogen salt of potassium should have as many bands of selective reflexions as there are isotopes (potassium chloride, 2; potassium bromide, 2; and potassium iodide, 1). Associating the lighter isotopes with the band of shorter wave-length, parallel lines are obtained on plotting atomic weight against the wave number ($1/\lambda$). These are discussed and support is advanced for the view that the isotope Cl^{37} is most abundant in rock-salt, whilst Cl^{35} is most abundant in sylvite.

J. S. C.

Atomic Weight of Carbon and Silver. G. DEAN (*J. Chem. Soc.*, 1924, **125**, 2656—2672).—The atomic weight of carbon has been determined from the ratio AgCN : Ag, a known weight of carefully purified silver cyanide being reduced to silver by heating in a current of hydrogen. From 21 experiments a mean value of 12·002 ± 0·001 was obtained, if Ag be 107·88 and N 14·008. By reducing silver cyanate to silver by heating in a current of purified moist air, the ratio AgCNO : Ag has been determined. The mean of 16 experiments gave C=12·003±0·001. By combining the results of the cyanide and cyanate series, new independent values for the atomic weight of silver, Ag=107·871, and the equivalent of cyanogen, (CN)=26·008, involving no other assumption than O=16, have been deduced. From the equivalent of cyanogen, assuming the atomic weight of nitrogen, that of carbon is found to be 12·000. The densities of metallic silver, silver cyanide, and cyanate have been determined.

M. S. B.

Atomic Weight of Hafnium. O. HÖNIGSCHMID and E. ZINTL (*Z. anorg. Chem.*, 1924, **140**, 335—336).—The atomic weight of hafnium was determined by analysis of a sample of the bromide containing according to *X*-ray spectroscopic measurements about 6% zirconium. The mean value found was 171·88; correction for the zirconium content yields the value 180·8.

S. K. T.

Atomic Weights of Zirconium and Hafnium. G. HEVESY (*Nature*, 1925, **115**, 335—336).—The zirconium samples used by Venable and Bell (A., 1917, ii, 479) contained from 0·7 to 1% of hafnium; these authors' corrected value for the atomic weight of zirconium is 91·3, in close agreement with that obtained by Hönigschmid and Zintl (see preceding abstract) and that predicted by Aston from positive-ray data. The figure 91·3±0·1 should be adopted.

Hönigschmid and Zintl's figures for the atomic weight of hafnium have been corrected for zirconium content of the material (0·16 and 0·57%), yielding a value of 178·6±0·1.

A. A. E.

Long-range Particles from Polonium. N. YAMADA (*Compt. rend.*, 1925, **180**, 436—439).—The ratios of the number of long-range particles to the number of α-particles of ordinary range, from polonium deposited on copper, nickel, and silver, have been deter-

mined. The values obtained are much smaller than those of Bates and Rogers (A., 1924, ii, 296), especially after removing occluded gases and water vapour from the metals, metallic screens, etc. The majority of the long-range particles observed by Bates and Rogers are to be traced to the copper on which the polonium was deposited and to the mica screens used. The particles which persist after removal of occluded gas, water, etc., are present to the extent of three or four in 10^7 α-particles of ordinary range, and their range is about 10—14 cm. in air. J. S. C.

Ionisation by α-Particles in Monatomic and Diatomic Gases. R. W. GURNEY (*Proc. Roy. Soc.*, 1925, **A**, **107**, 332—340).—To throw light on the discrepancy between the ionisation produced by α-particles in certain substances and that to be expected from current theories, measurements have been made of the total ionisation produced by definite beams of α-particles in xenon, krypton, argon, neon, helium, oxygen, hydrogen, and nitrogen. In the five monatomic gases the ionisation increases with increasing atomic number, which would be expected from their decreasing ionisation potentials. But in the diatomic gases the ionisation is less than in any of the monatomic gases, indicating that energy has been expended in other ways. The ratio of the value of the ionisation in air to that in the other gases is found to vary with the velocity of the α-particles. N. H. H.

Stopping-power of Gases for α-Particles of Different Velocities. R. W. GURNEY (*Proc. Roy. Soc.*, 1925, **A**, **107**, 340—349).—By selecting small portions of the range the relative stopping power of the five rare gases and of hydrogen and oxygen has been measured for α-particles of high, intermediate, and low velocities, separately. The values of the relative stopping powers tend to converge at the end of the range. The values for high velocities are in good agreement with the relative atomic stopping powers calculated by Fowler. The measurements of ionisation described in a previous paper (see preceding abstract) are discussed in the light of this result. N. H. H.

Ejection of Protons from Nitrogen Nuclei, Photographed by the Wilson Method. P. M. S. BLACKETT (*Proc. Roy. Soc.*, 1925, **A**, **107**, 349—360).—By means of a modified and automatic form of Wilson's condensation apparatus about 23,000 photographs of the tracks of α-particles in nitrogen have been taken from two directions at right angles. These have shown the tracks of about 270,000 α-particles of 8·6 cm. range and 145,000 α-particles of 5·0 cm. range. In addition to a large number of forks corresponding with elastic collisions between α-particles and nitrogen atoms, eight have been found which undoubtedly represent the ejection of a proton from a nitrogen nucleus. From measurement and from the fact that these eight forks are doubly and not trebly branched, it is inferred that the α-particle takes the place of the ejected proton in the nitrogen nucleus resulting in a particle of mass 17 and atomic number 8; that is, an isotope of oxygen. Since it has not been

detected by Aston's mass spectrograph, it is probably of rare occurrence or else possessed of a short life. Its life must, however, be greater than the time of effective supersaturation in the condensation chamber, which is about 1/1000 second. N. H. H.

Recoil Effect in Scattering of γ-Rays. D. Skobelzyn (*Z. physik*, 1924, **28**, 278—286).—The Wilson cloud-track method has been applied to the electrons emitted during the passage of γ-rays through matter, and the velocities of the electrons have been determined by the application of a magnetic field. The Compton theory of scattering was verified in the following particulars. (1) The energy imparted to the electron by radiation of frequency ν is very often only a small fraction of the value $h\nu$. (2) The velocity of the electron has always a forward component. (3) The velocities of the electrons diminish with increase of the angle between their path and that of the exciting radiation. S. B.

Absorption and Diffusion of γ-Radiation of Great Energy in Light Elements. J. Thibaud (*Compt. rend.*, 1924, **179**, 815—818; cf. A., 1924, ii, 515, 717).—For a single element the number of electrons dislodged on the K level is much greater than that on the L level; as in the case of X-rays, a γ-ray is more readily absorbed by an electronic level of greater energy. Although a study of the comparative emissive intensities of different elements leads to the inference that only the heavy elements are capable of yielding photo-electric spectra, photographs show that the photo-electric phenomenon may be excited in lighter elements. The fluorescence absorption of γ-rays seems to decrease less rapidly with N than Bragg's law would indicate; the suggestion is made that it may be proportional to N^2 rather than N^4. A fraction of the γ-radiation is diffused in the mass of the radiator; in a "corpuscular γ-ray spectrum" derived from a light element this effect is shown by the emission of two types of electrons. The first corresponds with the rays which have undergone change of wave-length, the others are "resonance electrons" (cf. Compton, A., 1923, ii, 280). The diffusion of γ-rays is difficult of observation. As with X-rays, diffusion by quanta appears to be of little importance in the case of γ-rays. The continuous base observed in the spectra of secondary β-radiation may be due to the degradation of these quanta. H. J. E.

Absorption of X-Rays. E. C. Stoner and L. H. Martin (*Proc. Roy. Soc.*, 1925, **A, 107**, 312—331).—By the use of a balance method, the absolute absorption coefficient of aluminium has been determined for the three wave-lengths 0·45, 0·631, and 0·708 Å. Primarily comparative to aluminium the absorption of copper, palladium, silver, and tin and the relative absorption of uranium oxide have also been investigated over a range of 0·3 to 0·71 Å. and the results compared with those of previous observers. The measurements are discussed in relation to current theories of X-ray absorption, notably the λ^3 (λ=X-ray wave-length) and Z^4 laws and the magnitude of the K and L absorption discontinuities.

N. H. H.

Statistical-mathematical Inquiry into the Sub-electron. H. DAECKE (*Physikal. Z.*, 1924, **23**, 624—631).—Mathematical. Owing to the failure of purely physical methods to decide the question as to the existence of a sub-electron, the author has applied a cyclic error method to an examination of published data, and concludes that values of e less than $4{\cdot}77\times10^{-10}$ are most probably integral sub-multiples of it. D. M. E.

Periodic Structural Regularities in Spectra as Related to the Periodic Law of the Chemical Elements. W. F. MEGGERS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 43—47).—The periodicity of structural regularities in spectra as related to the periodic law of the chemical elements is revealed in the verification of the displacement law of Kossel and Sommerfeld and the extension of Rydberg's alternation law. The structures are in accord with the quantum theory of spectral line emission as developed by Bohr and others. J. S. C.

Magnetic Atom Moments and Directional Quantisation. W. GERLACH (*Physikal. Z.*, 1924, **23**, 618—620).—An improved apparatus is described for studying the Debye–Sommerfeld quantisation in a magnetic field and for determining the magnetic moment of atoms. For silver, the value $M=5690$ gauss/cm. was obtained. Gold and copper behaved similarly to silver. Tin, lead, and antimony were unaffected by the magnetic field. In the case of nickel, the atomic stream was diffused, and it would appear that the atom has a magnetic moment of several magnetons. D. M. E.

Absorption Spectra of Pyrrole and its Derivatives. III. Influence of Amino and Carbamido Groups on the Absorption Spectra of Pyrrole Derivatives. G. KORSCHUN and (MME.) C. ROLL (*Bull. Soc. chim.*, 1925, [iv], **37**, 130—140; cf. A., 1923, ii, 107).—The absorption spectra of the ethyl esters of the following pyrrolecarboxylic acids were examined: 1-amino-2:5-dimethyl-, 1-carbamido-2:5-dimethyl-, 1-amino-2:3:5-trimethyl-, 1-carbamido-2:3:5-trimethyl-pyrrole-4-carboxylic acids, 1-amino-2:5-dimethyl- and 1-carbamido-2:5-dimethyl-pyrrole-3:4-dicarboxylic acids. The general conclusions reached are that auxochrome groups in the 1-position alter the distribution of residual valency in the pyrrole nucleus, and lose their auxochromic influence. Methyl and carbamido groups in the 1-position cause displacement of the absorption spectra towards the ultra-violet, whilst the amino group causes practically no displacement. A decrease in the degree of saturation of the substituent in the 1-position, for example by the formation of an enolic modification of the carbamido group under the influence of alkalis, displaces the absorption towards the red, whilst an increase in the degree of saturation, for example by salt-formation from the amino derivatives, causes a displacement in the opposite direction. F. G. W.

Spectrum of Chlorophyll in the Living Leaf. J. WŁODEK (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, **B**, 407—423).—The displacement of the chlorophyll spectrum of the living leaf

towards the infra-red region in comparison with that of a solution of chlorophyll appears to be attributable to the optical system of the tissue of the leaf, as also is the effacement of the boundaries of the absorption bands. The spectrum of the leaf chlorophyll is probably a mixed spectrum composed of a common with a reflected spectrum intermixed with unabsorbed light. The duality of the first absorption band of chlorophyll, observed with both the living and the killed leaf, is explainable by assuming that the spectrum of the chlorophyll is not that of a mixture of green pigments, but is composed of two distinct superposed spectra of neo- and allo-(*a*- and *b*-)chlorophylls. Under the influence of light, the spectra of leaf chlorophyll undergo change; the stripes of the first absorption band corresponding with both chlorophylls alter in width, this indicating either a change in the relative amounts of the two chlorophylls or the appearance of new spectra of unstable compounds of chlorophyll with carbon dioxide. T. H. P.

Neodymium Oxide. E. L. Nichols (*Proc. Nat. Acad. Sci.*, 1925, **11**, 47—52).—The spectrum of the glowing oxide studied with the spectrophotometer reveals ten or more crests on the brightness curve of the visible spectrum which are assumed to be the envelopes of groups in a much more complicated but almost wholly submerged structure. The crests fall into two sets such that the frequency differences between neighbours in a given set are multiples of 18·5, the Tanaka interval for neodymium. The luminescence of the oxide has been investigated over the temperature range 600—1000°. Comparison of the bulk and bead spectra shows that the various lines of neodymium are all parts of a single structure. The absorption spectrum of neodymium in aqueous solution shows no obvious sign of identity with either emission spectra. J. S. C.

Theory of Band Spectra. R. Mecke (*Z. physik*, 1924, **28**, 261—277).—It is shown that a formal analogy can be drawn between the representations of line and band spectra, both comprising three quantum numbers. Further, there is evidence of a regular alternation of odd and even multiplets from element to element in the periods of the periodic table, in band spectra as well as in ine spectra. The positive nitrogen bands may be regarded as the "arc" spectrum of the nitrogen molecule and contain a quintet system. The negative bands, or "spark" spectrum, contain a doublet system. S. B.

Isotope Effect in Band Spectra. I. R. S. Mulliken (*Physical Rev.*, 1925, [ii], **25**, 119—138; cf. A., 1924, ii, 3, 294, 295, 446, 640; Jevons, A., 1915, ii, 33; 1924, ii, 640; Loomis, A., 1921, ii, 530).—In a theoretical discussion of the isotope effect in band spectra of diatomic molecules, definitions are obtained of the origin of a band-system and of the origin of a band. The incidence of the vibrational and the rotational isotope effects is considered, and an explicit equation for band-heads is obtained. The quantum theory of band spectra is supported by confirmatory

evidence in the case of BO, SiN, CuH, CuCl, CuBr, and CuI. Applications of the isotope effect to the study of isotopy and the interpretation of band spectra, and its relation to the positive ray method, are examined. A. A. E.

Application of the Quantum Theory of Band Spectra to the First Negative Deslandres Group of Carbon. C. M. BLACKBURN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 28—34).—A discussion of the structure of the lines studied by Lemon from the point of view of the quantum theory of band spectra. Owing to the simplicity of the structure, the radiator of the bands probably approximates very closely to the dipole molecule. The molecule in question is in simple rotation about a non-precessing axis perpendicular to the line joining the nuclei. The moments of inertia of the molecule in the vibrationless state before and after emission are $8{\cdot}07\times10^{-40}$ and $6{\cdot}78\times10^{-40}$ g./cm.^{2}, respectively. J. S. C.

Fluorescence and its Applications. E. BAYLE, R. FABRE, and H. GEORGE (*Bull. Soc. chim.*, 1925, [iv], **37**, 89—115).—A self-starting, gas-filled, direct current, quartz mercury arc-lamp is described (cf. George, *Revue d'optique*, 1925, 1), and photographs are shown comparing its spectrum with those of the ordinary mercury arc-lamp and a high-frequency lamp (cf. George, *Compt. rend.*, 1920, **170**, 458). The above direct-current lamp gives the highest output of ultra-violet rays of wave-length around 3650, which is most suitable for use with a nickel oxide screen (cf. *U.S. Bur. Standards, Tech. Papers*, 1920, **148**). Various substances, chiefly in the solid state, were submitted to the action of the ultra-violet rays produced by the above lamp and screen. The fluorescence spectra were compared photometrically, over the range λ=4000—7600, at intervals of 200 Å., with rays of the same wave-length obtained from white light, to determine the distribution of luminous intensity in the spectrum under examination, and hence, using Gibson and Tyndall's coefficients of visibility (*U.S. Bur. Standards, Tech. Papers*, 1923), to calculate the total luminous intensity of the fluorescence spectrum. Solid sodium salicylate gives a violet fluorescence the intensity of which, taken as 20 units, forms a convenient standard of comparison. The fluorescence persists in aqueous solution, is perceptible in solutions of 1 : 25,000, and can be used for the detection of salicylic acid in milk. Salicylates show stronger fluorescence than *m*- and *p*-hydroxybenzoates. Etherification of the hydroxyl group destroys the fluorescence, and the latter is much more intense with the aryl than with the alkyl salicylates. Coumarin and its derivatives show only weak fluorescence, with the exception of æsculin. Novocaine hydrochloride shows a bluish-violet fluorescence, intensity 32, whilst stovaine and cocaine hydrochlorides remain dark. The colours and intensities of the following *iso*quinoline derivatives are tabulated: papaverine, bluish-white, 6; hydrastine, greenish-white, 55; narcotine, violet, very dark; narceine, violet-blue, 7; veratric acid, pale blue, 5; opianic acid, similar, 10; potassium opianate,

blue, 5; hydrastinine and cotarnine, nil; hydrastine hydrochloride, blue, 36; hydrastine salicylate, greenish-white, 55; hydrastinine hydrochloride, 4; and cotarnine hydrochloride, yellow, 35. Freshly-prepared hydrastine sulphate solution shows no fluorescence, the latter developing slowly in the cold, rapidly in the hot, and instantaneously on the addition of a few drops of hydrogen peroxide.

F. G. W.

Colour and Chemical Constitution. XIX. Organic Fluorescence. J. Moir (*Trans. Roy. Soc. S. Africa*, 1924, 12, 45—50).—All organic substances which are known to exhibit fluorescence contain an aromatic ring, although the presence of such a ring is not essential to the production of colour and the majority of aromatic substances do not fluoresce. For the production of fluorescence further factors are required in the nature and arrangement of the groups attached to the ring, and one of the groups must apparently be an auxochrome. The arrangement of the groups appears to be less important than their nature, when only one aromatic ring is present. Two ortho-groups alone do not cause fluorescence; it is apparently necessary that, in addition to the auxochrome, a second group attached to the ring by an atom having a double linking to another atom should be present. The fluorescence of α-naphthol, sodium salicylate, and sodium coumarate can be explained in this way. The non-fluorescence of *o*-nitrophenol and the fluorescence of *m*-nitrodimethylaniline present difficulties, and it is possible that spatial differences come into play. The striking fluorescence of the quinol derivatives previously described (A., 1923, ii, 108) and of umbelliferone is probably to be attributed to the co-operation of two pairs of factors. Substances which contain two aromatic rings doubly linked exhibit fluorescence without any auxochromes being present. The fluorescence is sometimes shown only in sulphuric acid solution, sometimes only in the solid state. Since it is impossible to assign a quinonoid structure to the solution of xanthene in sulphuric acid it is evident that fluorescence does not depend on unsaturation outside the ring, but wholly on the rings as such with the presence of two groups holding them in a rigid position, *i.e.*, on purely spatial factors. It is suggested that fluorescence is merely the reflexion of light from such rigid molecules acting as mirrors, and that only such molecules as are devoid of rigidity do not fluoresce.

The following data are given for the position of absorption-bands by transmitted light in solutions of the substances in concentrated sulphuric acid: xanthene, λ 360 (strong) and 425 (weak); dihydroanthracene, 352 and 400; dihydroacridine, 430 and 408 (narrow) and 340 (broad); dihydrophenazine, 398 (broad); phenoxazine, 417; xanthhydrol, 450 and 470 (weak); anthracene, 330 (broad); acridine, 355 (narrow); phenazine, 510 and 550 (weak); phenoxazonium salts, 460; anthraquinone, 403 (broad); acridone, 336 and 358 (both narrow); phenazine oxide, 501 and 544; xanthone, 340 and 405. The green solution of anthracene and dihydroanthracene has 701, whilst the corresponding quinhydrone of

dihydrophenazine probably has an absorption band above 760. The quinhydrone of phenoxazine has a band at 537 in sulphuric acid. R. B.

Absorption of Fluorescent Light by the Emitting Substance. T. Duseberg (*Physikal. Z.*, 1925, **26**, 157—166).—A narrow beam of light was sent vertically through a rectangular trough and the fluorescent light which was emitted horizontally was examined in a spectrophotometer after passing through a layer of the fluorescent solution. Light of wave-length of the maximum intensity was transmitted better than that on either side of it. The fluorescent light can again excite fluorescence in the second solution, the shorter wave-lengths being the more active. This furnishes the explanation of the fact that the maximum intensity of the fluorescent light is displaced towards longer wave-lengths by passage through a considerable layer or a concentrated solution of the substance. E. B. L.

Excitation of Phosphorescence by High-frequency Radiation. E. Rupp (*Ann. Physik*, 1924, [iv], **75**, 369—390).—On Lenard's photoelectric theory of phosphorescence, a conductivity change should accompany the excitation of a phosphorescent body. In the present paper, the conductivity changes in zinc sulphide induced by excitation by X-rays and γ-rays are described, and are correlated with the light emission from the sulphide. The problem is discussed whether such high-frequency radiations excite the "phosphor" by direct photoelectric action, or indirectly by the secondary action of high-velocity electrons ejected from the body of the material. S. B.

Effect of Heat Treatment upon the Cathode Luminescence of Fluorite. F. G. Wick and J. M. Gleason (*J. Opt. Soc. Amer.*, 1924, **9**, 639—648).—The effect of preliminary heating on the rate of decrease of the intensity of the luminescence from fluorite has been examined, when excited by continuous bombardment by cathode rays. Heating at 600° increased the duration of phosphorescence and decreased the rate of its decay. Fluorite subjected to surface fusion, however, had a shortened period of phosphorescence. S. B.

Critical Potential of Methane and its Absorption in the Ultra-violet. G. Glocker (*Proc. Nat. Acad. Sci.*, 1925, **11**, 74—77; cf. A., 1924, ii, 374).—No part of the maximum in the current potential curve obtained in three- or four-electrode tubes filled with methane can be due to a resonance potential. Absorption measurements fail to detect any absorption in the required region (for 5 volts, 2400 Å.) and further proof is afforded by Lenard photoelectric experiments. The various theoretical possibilities are discussed. J. S. C.

Exact Magnitude of the Electric Moment of Dipolar Molecules, and the Chemical Significance of Orientation Polarisation. L. Ebert (*Z. physikal. Chem.*, 1925, **114**, 430—440).—The uncertainty in the value of the electric moment, μ, is discussed.

Different values are obtained for μ by applying the classical gas theory and the quantum theory, respectively, to molecular rotation. For diatomic molecules, $\mu_{quantum}$=about 0·5 μ_{class}. The values calculated from Gans' orientation-polarisation theory by Smyth (cf. A., 1924, ii, 810) are uncertain on account of the incompleteness of the polarisation balance. The question of the deformation of atoms and ions is discussed. The different deformabilities of the halogens are clearly reflected in the values of P_0+P_A for their compounds, which in general diminish in the series Cl $\longrightarrow$ Br $\longrightarrow$ I.

It is assumed that a central atom surrounded by similar atoms forms an electrically symmetrical complex, if co-ordination-saturation is attained. If saturation is not reached, then P_0+P_A, or the moment, decreases with the approach of that symmetry which corresponds with the maximal co-ordination number. The dipolar character of a molecule is to be regarded as an indication of an association tendency. L. L. B.

Dielectric Constants of Liquid Mixtures. M. GRÜTZMACHER (*Z. Physik*, 1924, 28, 342—354).—The dielectric constants of chloroform, carbon tetrachloride, carbon disulphide, toluene, benzene, and of binary mixtures of these, have been measured. The constants for the mixtures cannot be calculated satisfactorily by any formula so far proposed. S. B.

Method of Measuring the Dielectric Constants of Liquids. L. A. SAYCE and H. V. A. BRISCOE (*J. Chem. Soc.*, 1925, 127, 315—322).—The apparatus consists of a container shaped like an elongated Dewar flask, in which the liquid fills the annular space, the inner walls being silvered so as to form the plates of a condenser. For the measurement of the capacity a variable condenser (C_3) is connected in parallel with an inductance (L_3). To this circuit is loosely coupled an oscillatory circuit (L_1C_2) in which oscillatory currents are maintained by means of a triode valve. Resonance between the two circuits is then indicated by a sudden drop in the anode current of the triode circuit. The dielectric container of unknown capacity (C_4) is then coupled in parallel with C_3, and the reduction that has to be made in C_3 in order to restore resonance is a measure of the capacity of C_4. Details are given of the construction of a suitable wide-range condenser capable of very accurate adjustment. The method is tested for benzene, for which the dielectric constant is 2·2389 at 25°, using a frequency of 65×10^3 cycles per sec. W. H.-R.

Dielectric Constant of Water in [the presence of] Strong Electrolytes. H. ZAHN (*Z. Physik*, 1925, **31**, 362—372).—By a development of the work of Schaefer the difference in ϵ between two different electrolytes of the same conductivity can be measured by measuring the change of intensity of a field in passing through a cylinder of the dielectric. It is claimed confidently that the dielectric constant of water in a saturated lithium chloride solution is smaller than that in a dilute sodium chloride solution of the same conductivity. Exact numerical values are not yet possible;

ϵ is certainly <57, probably <42, and may even be considerably less. R. A. M.

Magneto-chemical Phenomena. A. SCHÜKAREW (*Z. physikal. Chem.*, 1925, **114**, 500; cf. this vol., ii, 47).—Further observations on the magneto effect are recorded. L. L. B.

Effect of Pressure on Refractive Index of Organic Liquids. I. EISELE (*Ann. Physik*, 1925, [iv], **76**, 396—402).—Two hollow prisms were employed, in one of which the liquid was submitted to pressure. Monochromatic light traversing the prisms was examined by an interferometer and the shift in the bands on increasing the pressure was measured. The relationship found does not agree with any formula connecting refractive index and compressibility, but the results lie between the values calculated from the Beer and Lorentz formulas. E. B. L.

Rotation Dispersion. II. J. LIFSCHITZ (*Z. physikal. Chem.*, 1925, **114**, 485—499; cf. A., 1923, ii, 525).—A further investigation of the relation between rotation dispersion, light absorption, and stereo-constitutive structure. A series of metallic complexes of active *d*-alanine, *l*-propylenediamine, and *l*-aspartic acid has been studied polarimetrically, and the effect of different modes of linking on the rotatory power is discussed. It is shown that homopolar and heteropolar principal valencies have characteristically different optical effects, and that secondary valencies are different from both. For internal complex salts (characterised by containing a metal atom connected by both primary and secondary valencies) there are special rules. It is concluded that primary and secondary valencies are not optically similar in character, and that Werner's evidence as to their identity is unacceptable. By isolation of the partial antipodes of the *d*-alanine complex of cobalt, direct evidence seems to be given of a relative asymmetric synthesis by formation of cleavable metal complexes from inactive metallic salts and active co-ordinated molecules, and at the same time a new method seems to be found for the preparation of active internal complex salts. It is pointed out that the investigation of rotation dispersion represents a crucial method for the exploration of stereo-constitutive questions. L. L. B.

Rotatory Dispersion of certain Normal Alkyl Hexahydromandelates. C. E. WOOD and M. A. COMLEY (*J. Chem. Soc.*, 1924, **125**, 2630—2646).—To determine the effect on rotatory dispersion of the substitution of the *cyclo*hexyl group for the methyl group of lactic acid (cf. T., 1923, **123**, 600) the optical rotations of the nine esters, from methyl to *n*-nonyl, of hexahydromandelic acid have been studied over as wide a temperature range as possible. All the esters exhibit complex rotatory dispersion which, in the higher members, approaches the condition for anomaly. The esters in general retain the sign of rotation of the acid from which they are derived. Molecular dispersion is shown to be chiefly dependent on the groups immediately surrounding the asymmetric centre, temperature and lengthening of the chain producing only secondary

effects. The molecular dispersion of the lactates is not very different from that of the hexahydromandelates. Large differences, however, are observable in the molecular rotation. The temperature coefficient of the latter is negative for the hexahydromandelates and positive for the lactates, and the numerical value of the first is decidedly greater than that of the second. In general, the molecular rotation appears to decrease to an approximately constant value on ascending the series, irregularities being observed in the *n*-butyl and *n*-octyl esters. Experimental details of the preparation and resolution of hexahydromandelic acid and of the preparation of the different esters have been given. M. S. B.

Rotatory Dispersive Power of Organic Compounds. XIII. Significance of Simple Rotatory Dispersion. Rotatory Dispersion of Camphorquinone and of Sucrose. T. M. Lowry and E. M. Richards (*J. Chem. Soc.*, 1924, **125**, 2511—2524).—In view of recent criticism, the utility of the simple dispersion formula $\alpha=k/(\lambda^2-\lambda_0^2)$ (T., 1913, **103**, 1067; Lowry and Dickson, A., 1914, ii, 786) has been explained. The graphical and numerical methods of testing it have been described, and the casual and systematic errors and limits of application discussed. A complex dispersion may appear to be simple if the partial rotations are all controlled by identical or closely similar dispersion constants. A new method has been described for distinguishing between simple and complex rotatory dispersion, depending on Drude's postulate that the wave-lengths of his dispersion equations coincide with the wave-lengths of maximum absorption of light. The genuine hyperbolic curve of the simple dispersion formula can be distinguished from the false hyperbola of the complex dispersion, controlled by two natural frequencies, because the latter, in the region of longer wave-lengths, will be directed towards an imaginary asymptote lying between the real asymptotes of the component partial rotations, whilst the former will have as its asymptote the central line of a real absorption band. The method is limited to equations in which the value of the dispersion constant is not less than about $\lambda_0^2=0{\cdot}055$ by the difficulty of making exact measurements of selective absorption beyond $\lambda=2327$ Å. Measurements have been made of the rotatory dispersion of camphorquinone and sucrose, and the results discussed from the point of view of the new method of testing. M. S. B.

Diffusion of Light in Fluids. Y. Rocard (*Compt. rend.*, 1925, **180**, 52—53).—In the preparation of optically pure liquids by filtration, the size of the filter-pores is of little importance, but the filtration must be very slow. If a parallel beam of light traverses a liquid in the direction *Ox*, and is observed from a distant point on *Oy*, depolarisation (ρ) is defined as the ratio of the intensity of the light vibrating along *Ox* to that vibrating along *Oz*. For optically pure water, $\rho=0{\cdot}11$ for green light, and for freshly-prepared water the value of ρ is little affected by wave-length. A slight fluorescence is produced owing to gradual solution of the glass of the containing vessel, as a result of which ρ may rise to

0·18 in violet light. For benzonitrile ρ=0·65 for red light, whilst for nitrobenzene ρ=0·68, 0·67, 0·68, and 0·74 for red, yellow, green, and blue light, respectively. Theoretical reasoning shows that ρ should be little affected by a high magnetic field in agreement with the results of Martin (this vol., ii, 90). W. H.-R.

Electrical Double Refraction of Gases. N. Lyon (*Z. Physik*, 1924, **28**, 287—298).—According to the Born dipole theory, the Kerr constant of a gas should increase more rapidly than its density at high pressures. The electrical double refraction of carbon dioxide has accordingly been measured in the pressure interval 10—50 atm. using a potential difference of 30,000 volts, but the double refraction was found to be closely proportional to the density of the gas throughout the range. S. B.

Pyrrole and Melanins. Spectrophotometric Studies. G. Galleranı (*Arch. ital. Biol.*, 1924, **72**, 189—207; from *Chem. Zentr.*, 1924, ii, 2168).—Studies on the absorption spectra of pyrrole and of melanins and on the effect of chemical changes on these spectra confirm the relationship between these substances. The absorption curve of ozonised pyrrole resembles that of oxyhæmoglobin. Pyrrole-black obtained by oxidation in the presence of adrenaline is similar to the melanins. After injection of pyrrole or of 2 : 5-dimethylpyrrole, the urine of dogs shows the melanin curve. Pyrrole-black is regarded as an intermediate stage between pyrrole and the melanins. G. W. R.

Quantum Theory and Molecule Formation. M. Born and J. Franck (*Z. Physik*, 1925, **31**, 411—429).—Triple collisions are required for a quantum mechanism of additive reactions, but not for reactions involving displacement or adsorption. This fact throws light on the phenomena of catalysis and particularly on surface effects. The impact of a quantum of light and two atoms may be regarded as a triple collision. The formation of molecules is considered in detail, first from the point of view of classical mechanics and, secondly, from that of the quantum theory. The conception of a "quasi-molecule" is introduced. Two atoms behave as a loosely bound unit for a finite period after collision without either rotations or vibrations becoming quantised, the entity having a life-period of 10^{-12} to 10^{-13} sec. The evidence for the real existence of such molecules is discussed theoretically and various optical phenomena are quoted in support.

The conception of quasi-molecules leads in the extreme case to a condition whereby an equilibrium between attractions and repulsions follows from classical mechanics. No alternative quantum state could exist, so that any disturbance would disrupt the quasi-molecule, which must therefore be regarded as labile from the point of view of quantum mechanics. A quantum-theory criterion of stability will therefore require that a stable molecule shall show a neighbouring energy state greater than the initial state by at least one quantum number.

The idea of chemical affinity is thus meaningless unless the

criterion of energy levels is fulfilled. From these considerations the notion of a true molecule gains in precision. R. A. M.

Valency of Boron. R. C. Rây (*J. Indian Chem. Soc.*, 1925, **1**, 133—139).—From its position in the periodic classification, boron should possess a positive valency of three and a negative valency of five, the latter being apparent in the case of its hydrides and their related compounds. The stability of the complex $\rangle B{:}B\langle$ has previously been shown (T., 1922, **121**, 1088) and to the hydrides of boron the following formulæ may, therefore, be assigned:

B_2H_6, $H_3B{:}BH_3$; B_4H_{10}, $H_3B{:}BH_2{\cdot}BH_2{:}BH_3$;
B_5H_9, $H_3B{:}BH{:}BH{:}BH{:}BH_3$; B_6H_{10}, $H_3B{:}BH{:}BH{:}BH{:}BH{:}BH_3$;
$B_{10}H_{14}$, $H_3B{:}BH{:}BH{:}BH{:}BH{:}BH{:}BH{:}BH{:}BH{:}BH_3$.

The borohydrate, $H_4B_2(OH)_2$, and the halogen derivatives, B_2H_5X and $B_2H_4X_2$, would be represented by $H_2B(OH){:}BH_2(OH)$, $H_3B{:}BH_2X$, and $XH_2B{:}BH_2X$, respectively. The possibility of boron functioning as a quinquevalent element on the Lewis–Langmuir theory has been discussed (Böeseken, A., 1923, ii, 406); on Bohr's theory, the boron atom consists of the helium structure of two electrons revolving in one-quantum orbits and three electrons in two-quantum orbits. These three electrons can each share the outer ring of three halogen atoms, thus completing their octets, or five additional electrons can gather round the boron atom to complete its octet. The non-existence of BH_5 has been explained by Rankine (A., 1922, ii, 635). Further examples of quinquevalent boron are cited from the literature. J. W. B.

Valency Problem of Sulphur. VIII. H. Lecher.—(See i, 390.)

Electronic Theory of Valency and the Electrolytic Oxidation of Formaldehyde. C. del Fresno (*Anal. Fís. Quím.*, 1924, **22**, 545—550; cf. A., 1924, i, 612).—The electrolytic oxidation of formaldehyde is further discussed and a scheme is suggested in accordance with the Langmuir theory of atomic structure.

G. W. R.

Complexity of the Solid State. I. Behaviour of Pure Sulphur Trioxide. I. A. Smits and P. Schoenmaker (*J. Chem. Soc.*, 1924, **125**, 2554—2573).—The irregular behaviour of sulphur trioxide with regard to melting point and vapour pressure indicates a remarkable complexity. This has been studied by examination of the intensively dried ice-form, obtained by distillation and drying over phosphorus pentoxide so that the velocity of inner transformation becomes very small. After keeping for 56 hrs. at 18°, the vapour pressure at 0° had diminished by 71·4 mm., and by distillation the vapour pressure could be changed continuously from an initial value of 207 mm. to a final value of 22 mm. at 0°. As the vapour pressure diminished the initial melting point first rose and then fell. All these different solid phases belong to the ice-form, since they give melting ranges falling on the continuous three-phase line corresponding with the equilibrium, solid–liquid–vapour, for a dissociable compound. This can be explained

on the theory of allotropy by assuming that the system, sulphur trioxide, is composed of at least two different kinds of molecules, α and β, which not only change each into the other, but also form a dissociable compound αβ. After intensive drying, equilibrium is reached only slowly. When behaving as a unary system, the ice-form of sulphur trioxide is a little richer in the more volatile pseudo-component than the dissociable compound. A second metastable form, the low-melting asbestos form, and the stable or high-melting asbestos form have also been investigated and show similar phenomena. M. S. B.

Composition of Simple Substances as Revealed by Intensive Drying. A. Smits (*Chem. Weekblad*, 1924, **21**, 594—600; cf. *B.*, 1924, 855).—The vapour pressure of the high-melting form of sulphur trioxide, m. p. ±60°, has been determined, after intensive drying and partial distillation, at 50°. The vapour pressures were 59·1 cm. mercury before distillation, 3·7 cm. one hour after distilling off part of the material, 29·1 cm. 43 hrs. after distillation, and 49·4 cm. 761 hrs. after distillation. These results are compared with those obtained with mixtures of chlorine and bromine at −80°, and are held to indicate that this form of sulphur trioxide is a mixture of two different modifications and of a compound of the two. S. I. L.

Complexity of the Solid State. II. Behaviour of Phosphorus Pentoxide. I. A. Smits and A. J. Rutgers (*J. Chem. Soc.*, 1924, **125**, 2573—2579).—Determinations have been made of the vapour pressure of the crystalline sublimate of intensively dried phosphorus pentoxide. This was shown to vary with the velocity of distillation. Above 400°, the very volatile metastable forms are transformed into a more stable modification, and the vapour pressure falls continuously to 0·02 cm. of mercury, but, as before, the values depend on the previous history. According to the old views on phase equilibria, the stable modification should melt at a higher vapour pressure than the highest exhibited by the metastable form. On the contrary, however, it shows an initial melting point with a much lower vapour pressure, namely, 0·59 atm. at 563°, whilst the metastable modification gives about 2 atm. at 370°. It also melts over a large temperature range. In this respect, phosphorus pentoxide resembles sulphur trioxide (cf. preceding abstracts). The crystalline state evidently consists of mixed crystals built up from molecules of different kinds, and the pure substance behaves as a unary system only when inner equilibrium is established. M. S. B.

Systematic Doctrine of Affinity. XXX. Heats of Formation of Intermetallic Compounds. VI. Tin Alloys. W. Biltz and W. Holverscheit (*Z. anorg. Chem.*, 1924, **140**, 261—276).—The heats of formation of alloys of tin with calcium, magnesium, and sodium were measured by the method previously described (cf. A., 1924, ii, 482), a solvent of ferric chloride in hydrochloric acid being used. The results, in Cal. per g.-mol.,

together with the densities of the alloys at 25°, were: $CaSn_3$, 43 (*d* 5·989); Mg_2Sn, 49 (*d* 3·625); $NaSn_2$, 15 (*d* 4·725); NaSn, 11 (*d* 3·990); Na_4Sn_3, 36 (*d* 3·570); Na_2Sn, 12 (*d* 3·111); Na_4Sn, 21 (*d* 2·315). The alloy with the highest heat of formation (Mg_2Sn) is the only one of the above which is formed from its components with an increase in volume; the sodium alloys are formed with a percentage contraction which increases with increasing sodium content. The curve of the heats of formation of the sodium alloys against the valency numbers exhibits a change in gradient (cf. *ibid.*); this supports the complex theory of intermetallic compounds. S. K. T.

Theoretical Stoicheiometry of the Intermolecular Forces and the Space Occupied by the Molecules of Organic Compounds. I—II. E. Wöhlisch (*Physikal. Z.*, 1925, **26**, 170—176, 177—184).—A study of the molecular volumes of isomerides and the diameters of the molecules as calculated by several different methods. The volumes of the molecule calculated from van der Waals' equation and from the viscosity of the vapour show a dependence on constitution, as also do the values for the volume at the critical temperature and the b. p. in certain cases; values obtained from the molecular refraction and the surface tension and heat of vaporisation were useless for the purpose. Rise in b. p. accompanies diminution in the space between the molecules, even when an increase in the total molecular volume produces a rise in b. p. Acids have larger volumes than the isomeric esters and smaller spaces between; similarly, the molecules of the alcohols are larger than those of the isomeric ethers; branched hydrocarbons have smaller volumes than simple chains; addition of chlorine to a carbon atom reduces the volume of the molecule. E. B. L.

X-Ray Investigation of the Lower Members of the Fatty Acid Series. R. E. Gibbs (*J. Chem. Soc.*, 1924, **125**, 2622—2625).—*X*-Ray measurements of the d_1, d_2, d_3, and also d_4 spacings have been extended to the lowest members of the fatty acid series (cf. Müller, T., 1923, **123**, 2043; Piper and Grindley, A., 1923, i, 1056). For the higher members, d_1 varies directly with the number of carbon atoms and is evidently related to the length of the chain. At hexoic acid deviations from the linear law appear and increase gradually down to propionic acid. An abrupt change occurs at acetic acid. This corresponds with the change observed in the freezing points (Massol, A., 1896, i, 408). The side spacings for the even acids, d_2, d_3, and d_4, change only to a small extent, but the odd acids show less regularity. The results are discussed from the point of view of the three possible types of chain suggested by Müller and Shearer (T., 1923, **123**, 3156). Mention is made of further work which demonstrates the true crystalline nature of stearic acid. M. S. B.

Compton Effect with no Box Around the Tube. P. A. Ross and D. L. Webster (*Proc. Nat. Acad. Sci.*, 1925, **11**, 56—61; cf. following abstract).—Observations of the spectra of scattered

X-rays, the scattering occurring in a compartment large enough to make the inverse square law alone suppress the scattered rays from light elements beyond detection, fail to detect the peak reported by Duane. The position of the Compton line agrees with the computed position within the limits of experimental error. The photographs with aluminium as scatterer are better defined than those obtained with sulphur. The present status of the tertiary-ray hypothesis is reviewed. J. S. C.

Compton Effect: its Relation to Duane's Box Effect. P. A. Ross and D. L. Webster (*Proc. Nat. Acad. Sci.*, 1925, **11**, 61—64; cf. Duane and collaborators, *ibid.*, 1924, **10**, 374—379).—Evidence is reviewed definitely contrary to Duane's box-effect theory as an explanation of the Compton peaks, and leaves Compton's theory of the scattering of quanta by single electrons as the only hypothesis yet advanced capable of explaining their existence. J. S. C.

Röntgenographic Measurement of Absolute Dimensions of a Single Crystal in Bodies of Fine Crystalline Structure. N. Seljakow (*Z. Physik*, 1925, **31**, 439—444).—Mathematical. An expression is deduced similar in form to one published without proof by Scherrer. The results given by the expressions differ by about 2% only. R. A. M.

Röntgen-Spectroscopic Determination of the Proportion by Weight of an Element in Mixtures and Compounds. R. Glocker and W. Frohnmayer (*Ann. Physik*, 1925, [iv], **76**, 369—395).—A photograph of the absorption spectrum of the material for *X*-rays is obtained and the ratio of the density at the edge of the band to the density just outside it measured. Crystals, powders, solutions, sheets, etc. can be used. The method is particularly applicable when an element of high atomic weight has to be determined in the presence of elements of low atomic weight; also when only a small quantity of the material is available or when ordinary analytical methods are tedious. The degree of accuracy is about ± 5% of the correct weight. Thus, barium in a glass gave 5·45% as against 5·8% by chemical analysis; the exposure necessary was 90 mins., using a water-cooled Coolidge tube fed with 5 milliamps. at 55,000 volts. E. B. L.

Orientation of Ammonium Iodide by Muscovite Mica. L. Royer (*Compt. rend.*, 1925, **180**, 448—450; cf. this vol., ii, 110).—The orientation of ammonium iodide on the two surfaces of a cleaved crystal of muscovite mica has been investigated. Each of the two planes separated by cleavage gives rise to one or the other of two possible orientations. The layers of molecules are individually deprived of a plane of symmetry but are symmetrical one to the other by reference to the plane (010). The addition of ammonium iodide permits of the exact determination of the lattice structure of mica and of the molecular magnitudes of its mesh. J. S. C.

Molecular Symmetry in Crystal Structure. J. H. SMITH (*Nature*, 1925, **115**, 334—335).—Sodium and potassium chlorate, bromate, and iodate exhibit structural relations similar to those known to exist among the alkali polyhalides, and falling into two groups, the cæsium chloride and the sodium chloride group, respectively. Sodium chlorate and bromate and potassium chlorate belong to the latter, potassium bromate and iodate, and probably sodium iodate, to the former. The half-molecule parallelepipedon of potassium chlorate has edges 3·56, 3·69, 3·69 Å. Potassium bromate is ditrigonal pyramidal (pseudocubic), with edge of one molecule pseudocube 4·46 Å. The edges of the one molecule parallelepipedon of monoclinic (pseudocubic) potassium iodate are 4·57, 4·50, 4·50 Å. It is inferred that the complex radicals act as single units and the molecule behaves as an electric doublet. Since the symmetry is independent of the constituent atoms in the radical, it is probable that the crystal-forming forces are electrostatic attractions independent of any structural axes the radicals may possess. A. A. E.

Relationship between the Fine Structures of the Two Crystalline Forms of Carbon and Zinc Sulphide. J. BECKENKAMP (*Z. anorg. Chem.*, 1924, **140**, 277—291).—A comparison of the crystal forms of diamond and zinc blende and of graphite and wurtzite, based on the considerations previously put forward by the author (cf. this vol., ii, 90), supports Bragg's atomic arrangement for graphite. The observed axial ratios of the molecule are in agreement with both the Bragg and the Debye–Scherrer structures. It is shown that diamond and zinc blende must be considered chain compounds, whereas graphite represents a typical ring compound; the structures of these molecules are described in detail. S. K. T.

Symmetry between Growth and Diminution in Size of Crystals. G. FRIEDEL (*Compt. rend.*, **179**, 1924, 796—799).—A cylindrical cavity, 2 mm. in diameter and 5 mm. deep, ending in a roughly hemispherical surface was made in a crystal of alum. The whole crystal, including the sides but not the bottom of the cavity, was then varnished, and an alum solution, not quite saturated, allowed to flow through the cavity. Subsequent examination showed octahedral, cubic, and dodecahedral facets arranged in the form of a "negative crystal" at the bottom of the cavity. The dominant faces were octahedral, the cubic and dodecahedral faces occurring principally on the edges and summits. It is concluded that crystal growth from a saturated solution and the diminution in size undergone in a solution which is not quite saturated are approximately symmetrical processes as regards ratios of increase and decrease between the various faces of the crystal. H. J. E.

Modification of Crystal Faces owing to their Syncrystallisation with Foreign Matter Dissolved in the Mother-liquor. P. GAUBERT (*Compt. rend.*, 1925, **180**, 378—380).—Discussion of hypotheses. The production of cubes, instead of octahedra, of lead nitrate by its crystallisation from a saturated solution of methylene-

blue is attributed to orientation of crystals of the former on those of the latter, and it is stated that all other cases of modification by syncrystallisation can be similarly explained; the faces are not modified by the presence of isomorphous substances. F. M. H.

Isomorphism between Tervalent Thallium and Rare Earth Metals. F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, i, 8—14).—The double sulphates

$$NH_4Tl(SO_4)_2,4H_2O$$

and $NH_4La(SO_4)_2,4H_2O$ form monoclinic crystals, the crystallographic constants being, respectively, $a:b:c = 1{\cdot}080:1:1{\cdot}017$, $\beta=104°\ 26'$, and $a:b:c=0{\cdot}3509:1:0{\cdot}9145$, $\beta=97°\ 36'$; the respective molecular volumes of the two salts are 152·4 and 151·5. The salts form mixed crystals, the limiting solubility of the latter in the former being about 11·7%. The double sulphate, $NH_4Nd(SO_4)_2,4H_2O$, also dissolves to the extent of 11% in $NH_4Tl(SO_4)_2,4H_2O$. Unsuccessful attempts have been made to replace metals of the rare earths in the double nitrates

$$Mg_3R_2^{\cdots}(NO_3)_{12},24H_2O$$

by tervalent thallium. The ammonium in ammonium thallic sulphate, $(NH_4)_3Tl(SO_4)_3$ (cf. Marshall, A., 1903, ii, 21), is capable of partial isomorphous substitution by univalent thallium.

T. H. P.

Deformation- and Recrystallisation-structure of Metals. R. GLOCKER (*Z. Physik*, 1925, **31**, 386—410; cf. A., 1924, ii, 518).—A röntgenographic investigation of the effect of rolling and subsequent heat treatment on the surface of metallic silver. Photographs are given showing the interference patterns obtained with a plate of rolled silver before and after heating for various periods at temperatures up to 850°. Short heat treatment has little effect, but 10 mins. at 140—150° causes a definite change in the photograph, black spots being superposed on the original *X*-ray diagram. Recrystallisation is indicated by the disappearance of some of the intensity maxima. A graphical method of interpretation is given and the experiments are discussed fully and the orientation of the crystals under various conditions is worked out in detail.

In the rolled surface the [112] direction is parallel to the direction of rolling and the [011] plane occurs on the rolled plane of the metal. If the heating is continued long enough or is at a high temperature, complete recrystallisation occurs when the regular orientation of the rolled surface disappears entirely. By less drastic heating an intermediate stage occurs, in which the [112] direction is still parallel to the direction of rolling, but instead of a [011] plane in the surface a [113] plane is found, *i.e.*, the cube edge is shifted to a position symmetrical to both direction and plane of rolling. The new surface structure disappears with further heating. R. A. M.

Fatty Acids. G. FRIEDEL (*Compt. rend.*, 1925, **180**, 409—411).—Smectic structure is intermediate between amorphous structure and crystalline structure. A smectic substance is characterised by the possession of a single direction, perpendicular to which its molecules

are arranged in equidistant planes, the distribution of the molecules in every plane being irregular. *X*-Ray or, more simply, microscopical examination shows that fatty acids, particularly palmitic acid (cf. Trillat, this vol., ii, 187), are crystalline and not smectic.
W. E. E.

Molecular Weight of Cholesterol. J. R. Partington and S. K. Tweedy (*J. Chem. Soc.*, 1925, **127**, 496—498).—The mean molecular weight of cholesterol determined from the elevation of the b. p. in benzene and in alcohol, and by the depression of the f. p. in benzene, is 423, showing that some association takes place in these solvents. A. R. P.

Cryoscopy in Sodium Sulphate Decahydrate. E. E. Turner and W. H. Patterson (*Trans. Faraday Soc.*, 1924, **20**, 345—347).—The molecular weights of a number of salts have been determined using sodium sulphate as cryoscopic solvent (cf. Löwenherz, A., 1896, ii, 149). The most probable value of the depression constant, K, is 32·5, but for carbamide, which was used as a standard, the depression is not strictly proportional to the concentration. The molecular weight M is given by the relation $M=100Kw/W\Delta$, where w is the weight of solute, W the combined weight of solute and sodium sulphate decahydrate, and Δ the observed depression of the transition temperature. Sodium nitroprusside, ferrocyanide, aluminoxalate, ferrioxalate, and chromioxalate exist as simple molecules, in agreement with the work of Burrows (T., 1919, **115**, 1429). Borax and sodium oxalate give abnormally low results.
W. H.-R.

Effects of certain Elements on the Electrical Resistivity of Copper. A. L. Norbury (Inst. Metals, Mar., 1925; advance copy, 4 pp.).—The effect of dissolved elements on the electrical resistivity of copper is small when the affinity of the element for copper is small, but the resistivity of the metal is increased greatly when the alloying element has a great affinity for copper. [Cf. *B.*, 1925, 245.]
A. R. P.

Thermal and Electrical Conductivities of some Pure Metals. F. H. Schofield (*Proc. Roy. Soc.*, 1925, **A**, **107**, 206—227).—The thermal and electrical conductivities of commercially pure aluminium, copper, magnesium, nickel, and zinc have been determined at temperatures of 100° and higher. In determining the thermal conductivity lateral heat loss was eliminated by use of the guard-ring principle. The thermal conductivity of aluminium was found to increase with rising temperature; that of nickel to decrease at first and then above 500° to show an increase. The other metals showed on the whole slight decreases of conductivity with temperature. The values of Lorenz's function $K/\lambda T$ (K and λ being the thermal and electrical conductivities and T the absolute temperature) for copper, magnesium, and zinc were practically constant at all temperatures; that for aluminium showed a rise with increasing temperature; that for nickel a rise to 300°, above which temperature it remained nearly constant except for an

abnormal value at 400°. The results are compared with those of previous workers who, however, for the most part employed lower temperatures. N. H. H.

Effect of Changes in Total Carbon and in the Condition of Carbides on the Specific Resistance and on some Magnetic Properties of Steel. E. D. CAMPBELL and G. W. WHITNEY (*J. Iron and Steel Inst.*, 1924, **110**, 291—311).—Two series of steel bars, one with and one without chromium, were prepared, the composition of the individual specimens of each series differing only with regard to the carbon; this was done by heating carburised bars with uncarburised in an atmosphere of moist hydrogen for several days at 950° and cooling in dry hydrogen. In this way, part of the carbon was removed from the bars rich in this element and redeposited in those poor in carbon. In the pure iron–carbon series the specific resistance of the annealed metal is a linear function of the carbon content up to 0·9%, at which point there is an abrupt rise followed by a slightly more rapid linear rise than before. In the chromium–iron–carbon series, increase of carbon content at first decreases the resistance due to the precipitation of the chromium from solid solution as a double iron–chromium carbide, then, after passing the eutectoid point, increases the resistance linearly with the carbon content. In hardened alloys of both series, the specific resistance increases more rapidly than the carbon content, indicating a lowering of the molecular weight of the carbides with increase of atomic concentration, or a decrease in their stability. Experimental evidence is given in support of a new theory of the mechanism of remanent magnetism. A. R. P.

Optical Study of Indanyl Bases. C. COURTOT and A. DONDELINGER (*Bull. Soc. chim.*, 1925, [iv], **37**, 115—130).—The following densities and refractive indices are recorded: indanylamine, d_4^{15} 1·0380, n_D^{15} 1·5619; *N*-methyl-, 0·9981, 1·5411; *N*-dimethyl-, 0·9803, 1·5357; *N*-ethyl-, 0·9846, 1·5342; *N*-diethyl-, 0·9542, 1·5218; *N*-phenyl-, 1·0910, 1·6215; *N*-*o*-tolyl-, solid [*M*]= 72·79 in benzene; *N*-*m*-tolyl-, 1·0742, 1·6122; *N*-*p*-tolyl-, solid, [*M*]=73·02 in benzene; *N*-xylyl-, 1·0600, 1·6037; *N*-phenyl-*N*-methyl-, 1·0790, 1·6165; *N*-phenyl-*N*-ethyl-, 1·0647, 1·6065; and *N*-methyl-*N*-benzyl-indanylamine, 1·0438 and 1·5775, respectively. The α-indanyl group behaves, refractometrically, as an aliphatic group, causing no anomaly in the molecular refractions of secondary or tertiary bases when the remaining groups attached to the nitrogen atom are aliphatic or alicyclic. In the indanylalkylarylamines, the molecular refractions agree with those calculated using Brühl's constants, but show an exaltation of 1·58—1·64 units above the value calculated using Eisenlohr's constants. Phenyl-, *o*-, *m*-, and *p*-tolyl- and xylyl-indanylamines show an exaltation of 0·67—0·88 (liquid) and 1·41—1·64 (in benzene), this being apparently characteristic of the phenylindanyl group, and independent of the positions of substituents in the phenyl group. The absorption spectra of the above bases are figured, as well as those of *o*-, *m*-, and *p*-nitrophenyl-, diphenyl-, and β-naphthyl-

indanylamines. The latter shows a bluish-violet fluorescence. The indanyl group is a stronger chromogen than the benzyl, but weaker than the phenyl group. F. G. W.

Effect of Temperature on the Anomalous Reflexion of Silver. M. DE SÉLINCOURT (*Proc. Roy. Soc.*, 1925, **A**, **107**, 247—254).—On the assumption that the anomalous reflexion coefficient of silver which occurs at about 3200 Å. is, in terms of the classical electro-magnetic theory, due to the inability of the "free" electrons to vibrate with frequencies corresponding with this region, the effect of the temperature of the silver has been determined, since it is to be expected that if the restoring force on the vibrating electrons varies with the distance between them and neighbouring atoms and electrons, the limiting frequency on either side of this band will vary as the metal contracts or expands. At the temperatures measured ranging from −183° to +150°, the band was found to be shifted towards the longer wave-lengths with increasing temperature, which corresponds with the view that with increasing distance between the atoms the restoring force and hence the frequency is diminished. The width of the band was found to vary with temperature, from which it is inferred that the particles controlling the electrons have an amplitude of oscillation of the same order as the atom. To explain this, a restatement in terms of the quantum theory is considered probably necessary. N. H. H.

Specific Heats. S. WIESNER (*Ann. Physik*, 1925, [iv], **76**, 439—443).—The author imagines the atoms of a substance in process of melting as forming aggregates, the rotation of which takes up the energy supplied—the latent heat of fusion. If d is the difference between the specific heats of the solid and liquid and r the atomic refraction, he shows that $r\sqrt{d}$=const.=3. E. B. L.

Specific Heat of Liquids. R. N. GHOSH (*J. Indian Chem. Soc.*, 1925, **1**, 123—124).—An empirical formula, $E=3NkT+N/2\,.\,x/(e^x-1)$, where $x=h\nu/kT$, N=number of atoms per unit mass, ν is Lindemann's constant, T the absolute temperature, and h and k are Planck and Boltzmann's constants, is proposed for the energy of a liquid per unit mass. From this equation $C_v=3Nk+\frac{1}{2}Nk\,.\,e^x x^2/(e^x-1)^2$, and the value of C_v is calculated for fourteen elements in the liquid state. J. W. B.

Heats of Combustion of Decahydronaphthalenes and β-Decalones. W. A. ROTH and R. LASSÉ (*Annalen*, 1924, **441**, 48—53).—A thermal examination of Hückel's products (this vol., i, 258). Between *cis*- (1499·9) and *trans*-decalins (1496·9) there is a difference of 3 kg.-cal. per mol. in heat of combustion. The *cis*- and *trans*-β-decalones (β-ketodecahydronaphthalenes) give equal values (1400·2 kg.-cal. per mol.). *cis*-Decalin is thermically identical with Willstätter and Hatt's preparation (A., 1912, i, 545; Roth and von Auwers, A., 1915, ii, 146). C. H.

Recent Measurements of the Joule Effect for Carbon Dioxide. F. G. KEYES and F. W. SEARS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 38—41).—The Joule effect for carbon dioxide is considered

from a thermodynamic point of view and theoretical equations are developed, the experimentally determined temperature changes being in fair agreement with those predicted. A convenient form of apparatus is described in which the fall in temperature is measured by means of a ten-junction copper–constantan thermocouple.

J. S. C.

Pyrophoric Phenomenon in Iron. A. Smits and G. Wallach (*Rec. trav. chim.*, 1925, **44**, 130—131).—By reducing ferrous oxide with hydrogen at temperatures varying between 575° and 800° and cooling in hydrogen, it is found that, on heating for 1 hour, the pyrophoric properties begin to decrease from 650° and rapidly disappear above 710°; this corresponds with the rapid alteration in the internal condition of iron at about 760°. F. M. H.

Osmium Tetroxide. H. von Wartenberg (*Annalen*, 1925, **441**, 318; cf. this vol., ii, 231).—Ruff and Tschirsch (A., 1913, ii, 416) have already recorded the b. p. of osmium tetroxide as 130°, from vapour-pressure determinations by extrapolation. R. B.

Boiling Point Relations for Fused Salts. R. Lorenz and W. Herz (*Z. anorg. Chem.*, 1924, **141**, 131—132; cf. A., 1921, ii, 486; 1922, ii, 739).—The relation $T_{(p=15)}/T_s=0{\cdot}765$ (where T is the absolute b. p. at 15 mm., and T_s the b. p. at 760 mm.), which has been shown to hold for fused salts, has now been verified from the experimental data of von Wartenberg and his collaborators for a large number of halides. Good agreement is obtained in nearly every case, the few deviations being probably due to experimental difficulties. L. L. B.

Melting Point and Vaporisation of Graphite. E. Ryschkewitsch (*Z. Elektrochem.*, 1925, **31**, 54—63).—Carbon rods containing less than 0·1% of impurity and narrowed in the middle were heated electrically in an atmosphere of argon. The course of the operation was followed by a kinematograph camera taking 25 pictures per sec. No gradual diminution of the cross-section of the rod occurred, but a bright line appeared at the narrowest part where, less than 1/10 sec. afterwards, the rod parted and formed an arc. Small globules of carbon having equal densities were found in the vicinity of the arc at the conclusion of the experiment. These observations show that the rod parted by fusion and not by sublimation. Simultaneous measurements were made of the current density, the pressure, and the temperature, the latter by means of a radiation pyrometer. The temperature of the rod taken just at the moment of parting was found to be independent of the pressure (0·21 to 0·935 atm.) and from it the m. p. was estimated to be $3800\pm100°$ Abs. Measurements were also made of the temperature of the arc formed when the rod parted. This was found to be independent of the current density but dependent on the pressure. It varied from 3450° Abs. at 0·005 atm. to 4330° Abs. at 1·5 atm. Those values above 3800° Abs. (about $\frac{1}{3}$ atm.) are considered to be the b. p. of graphite at different pressures. N. H. H.

Melting and Heat of Vaporisation of Graphite. K. FAJANS (*Z. Elektrochem.*, 1925, **31**, 63—70).—Theoretical. The presence of less than 0·1% of impurity in the graphite used by Ryschkewitsch (cf. preceding abstract) is shown to have a negligible effect. It must be assumed that the positive crater of the arc at pressures above about $\frac{1}{3}$ atm. is covered with a very thin layer of liquid carbon and the temperature of the crater measured above this pressure is its boiling point. For determining the vapour-pressure curve and from it the heat of vaporisation the arc method is considered better at the present than measurements of the rate of vaporisation of carbon filaments. The heat of vaporisation obtained by Kohn and Guckel using the arc method is used to calculate the heat of sublimation of diamond, the value obtained being very near that previously given by the author (cf. A., 1920, ii, 469) namely 150 cal. at the ordinary temperature. N. H. H.

Influence of Pressure on the Freezing Point of *p*-Nitrotoluene, *m*-Dinitrobenzene, and Guaiacol. N. A. PUSHIN (*J. Chem. Soc.*, 1924, **125**, 2628—2630).—By the manometric method of Tammann ("Kristallisieren und Schmelzen," 1903, 192—194), the m. p. of *p*-nitrotoluene has been found to increase from 51·5° to 122·4° as the pressure increases from 1 to 3000 kg./cm.^{2}, that of *m*-dinitrobenzene from 89·8° to 138·0° between 1 and 2000 kg./cm.^{2}, and the m. p. of guaiacol from 28·3° to 60·5° for the same range of pressure. The values found for guaiacol are in close agreement with those calculated from Denecke's equation (A., 1920, ii, 10). M. S. B.

Numerical Values of Chemical Constants and Frequencies of Elements. A. C. EGERTON (*Proc. Physical Soc.*, 1925, **37**, 75—83; cf. A., 1920, ii, 84).—The chemical constant C is given by the Sackur relation $C=3/2\log M-C_0$, where $C_0=\log 2\pi^{3/2}R^{5/2}/N^4h^3$. The value of C_0 calculated from the accepted radiation constants is $-1\cdot589$. The weighted mean of observations on 10 elements leads to an experimental value $1\cdot596\pm0\cdot008$. This value leads to figures for both Stephan's and Wien's constants, which agree with the latest experimental values. The data relating to the chemical constants of 61 elements have been collected and tabulated together with values of $\beta\nu$ (characteristic temperature) based on (*a*) the Lindemann melting-point formula, (*b*) the coefficient of expansion, and (*c*) observations. Values based on specific heat data are given and the relative accuracies discussed. The Lindemann formula gives the closest approximation to experiment. If $\beta\nu$ is plotted against $\log M$ (atomic mass) for various similar elements a linear relation is generally applicable. The evidence is inadequate for a discussion of the relationships between the characteristic frequencies of the elements. R. A. M.

Theoretical Stoicheiometry of Molecular Volume, Intermolecular Attraction, Viscosity, and Ionic Mobility of Liquid Organic Compounds. E. WÖHLISCH (*Biochem. Z.*, 1924, **153**, 120—128).—A brief theoretical review from the point of view of the

kinetic theory of results published elsewhere. Acids have a larger specific molecular volume (Φ) and a smaller total volume (V) than the isomeric esters, whilst for the alcohols Φ is greater than and V is less than the corresponding values for the isomeric ethers. Addition of methyl groups or chlorine atoms lowers Φ and increases V. The ratio Φ/V is greater for isomerides of high than for those of low b. p., and increases in homologous series. Of two isomerides, that with the higher b. p. has the higher coefficient of internal friction, since it has a larger molecule and a lesser intermolecular volume ($V-\Phi$). The internal friction of liquids increases in homologous series. Molecular association leads to an increase in Φ and a diminution in ($V-\Phi$). The non-applicability of the Stokes–Einstein equation to the ionic mobilities of certain isomeric ions is correlated with the intermolecular attraction between solvent and solute molecules, in the sense that the attractive forces affect the ionic mobility in the same way as an increase in molecular radius (cf. Lorenz, "Raumerfüllung und Ionenbeweglichkeit," Leipzig, 1922). J. P.

Specific Volume of Steels. J. H. ANDREW and A. J. K. HONEYMAN (*Iron and Steel Inst., Carnegie Schol. Mem.*, 1924, **13**, 253—266).—The effect of varying heat treatment on the specific volume of carbon- and nickel-chromium-steels was investigated. For annealed carbon steels the specific volume $v=0{\cdot}12712+0{\cdot}00052a$, where a is the percentage of carbon. That of Fe_3C is 0·1306. The effect of quenching both kinds of steel from various temperatures is recorded. The specific volume of fully tempered martensite is the same as that of the corresponding pearlite, indicating that in both conditions of the steel the cementite possesses the same crystalline form. CHEMICAL ABSTRACTS.

Liquid Densities at Various Temperatures. J. J. VAN LAAR (*Z. anorg. Chem.*, 1924, **140**, 52—60).—Polemical against Saslawsky (A., 1924, ii, 452). L. J. H.

Density Determinations of Rock-salt Crystals. W. GEISS (*Ann. Physik*, 1925, [iv], **76**, 403—408).—The density was determined by weighing in air and in benzene and also by flotation in a mixture of benzene and bromoform. The results obtained were: $d_4^{18}=2{\cdot}1644\pm0{\cdot}5^{o}/_{oo}$; coefficient of linear expansion between 0° and 50°$=40\times10^{-6}$, from which the lattice constant$=2{\cdot}81400[1+0{\cdot}000040(t-18)]$. E. B. L.

Density of Rhodium. T. K. ROSE (Inst. Metals, Mar., 1925; advance copy, 2 pp.).—Pure rhodium melted in the oxy-hydrogen flame and forged hot has d_4^{20} 12·472 in a vacuum. An ingot forged up from sponge had d_4^{20} 12·222. A. R. P.

Vapour Pressure of Tellurium. J. J. DOOLAN and J. R. PARTINGTON (*Trans. Faraday Soc.*, 1924, **20**, 342—344).—The vapour pressure of tellurium has been determined by a modification of the method of von Wartenberg (A., 1913, ii, 670). The metal was heated in a stream of nitrogen and the loss in weight determined

at three fixed temperatures and at least three rates of flow at each temperature. Assuming that the molecule of tellurium is diatomic, the vapour pressure is calculated as $1{\cdot}86\times10^{-2}$, $4{\cdot}40\times10^{-3}$, and $6{\cdot}10\times10^{-4}$ atmospheres at 671°, 578°, and 488°, respectively. The mean value for the heat of volatilisation per gram-mol. is 26·5 cal.

W. H.-R.

Saturated Vapour Pressure of Hydrocyanic Acid. R. Hara and H. Sinozari (*Tech. Rep. Tôhoku Imp. Univ.*, 1924, **4**, 145—152).—Pure hydrocyanic acid, b. p. 25·7°, was obtained by the action of sulphuric acid (*d* 1·39) on potassium cyanide, the vapour being passed over calcium carbonate and anhydrous calcium chloride before condensation; its polymerisation may be prevented by preserving it in contact with anhydrous calcium chloride. By a modification of the isoteniscopic method of Smith and Menzies (A., 1910, ii, 1036), the vapour pressure was determined within the limits 0—46°. The observed values are in satisfactory agreement with those calculated from the formula $\log P=-1836{\cdot}63/T^{1{\cdot}05}+7{\cdot}5030$.

C. S.

Vapour Pressure of Germanium Hydride. R. Schenk and A. Imker (*Ber.*, 1925, **58**, [*B*], 271—272).—Redetermination of the vapour pressure curve of germanium hydride indicates the b. p. −90° to −91°, which is in harmony with the value (−88·5°) given by Paneth, Haken, and Rabinovitsch (this vol., ii, 60). The lower value observed previously (A., 1922, ii, 855) is ascribed to the preservation of germanium hydride over-night in contact with mercury whereby partial decomposition is caused with liberation of hydrogen.

H. W.

Determination of Surface Tension by the Ring Method (Torsion Balance). P. L. du Noüy (*Biochem. Z.*, 1925, **155**, 113—118).—The author describes the standardisation and use of his apparatus for reading off directly in dynes/cm. the surface tension of liquids. The instrument is based on the ring method, is worked like a torsion balance, and has been used for a large number of determinations of the surface tension of colloidal liquids, chiefly blood-serum. The figures obtained agree within 0·1 dyne/cm. with those of other authors.

P. W. C.

Relation between the Hardness of Metals and Temperature. F. Sauerwald and K. Knehans (*Z. anorg. Chem.*, 1924, **140**, 227—242).—The absolute hardness, in terms of the work of compression, of various metals was determined over a wide range of temperature. For copper, tin, antimony, lead, and aluminium, the hardness is a linear function of the temperature, but with nickel, magnesium, zinc, and iron the curves are irregular. For nickel and magnesium the curves are composed of straight lines, but with zinc and iron the relationship is more complicated. Provisionally the breaks are considered to indicate polymorphism, although this is not always clear. The recoil curves show a general similarity to those for the hardness for the latter group. With the former they decrease with

rising temperature except that for each metal there is a characteristic break during which the recoil is independent of temperature.
L. J. H.

Piezochemical Studies. XXVII. Relation between Diffusion-velocity, Viscosity, and External Pressure. E. COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1925, **114**, 441—452; cf. A., 1924, ii, 521).—A method is described for the determination of viscosity at high pressures in an Ostwald viscosimeter, enclosed in a pressure chamber. It was found that the viscosity of mercury at 20° was raised by 4·8% by a pressure of 1500 atm., and since in similar circumstances the diffusion velocity of cadmium through mercury decreases by 5%, it is concluded that the product of diffusion-velocity and viscosity is constant, independent of the external pressure. L. L. B.

Viscosity of Binary Mixtures. D. B. MACLEOD (*Trans. Faraday Soc.*, 1924, **20**, 348—369).—The viscosities of binary mixtures of liquids can be expressed by the equation $\eta=\eta_1 m_1 x_1/x+\eta_2 m_2 x_2/x$, where η_1 and η_2 are the viscosities of the constituents, m_1 and m_2 their molecular percentages, x_1 and x_2 their amounts of "free space" per c.c., and x the free space of the mixture. The values of x_1 and x_2 can be calculated from the densities and viscosities at two different temperatures, and the value of x is given by the equation $x=x_1 v_1+x_2 v_2 \pm C$, where v_1 and v_2 are the volume percentages and C the change of volume per c.c. on mixing. In normal mixtures in which the volume change is small, the curve connecting viscosity and composition is a sagged one, the amount of the sagging depending on the relative viscosities. When contraction occurs on mixing, the curve rises to a maximum, the position and magnitude of which depend on the amount of contraction and on the viscosities, and consequently also on the temperature. When the constituents have almost equal viscosities the maximum occurs at almost equimolecular proportions, but otherwise the maximum tends to form near the viscous end of the curve, unless the constituents differ very markedly in viscosity, when the curve becomes S-shaped. Minima on the curve are usually accompanied by expansion on mixing. The formation of compounds causes a greater loss of free space than is indicated by the change in density, and the calculated results are therefore too low. The equations have been tested by means of existing data for a number of binary mixtures of organic liquids. W. H.-R.

Viscosity and Allotropy of Glass. H. LE CHATELIER (*Ann. Physique*, 1925, [x], **3**, 5—21).—A critical discussion of the work of Washburn and Shelton (*Univ. of Illinois Bull.*, No. 140, 1924, **21**, 1) and of English (*J. Soc. Glass Tech.*, 1924, **8**, 205) on the viscosity of glasses. The relation between the temperature and the log. log. of the viscosity is given by a linear equation of the type log. $\log.\eta=M[(t-1000)/1000]+N$ (M being a constant and N the viscosity at 1000°). For the glasses examined by English and for certain of those examined by Washburn and Shelton, two such

linear expressions are required, one for the upper, and a second for the lower temperature zone, indicating a transformation point at a temperature in the region of 1000°. The results of English, for lime and magnesia series of the molecular type $3SiO_2,xRO,(1-x)Na_2O$, show a simple linear relationship between the parameters M and N and the proportion of lime or magnesia molecules present. [Cf. *B.*, 1925, 242.] A. COUSEN.

Solid Solutions of Compounds of Elements of Different Valencies. G. BRUNI and G. R. LEVI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 377—384).—The results of X-ray analysis confirm the conclusion reached from those of thermal analysis (cf. Tacchini; this vol., ii, 122) that lithium and magnesium fluorides form solid solutions, the mixed crystals undergoing decomposition at a low temperature. At the ordinary temperature, solid solutions of the lithium fluoride type containing up to 20% MgF_2 may be prepared. The replacement of a certain number of magnesium fluoride molecules by a corresponding number of double lithium fluoride molecules causes neither appreciable change in the lithium fluoride space lattice nor the appearance of new lines in the corresponding X-ray photograms, but, just as in other similar cases, the formation of the mixed crystals is accompanied by a slight increase in the volume of the elementary cell. T. H. P.

Measurement of the Change in Volume in Metals during Solidification. H. ENDO (*Sci. Rep. Tôhuku Imp. Univ.*, 1924, **13**, 193—218).—Measurements have been made of the change in volume on solidification for a number of metals of low m. p. In the method employed, the metal is suspended in an inactive liquid during solidification or melting and the change in buoyancy determined. Results are given for mercury, sodium, potassium, rubidium, tin, bismuth, thorium, cadmium, lead, gold, silver, copper, and aluminium. When the change in volume per unit mass is plotted against the atomic weight, a periodic curve similar to the curve for atomic volume is obtained. [Cf. *B.*, 1925, 248.] C. S.

Measurement of the Change in Volume in Alloys during Solidification. H. ENDO (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **13**, 219—227).—Using the method described in a previous paper (preceding abstract) measurements of the change in volume during solidification have been made for silumin, duralumin, copper–aluminium alloys, brass, and bronze. The mean coefficient of cubical expansion between 20° and 500° was also determined. [Cf. *B.*, 1925, 248.] C. S.

Modification of the Structure of Aluminium Alloys containing Large Proportions of Silicon. N. PARRAVANO and A. SCORTECCI (*Atti Congr. Naz. Chim. Ind.*, 1924, 291—294).—Fusion of aluminium–silicon alloys with 1% of sodium or calcium modifies the structure of the metal so that, on cooling, the constituents are indistinguishable under the highest magnifications. Similar effects are produced in the same way in aluminium–silicon

alloys containing small proportions of other metals, the mechanical properties being improved at the same time. [Cf. *B.*, 1925, 247.]
T. H. P.

Intermetallic Reactions in a Lead-base Bearing Metal. O. W. ELLIS (*Nature*, 1925, **115**, 382).—A study of the influence of pouring temperatures and mould temperatures on the microstructure of a lead-base bearing metal. [Cf. *B.*, 1925, 286.]
A. A. E.

Influence of Lead and Tin on the Brittle Ranges of Brass. D. BUNTING (Inst. Metals, Mar., 1925; advance copy, 10 pp.).—The presence of lead in brass causes a general decrease of toughness and raises the upper limit of the brittle range. Addition of small quantities of tin to α-brass increases its impact strength and reduces considerably the brittle range, but larger quantities cause the separation of the brittle γ or δ constituent and a consequent great increase of brittleness. [Cf. *B.*, 1925, 246.] A. R. P.

Recrystallisation Phenomena [in Aluminium]. H. RÖHRIG (*Z. Metallk.*, 1925, **17**, 63).—Annealing rolled sheets of aluminium at 220—350° results in rapid recrystallisation and the growth of very large crystals differently oriented from those produced by annealing at a higher temperature. This behaviour is similar to that previously observed in the case of silver. [Cf. *B.*, 1925, 246.]
A. R. P.

Gas Solubility and Hydration. W. MANCHOT [with M. JAHRSTORPER and H. ZEPTER] (*Z. anorg. Chem.*, 1924, **141**, 45—81; cf. this vol., ii, 233).—The solubility of nitrous oxide and acetylene in aqueous solutions of electrolytes (including chlorides, bromides, nitrates, sulphates, phosphates, and iodates) has been determined at 25° over a wide range of concentration. The order of the effects of anions and cations is in agreement with the statements of previous investigators. The solubilities are always calculated for equal weights of water in the solutions, contrary to earlier investigations, where only the volume of the solution is considered. The present method has the advantage that a direct comparison is obtained with the value for the solubility in water, and it is possible to express in mols. of water the lowering of solubility caused by 1 mol. of dissolved substance. This value decreases with increasing concentration of salt.

The quantities of water "inactivated" by 1 mol. were found to be the same for nitrous oxide and acetylene, within the limits of error. Acetylene shows small variations with nitrates, which are probably due to chemical reaction. The quantity of water required by 1 mol. of salt is somewhat greater at 0° than at 25°. The influence of nitric, hydrochloric, and sulphuric acids on the solubility of nitrous oxide was studied, and found to be different from that of salts; with rising concentration, the solubility falls at first, reaches a minimum, and then increases. Some non-electrolytes produce a decrease in solubility, others an increase. An attempt has been made to calculate the number of mols. of water required by the

various ions, and satisfactory agreement obtained by several different methods. L. L. B.

Solubility of Lead Chloride in Acetic Acid. W. Herz and E. Martin (*Z. anorg. Chem.*, 1924, **140**, 339—340).—The solubility of lead chloride in acetic acid solutions decreases at first slowly and then rapidly as the acid concentration approaches 14·9*N*. The solution in glacial acetic acid gives only a brown coloration with ammonium sulphide. S. K. T.

Solubility of Mercury Halides in Mixtures of Glycerol and Water. E. Moles and M. Marquina (*Anal. Fís. Quím.*, 1924, **22**, 551—554).—The solubility of mercuric chloride in water at 25° is 0·26 g.-mol. per litre, whilst that of mercuric bromide at the same temperature is 0·0170 g.-mol. per litre. The solubilities of mercuric chloride and bromide in mixtures of glycerol and water are recorded. In both cases, the solubility increases with the proportion of glycerol. G. W. R.

Solubility in Mixed Liquids. G. Pleuger (*Physikal. Z.*, 1925, **26**, 167—170).—The solubility of benzamide and aceto-*p*-toluidide has been measured in mixtures of alcohol–water, alcohol–carbon disulphide, alcohol–carbon tetrachloride.

In general, at temperatures well below the melting point of the substance, the solubility is greater than would be expected from the mixture rule, and in several cases a most decided maximum is observed. There appears to be no connexion between the change of solubility and the dielectric constants. E. B. L.

Piezochemical Studies. XXVIII. Solubility Determination at High Pressures by means of Conductivity Determination. E. Cohen and J. C. van der Bosch (*Z. physikal. Chem.*, 1925, **114**, 453—499).—A conductivity method is described whereby the solubility of solids may be determined with great accuracy at high pressures. The principle of the method depends on the fact that the relation between the conductivity, κ, and the concentration C, of the solution may be expressed by the equation $\kappa = a + bC + dC^2 + eC^3$. Thallous sulphate was selected for experiment, on account of the marked influence of pressure on the solubility, and the resistances of a large number of solutions of different concentrations were determined at 30° and at pressures up to 1500 atm. For each pressure the equation $\kappa = f(C)$ was calculated. It was found that the results could be expressed by the following curve: $C = 5{\cdot}831 + 0{\cdot}003295p - 0{\cdot}000000109p^2$, and that at 1 atm., $(dC/dp)_{1\text{atm.}} = 0{\cdot}003295\%$. The agreement between the solubility found by the conductivity method and by the direct method (cf. A., 1923, ii, 386) is excellent. The disadvantages of the method are that it can only be applied to electrolytes, and that it is very tedious, owing to the long time taken to attain solution equilibrium. L. L. B.

Salting-out. E. A. Hafner and L. von Kürthy (*Arch. exp. Path. Pharm.*, 1924, **104**, 148—169).—The salting-out of phenol

from aqueous solution is selected as a typical example of the process under consideration. Interferometric measurements show that phenol solutions differ from solutions of other substances (*e.g.*, dextrose, potassium chloride) in that the displacement of the interference bands is not a linear function of the concentration of the solution. This is attributed to the aggregation of the phenol molecules, a view which is supported by the fact that departure from proportionality also appears with concentrated solutions of potassium chloride. A similar aggregation of phenol molecules occurs, according to interferometric measurements, when electrolytes are added to phenol solutions in amount insufficient to salt out the phenol, *i.e.*, the salting-out process commences before the actual separation of the phenol. This aggregation is considered to be a result of the polarisation of the molecules present in the solution, which is brought about by the introduction of an electric charge (electrolyte solution). The substance (phenol) with the smaller dielectric constant has the smaller polarisability and hence moves towards, and collects at, points where the strength of the electric field is small. Salting-out is thus a function of the dielectric constants of solvent and solute and will occur more readily the greater the difference between the values of these constants; other factors (such as hydration of ions) may, however, be present and obscure this relation. E. S.

Sorption of Ammonia and Carbon Dioxide by Glass. D. H. Bangham and F. P. Burt (*J. Physical Chem.*, 1925, 29, 113—129; cf. A., 1924, ii, 392).—Measurements of the rate of sorption of ammonia by glass wool of known surface area at 0° and different pressures are found to agree, over the experimental range investigated, with the equation, $s^m = kp^s\int_0^t p.dt$, where s is the sorption value in c.c. of gas sorbed (reduced to n.t.p.) and p_t the momentary pressure, both at the time t, and m is a constant of about 12. With carbon dioxide, the value of m varies with the pressure. M. B. D.

Adsorption from the Standpoint of Capillarity. W. A. Patrick and N. F. Eberman (*J. Physical Chem.*, 1925, 29, 220—228; cf. this vol., ii, 193).—The adsorption of water from its solution in *n*-butyl alcohol by silica gel has been determined at 1°, 26·2°, and 50° for concentrations of water up to the solubility limit. The adsorption can be represented by the formula $V = K(S\sigma/S_0)^{1/n}$ (cf. A., 1920, ii, 417), in which V is the volume of liquid solute adsorbed per gram of gel, S the equilibrium concentration of the solute in the solution, K and $1/n$ are constants, σ is interfacial tension, and S_0 a constant, which has a value, in general, less than the actual solubility of the solute. The equation can be deduced theoretically, using Rayleigh's equation connecting the vapour pressure of a liquid with the radius of curvature of its surface. M. B. D.

Anomalous Adsorption of Dyes by Wool and Cotton. J. B. Speakman and A. E. Battye (*J. Text. Inst.*, 1925, **16**, 53—60 T).—The anomalous adsorption by wool of basic dyes such as night-blue

and Victoria-blue described by Biltz and Steiner (A., 1910, ii, 830) is associated with the observation of Gee and Harrison (*Trans. Faraday Soc.*, 1910, **6**, 42) that untreated wool has a negative charge and acid-treated wool a positive charge when immersed in water. The process of dyeing is regarded as due to adsorption of dye by a neutralisation of the charge on the adsorbent and also to those unknown forces which are responsible for normal adsorption. Increasing the concentration of a solution of night-blue increases its acidity, and since this represses the negative charge on the wool, the latter has a decreasing adsorptive power for the dye. The adsorption of the dye is therefore dependent on the relation between the rate of increase of the normal adsorption and the rate of decrease of the adsorption due to the electrical charge of the fibre. The anomalous adsorption described by Biltz and Steiner is an instance where the adsorption due to the electrical charge has a dominating influence. In buffered solutions of night-blue, adsorption increases regularly with increase of concentration. A. J. H.

Behaviour of Hydrated Aluminium Oxide towards Dyes. J. K. Wood and A. Wooller (*J. Soc. Dyers and Col.*, 1925, **41**, 47—53).—Carefully purified samples of hydrated aluminium oxide prepared under varied conditions of temperature and concentration by addition of ammonia or sodium hydroxide to aqueous solutions of aluminium chloride or acetate are found to adsorb acid but not basic dyes. Hydrated aluminium oxide prepared from the acetate readily adsorbs basic dyes if a trace of alkali is added, but that prepared by means of sodium hydroxide strongly adsorbs basic dyes only when previously ignited; in each case the adsorbed dye is readily removed by washing with water. The adsorption of basic dyes from aqueous solution is not affected by the presence of sodium sulphate, but is favoured by the presence of potassium citrate and particularly by sodium phosphate. Quantitative measurements in the presence of sodium phosphate at a measured hydrion concentration are described. Magenta is more strongly adsorbed than methylene-blue, the latter being more easily removed from the hydrated oxide by washing. Basic dyes adsorbed by hydrated aluminium oxide are removed by washing with water containing sodium chloride, sodium sulphate, or sodium acetate, but not by washing with water containing phosphate or free alkali. Hydrated aluminium oxide containing comparatively large amounts of chlorine decolorises aqueous solutions of methyl-orange and orange-IV, but with preparations containing less than 0·05% of chlorine a certain minimum concentration of dye was necessary before any adsorption occurred. Samples of hydrated aluminium oxide containing 0·56% of chlorine were shaken up with 5% solutions of sodium phosphate, potassium citrate, sodium sulphate, potassium dichromate, and sodium acetate, were then thoroughly washed with distilled water and dyed with ponceau-2R; the amount of dye adsorbed was found to increase in the order of the solutions named, those samples treated with phosphate and acetate having a white and an intense brick-red colour, respectively; in this behaviour

hydrated aluminium oxide resembles wool. Measurements of the adsorption of acid dyes such as picric acid, naphthol-yellow S, brilliant-crocein R, orange II, ponceau-2R, amaranth, and brilliant-crocein 9B are described. The mode of preparation of hydrated aluminium oxide has less influence on its dyeing properties than is the case with stannic and titanic acids (cf. Wood and Morley, A., 1923, ii, 425, 426). The behaviour to acid dyes is largely determined by the presence of acidic impurities (cf. Michaelis and Rona, A., 1919, ii, 496). A. J. H.

Theory of Dyeing. G. Rossi and A. Basini (*Annali Chim. Appl.*, 1925, **15**, 4—16).—The authors regard dyeing as a simple process of adsorption of the colouring matter by the fibre. Dyeing may occur when the adsorption compound is insoluble in water, that is, when the affinity of the secondary valencies of the fibre towards those of the colouring matter is greater than that of the latter for the secondary valencies of the solvent. If this is not the case, dyeing is possible only with the intervention of mordants which, behaving like substantive dyes towards the fibres, give absorption compounds with increased affinity of their secondary valencies towards those of the dye; the same effect is produced if the mordant and dye yield compounds the secondary valencies of which have a greater affinity for those of the fibre than for those of the solvent.

That the generation of heat during the dyeing process cannot be regarded as evidence in favour of the salt-formation theory of dyeing is shown by the observation that the coagulation of colloidal arsenic trisulphide is accompanied by thermal change. Other experimental results supporting the authors' theory are: (1) the quantity of dye adsorbed by fibres immersed in dye-baths containing stabilising emulsoids is less than that which the same fibres are able to adsorb in absence of stabilisers, and (2) the proportion of dye combining with the fibre varies, within certain limits, with the concentration of the bath. T. H. P.

Adsorption. F. Schelte (*Z. physikal. Chem.*, 1925, **114**, 394—412).—The isotherms representing the adsorption of methyl-violet, ethyl-violet, diamond-fuchsin, and methylene-blue by window and lead glass are found to be of the usual form. The surface of the glass powder was determined by the method of Schmidt and Durau (A., 1924, ii, 238), which involves the determination of the solubility of the glass in dilute alkali; it was found that this solubility depends, not only on the chemical composition, but also on the previous thermal history of the glass. The adsorption for the two glasses was found to be different. Expressed as percentage of surface covered, the values for methyl-violet, ethyl-violet, diamond-fuchsin, and methylene-blue on window glass are 196·6, 164·8, 198, and 136·4, respectively, whilst the corresponding values on the lead glass are 192, 140·3, 75·2, and 79·5, respectively. The extent of the adsorption does not depend only on the magnitude of the surface area, but on the chemical composition and physical properties of the adsorbent. L. L. B.

Adsorption Compounds. V. R. HALLER (*Kolloid-Z.*, 1925, **36**, 86—92; cf. A., 1924, ii, 93).—In a group of acid triphenylmethane dyes, the introduction into the benzaldehyde nucleus of a sulphonic group increases the dispersion, although this is diminished by the introduction of a halogen or nitro group. The aluminium, iron, and chromium lakes are polydisperse, the lower degree of dispersion giving a blue and the higher a reddish-violet. Wool is dyed in reddish colours and cotton in blue. E. M. C.

Adsorption. IX. Adsorption by Soil. P. N. PAVLOV (*Kolloid-Z.*, 1925, **36**, 78—81).—The form of the curve representing the adsorption of ammonium chloride from aqueous solution by soil depends on the relative amounts of soil and solution. In accordance with the author's criteria (cf. A., 1924, ii, 833) the action is a complex chemical process, probably involving a series of reactions in which almost insoluble double salts are formed, each of which is stable over a definite range of concentration. E. M. C.

Vapour Pressure–Water Content Diagram and Adsorptive Power of Aniline-black. P. P. KASAKEVITSCH (*Kolloid-Z.*, 1925, **36**, 82—85).—The vapour pressure–water content curves of aniline-black are quite smooth and show considerable hysteresis. At all stages of humidity the water content for drying is about twice that for wetting. The importance of the slowness of many adsorption reactions is emphasised and it is shown that the amount of hydrochloric acid removed from solution by aniline-black in one month is independent of the final concentration of acid.

E. M. C.

Capillarity, Evaporation, and Efflorescence. K. SCHULTZE (*Kolloid-Z.*, 1925, **36**, 65—78).—The rate of evaporation of water from circular capillaries is proportional to the area of the cross-section, and falls off rapidly with the depth below the mouth of the tube. The rate of evaporation is considerably greater from tubes of irregular cross-section, and it is suggested that the shapes of the capillaries are important factors in determining the course of evaporation from granular and porous materials. Efflorescences were obtained during the evaporation both of salt and of colloidal solutions. E. M. C.

Behaviour of Oil and Oleic Acid with Water. IV.—VI. J. F. CARRIÈRE (*Rec. trav. chim.*, 1925, **44**, 121—129; cf. A., 1924, i, 461).—The behaviour of a pure oil with water is contrasted with that of an oil containing a trace of oleic acid. Anomalies in the behaviour of oil and water, which certain observers have attributed to hydrolysis, are now explained as due to the presence of impurities. The interfacial tensions of neutral oil/water, and of oleic acid/water, respectively, as given in the literature, require correction to about 26 and 10·5 dynes/cm. respectively at 20°. Traces of fatty acids in oil may be detected by the action of ammonia vapour after establishment of the oil/water equilibrium. [Cf. *B.*, 1925, 250.]

F. M. H.

Colours Due to Thin Films on Metals. U. R. Evans (*Proc. Roy. Soc.*, 1925, **A**, **107**, 228—237).—Experiments are described which support the view that the colours of thin films on metals are due to interference. Mallock's objection (*Proc. Roy. Soc.*, 1918, **A**, **94**, 566) that the temper colours on steel are not changed by polishing is countered by an experiment in which the colours are changed in the correct sequence by cathodic treatment in dilute hydrochloric acid. Raman's view (*Nature*, 1922, **109**, 105) that the colours are due to a granular structure is shown to be untenable, since the colours on molten lead can be obtained as easily when the oxide is molten as when it is solid. The sequence of colours obtained on iron and lead as above and also by exposing silver to iodine vapour and copper to hydrogen sulphide corresponds fairly well with that expected from the interference theory. Furthermore on removing the lead oxide film the colours seen by transmitted light are complementary to those seen by reflected light. The author considers that Tammann and Köster (A., 1922, ii, 831) were justified in using the interference principle to follow the velocity of the growth of films but that the principle may have been applied incorrectly.

N. H. H.

Densities of certain Aqueous Potassium Chloride Solutions as Determined with a New Pycnometer. H. C. Parker and E. W. Parker (*J. Physical Chem.*, 1925, **29**, 130—137).—A modified type of Sprengel pycnometer is described. The capacity is about 100 c.c. and it has a calibrated capillary stem which obviates the filling of the pycnometer to an exact volume. The densities of 0·099271*N*, 0·1*N*, and 0·01*N* solutions of potassium chloride are 1·004840, 1·004881, and 1·000372 respectively, based on the value 0·9998406 for water at 0°. The accuracy is about 1 part in a million parts.

M. B. D.

Densities of Solutions of Aluminium Chloride in Phosgene [Carbonyl Chloride]. A. F. O. Germann (*J. Physical Chem.*, 1925, **29**, 138—141; cf. A., 1924, ii, 674).—The density of pure carbonyl chloride at 0° and 25° is 1·4275 and 1·3685, respectively. The density of solutions of aluminium chloride in carbonyl chloride has been measured at these temperatures, and over the range investigated (0—50% aluminium chloride) varies linearly with the percentage of aluminium chloride present.

M. B. D.

Alteration of the Volume Contraction on Solution. J. N. Rakshit (*Z. Elektrochem.*, 1925, **31**, 97—101).—The contraction which occurs when various substances are dissolved in water and ethyl alcohol has been measured at different concentrations. A summary of previous work is given and the theory of the alteration of contraction with dilution discussed. The present results agree in general with van Laar's hypothesis.

N. H. H.

Neutralisation of Chloric Acid by Alkalis Studied by Viscosity Measurements. L. J. Simon (*Compt. rend.*, 1924, 179, 822—825).—Chloric acid, on neutralisation with sodium or potassium hydroxide, gives results similar to those previously

obtained with polybasic acids (A., 1923, ii, 219; 1924, ii, 335, 455). The differences previously observed between the two alkalis also apply to the present case. H. J. E.

Refractometric Studies of Neutralisation. F. S. HAMMETT (*J. Franklin Inst.*, 1925, **199**, 91—98).—The refractive index of mixtures of strong and weak mono-, di-, and tri-basic acids (hydrochloric, acetic, sulphuric, oxalic, phosphoric, and citric) and strong mono-acidic bases (sodium and potassium hydroxides) is a linear function of the salt concentration when excess of base is present. The linear relation also holds for excess of acid when the acids are monobasic, but not when di- or tri-basic acids are involved. This is ascribed to the formation of acid salts. L. F. G.

Electrolyte-free, Water-soluble Proteins. II. Effect of Carbon Dioxide. I. M. ADOLF and W. PAULI (*Biochem. Z.*, 1924, **152**, 360—372).—The preparation by electro-dialysis of highly purified serum-albumin, egg-albumin, and "glutin" (gelatin) is described. The conductivity of such pure proteins rises on contact with air, and is again lowered by electrodialysis to a constant value corresponding with the hydrogen ions and negative protein ions present. It is suggested that the increase of conductivity, which does not affect the hydrogen-ion concentration, the isoelectric

with positive hydrogen and negative hydrogen carbonate ions, respectively. J. P.

Distribution of Particles in Colloidal Suspensions. W. W. BARKAS (*Trans. Faraday Soc.*, 1925; advance proof).—The constants in the equation given by Porter and Hedges (A., 1923, ii, 743), viz. $\log_e n/(1-bn) + 1/(1-bn) = Ky + A$, are empirical. These constants should have values which depend on the size and mass of the particles, and an attempt has been made to determine them for suspensions of gamboge, copper, and silver. Sols containing particles between certain narrow limits of size were used, the determination of the distribution being carried out in a specially constructed cell by the method of counting. Values of K were determined, and from the equation $K = gNm(u-\gamma)/R_0Tu$ the values for the limiting radius of the gamboge, silver, and copper particles were found to be $1{\cdot}85 \times 10^{-5}$ cm. ($K = 120$), $4{\cdot}32 \times 10^{-6}$ cm. ($K = 80$), and $6{\cdot}47 \times 10^{-6}$ cm. ($K = 220$), respectively. These values were checked by measurement of the rate of fall of thin cloud in uncentrifuged solution, and good agreement was obtained with gamboge and copper particles. In the derivation of the equation it is assumed (1) that the particles are spherical, (2) that Stokes' law is obeyed, and (3) that the particles exist in the pure state in the solution. With regard to (1), it was observed with the larger particles of gamboge that the diffraction rings are of irregular intensity, from which it is inferred that these particles are not spherical. The formula of Porter and Hedges appears to hold within the limits of experimental error. L. L. B.

Law of Distribution of Particles in Colloidal Suspension. Specific Volume of a Gamboge Suspension. J. R. H. COUTTS (*Trans. Faraday Soc.*, 1925; advance proof).—Measurements of the densities of gamboge suspensions by means of a pycnometer show that there is no measurable change in volume in the formation of these suspensions. L. L. B.

Connexion between Osmotic Pressure, Swelling Pressure, and Adsorption. M. PÓLÁNYI (*Z. physikal. Chem.*, 1925, **114**, 387—393; cf. A., 1914, ii, 720).—The author has derived the relation $c'-c+(dc'/d\log_e C)_{c=\text{const.}}=c/RT \cdot dP/dc$, where c' is the crystalloid concentration in the solution containing colloid, c the crystalloid concentration in the crystalloid solution, C the colloid concentration, and P the swelling pressure or osmotic pressure. Its validity is confirmed within the limits of error by Loeb's data for gelatin phosphate. L. L. B.

Stability of Arsenious Sulphide Hydrosol and Velocity of Colloidal Particles Moving under the Influence of Gravity. A. DUMANSKI (*Kolloid-Z.*, 1925, **36**, 98—99).—The particles of an arsenious sulphide sol, kept under observation for 4 years, fell at a constant rate of 0·031 cm. per day. E. M. C.

Colloidal Lead Dioxide from Lead Tetra-acetate. A. GUTBIER and H. O. MEYER (*Z. anorg. Chem.*, 1924, **141**, 95—100).—Perfectly dry lead tetra-acetate, prepared by the method of Dimroth and Schweizer (cf. A., 1923, ii, 744), was found to decompose immediately in presence of water, giving lead dioxide. To prepare colloidal lead dioxide from the acetate, the latter (1·5 g.) should be slowly added, at the ordinary temperature and with rapid stirring, to a 0·3% solution of gum arabic (250 c.c.) to which 0·2*N*-ammonia solution (30 c.c.) has been added. The sol is filtered from small quantities of brown precipitate, and dialysed as rapidly as possible. The pure preparation is dark brown. A white precipitate of hydrated lead dioxide separates slowly on long keeping. L. L. B.

Colloidal Sugar. I. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 118—122).—When solutions of dextrose in commercial absolute alcohol or acetone are poured into a large excess of ether at the ordinary temperature, the crystallisation process passes through a marked colloidal stage, lasting about 2 hrs. The suspensions produced by pouring alcoholic dextrose solutions into benzene, toluene, or xylene are much more stable and show violet, deep blue, or green shades with a strong opalescence in the complementary colours. E. M. C.

Cholesterol and its Esters. E. KEESER (*Biochem. Z.*, 1924, **154**, 321—327).—Methods are described for preparing stable sols of cholesterol and lecithin. Both sols diminish the stability of negatively charged colloids. The activity of the sols of the fatty acid esters of cholesterol in diminishing the stability of negatively charged colloids is reduced as the length of the carbon chain in the homologous series is increased. A cholesterol sol has a considerably

lower surface tension than pure water. Its fatty acid esters are less active in lowering the surface tension of water, the activity again falling off as the molecular weight increases. The constant proportion existing in the organism between free cholesterol and its esters has an important bearing on the physical state of the body colloids. H. D. K.

Colloids and Mineral Waters. E. HENRIJEAN and W. KOPACZEWSKI (*Compt. rend.*, 1924, **179**, 909—912).—The surface tension of coloured negative colloid solutions is equal to, and that of positive colloid solutions is less than that of distilled water. A similar difference is found when distilled water is mixed with the colloid. On substituting mineral water for the distilled water, the effect is reversed; this is attributed to the presence of a positive colloid in the natural water. If a natural mineral water is replaced by an artificial preparation of identical chemical composition, no such reversal is observed. The conclusion is reached that the ferruginous mineral water used in the experiments (Spa, Source Pierre-le-Grand) contains an electropositive hydrosol of iron.
H. J. E.

Colloids and Mineral Waters. D'ARSONVAL and BORDAS (*Compt. rend.*, 1924, **179**, 912—913; cf. preceding abstract).—Certain mineral waters deposit sediment after being bottled. The deposition of sediment may be avoided by adding carbon dioxide in order to avoid both oxidation and precipitation from acid carbonates. Certain cases of deposition, however, do not seem to be traceable to these two causes. H. J. E.

Velocity Function of the Viscosity of Disperse Systems. I. W. OSTWALD (*Kolloid-Z.*, 1925, **36**, 99—117).—It is suggested that the term "structural viscosity" should be used quite generally in referring to the deviations from Poiseuille's law which are shown by certain colloidal solutions. Such deviations are shown in the influence of change of pressure or rate of flow on the viscosity. Even for colloids exhibiting "structural viscosity," measurements with the Ostwald type of viscosimeter are trustworthy. A simple pressure-viscosimeter is described for measuring the effect of variations in the rate of flow. The capillary viscosimeter is modified by using a short, narrow capillary with an upper bulb in the form of a flat lens and by increasing the length of the arms to 20—50 cm. The filling tube is wide and is graduated throughout its length. The instrument is calibrated for water for different heights of filling. If t_w and t_k are the times of flow for water and for the colloidal solution, for the same height, and if k_1, k_2, etc., are constants, the results for a large number of colloidal solutions may be expressed by $t_k = k_1 . t_w^n$ with an accuracy of 1—2%. In some cases better agreement is given by $t_k = t_w^n + k_2 . t_w^n$ or $t_k = k_3(t_k - t_w)^n$. Similar equations hold for measurements with the Hess and the Couette apparatus. The exponent n, which measures the "structural viscosity," is greater than 1; the highest value found was 1·75 for

a 1% caoutchouc sol in benzene. The constant k is generally less than 1, but may be greater. For colloidal solutions, such as those of gelatin, reduction of concentration or heating causes both constants to approach the value 1. Since colloidal solutions, like their dispersive media, probably give values for k less than 1 for higher pressures and turbulent motion, the complete relationship between velocity of flow and pressure will be represented by a sigmoid curve. E. M. C.

Physico-chemical Properties of Gelatin. Rotatory Power. F. VLÈS and E. VELLINGER (*Compt. rend.*, 1925, **180**, 439—442).—The mutarotation and rotatory power of gelatin gels at various p_H values have been investigated at 40° and at the ordinary temperature (12—15°). The diffusion of light by the gels and the resulting polarisation have also been studied in their relation to the p_H value of the gel. The light diffused is a maximum at the isoelectric point (p_H 4·7) and passes through minima at p_H values 2·6 and 13. Freshly-prepared samples exhibit mutarotation at the ordinary temperature, but not at 40°. The phenomenon is most pronounced at the isoelectric point. The rotatory power (negative) at 12—15° plotted as a function of p_H exhibits a pronounced maximum at the isoelectric point and two minima, one at p_H 3 and the other well on the alkaline side. The rotation is more pronounced for blue than for yellow light. At 40° there is a slight minimum at p_H 4·7. The mutarotation is due to the slow conversion of a system stable at 40° into one stable at 12—15°, the rate of change being retarded by the viscosity of the medium. The development of a maximum value in the rotation is attended by the parallel development of an opalescence, showing the change to be accompanied by a modification of the physical structure. The interpretation of the p_H–rotatory power diagram is considered. J. S. C.

Osmotic Pressure of Hæmoglobin. Explanation of the Effect of Acetic Acid, based on Donnan's Theory of Membrane Equilibrium. H. C. WILSON (*Biochem. J.*, 1925, **19**, 80—83).—When hæmoglobin is dialysed in an osmometer against acetic acid, there results a four- to six-fold increase in osmotic pressure above the value against distilled water. The hydrogen-ion concentration of the hæmoglobin solution is considerably less than that of the acetic acid solution. It is supposed that hæmoglobin acetate is formed. S. S. Z.

General Character and Electrical Properties of Gels. F. MICHAUD (*J. Chim. physique*, 1924, **21**, 386—395; cf. A., 1923, ii, 134; *Compt. rend.*, 1924, **178**, 993).—An electrical double layer exists at the surface of a gel which itself consists of a network of canals filled with liquid, the radii of the canals being less than that of the double layer. Adsorption occurs and is general; the negative charges only can penetrate the canals. Addition of alkali increases the charge on the double layer, the attraction between the charges is increased, and the canals expand to allow the positive charges to enter, as a result of which the gel expands. Conversely, acids produce contraction, but, if the acid is sufficiently strong, it may reverse

the sign of the double layer and expansion will then occur, as in the case of gelatin. The deformation of gels by electric currents is due to electrical osmosis, and prolonged passage of the current results in the drying of the gel at the anode, whilst liquid collects round the cathode. Conversely, a difference of potential is produced if the gel is pressed, owing to the liquid being forced along the canals. A complete explanation of the above phenomena must take account of both chemical and adsorption processes. Gels are an essential constituent of living matter, and certain muscular and nervous effects may be due to their properties. If a current is passed through a nerve, the latter is more excitable at the cathode, possibly owing to the production of liquid as in the case of gels. W. H.-R.

Electro-dialysis of Agar. E. H. HARVEY (*Amer. J. Pharm.*, 1925, **97**, 66—70).—By subjecting agar sols to a preliminary treatment with 0·5% acetic acid and water and then to electro-dialysis for 12 hrs. at 50°, the ash content on a dry basis was reduced from 3·75% to 0·81%. E. M. C.

Chemical Theory of the Protective Action of Sugars. II. D. L. SHRIVASTAVA, R. S. GUPTA, M. PRASAD, and S. S. BHATNAGAR (*J. Physical Chem.*, 1925, **29**, 166—177; cf. A., 1924, i, 942).—Adsorbed sugars (sucrose, arabinose, mannose, maltose, lævulose, and xylose) do not contribute to the rotation observed when the sugar is dissolved in a colloidal solution (cadmium, antimony, and arsenic sulphides, and selenium). Similar observations made with aluminium stearate and palmitate, zinc oleate, and magnesium oxide lead to the same conclusion. The change in optical activity is not due to mutarotation produced by the dissolving agents. M. B. D.

Conditions of Precipitation, by Electrolytes, of Selenium Hydrosol and Other Hydrosols. J. J. DOOLAN (*J. Physical Chem.*, 1925, **29**, 178—187).—The coagulating powers of various electrolytes have been determined for selenium and tellurium hydrosols. The results are not in accord with Whetham's law (A., 1900, ii, 62). M. B. D.

Ionic Conflict and its Relations with the Physico-chemical Constants of Plasma. A. H. ROFFO and L. M. CORREA (*J. Chim. physique*, 1924, **21**, 466—468).—Certain physiological properties of blood plasma depend on the value of the ratio (Na+K)/(Mg+Ca) formed by the four chief mineral elements. The value of this ratio is also responsible for the physical properties of some colloids. In determining the physical properties of plasma, it is necessary to add oxalate to prevent coagulation. Test portions of blood were treated with just sufficient oxalate to prevent coagulation and plasma was prepared by centrifuging. When this plasma was treated with quantities of sodium oxalate increasing from 1 to 10 mg., the surface tension gradually increased from 60·50 to 60·92 dynes, a more rapid increase to 70·4 dynes occurring when 12 mg. of sodium oxalate were added. The weights of the test portions are not stated. W. H.-R.

Dissociation of Chlorine into Atoms. M. TRAUTZ and F. GEISSLER (*Z. anorg. Chem.*, 1924, **140**, 116—148).—The amount of chlorine present in a porcelain vessel of known volume at atmospheric pressure was determined for temperatures between 1151 and 1264°, and compared with that calculated after making allowances for the departure of chlorine from the simple gas laws. From the temperature coefficient of the equilibrium constant the heat of decomposition is 59500±200 cal. The chemical constant calculated from the isochore lies between 0·54 and 2·27, which differs considerably from that calculated by Stern's formula. L. J. H.

Equilibrium of Gases in the Reaction of Explosives. N. YAMAGA (*J. Fac. Eng. Tokyo Imp. Univ.*, 1924, **15**, 207—271).—Calculations in the theory of explosives based on the analysis of the gaseous products are incorrect owing to the change of equilibrium constant during cooling. The equilibrium at the moment of explosion is that of the water-gas reaction. During cooling methane is formed by the reactions $CO+3H_2=CH_4+H_2O$, $CO_2+4H_2=CH_4+2H_2O$, and $4CO+2H_2O=CH_4+3CO_2$. These reactions occur only below 1500°, the stability temperature of methane. The equilibrium constants of the water-gas and methane reactions were calculated by the Nernst heat theorem, using the specific heat data of Piers and of Bjerrum. The constants given by these equations are compared with those given by the expressions of several other authors. All equations are satisfactory up to 2000° Abs. Above this, wide divergences occur except between the author's equations and that of Nernst. A consideration of the thermodynamic relations of gas mixtures based on van der Waals' equation shows that at high temperatures actual gas mixtures may be treated as ideal. On this basis a graphical method is developed by which the temperature and heat of explosion, and the equilibrium at the moment of explosion, may be derived from the analysis of the explosive and its heat of formation. F. G. T.

Equation for the Haber Equilibrium. L. J. GILLESPIE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 73—74).—The equations $\log Kp=(2679{\cdot}35+1{\cdot}1184p)1/T-(5{\cdot}8833+0{\cdot}001232p)$ and $\log Kp=(2172{\cdot}26+1.99082p)1/T-(5{\cdot}2405+0{\cdot}002155p)$ represent the values of the equilibrium constant over the temperature range 325—500° at pressures up to, and greater than, 100 atm. respectively. Attempts to obtain a single equation for high and low pressure data failed because of certain discontinuities. Haber's data for 30 atm. do not agree with the above equation. An explanation of the discrepancy is offered. J. S. C.

Electrolytic Dissociation of Dibasic Acids. II. Second Dissociation Constants. E. LARSSON (*Z. anorg. Chem.*, 1924, **140**, 292—300).—The second dissociation constants at 18° of 14 organic acids measured by the author's electrometric method (cf. A., 1923, ii, 55) are shown to agree with values calculated from the formula previously given, and with those obtained by other methods. The values for oxalic acid, $7{\cdot}1\times10^{-5}$, and maleic acid, $5{\cdot}1\times10^{-7}$,

are higher than those found by Chandler (cf. A., 1908, ii, 467), but are supported by other evidence. Bjerrum's n and r factors (A., 1923, i, 1059) are calculated for the acids investigated; those obtained for a series of dibasic α-thio-fatty acids indicate that the carboxyl groups in racemic acids are about 0·8 Å. nearer than in the corresponding *meso*-compounds. The value of n tends to increase as ethylenic linkages are introduced into the molecule. S. K. T.

Aqueous Solutions of Carbon Dioxide and Carbonic Acid. C. Faurholt (*J. Chim. physique*, 1924, **21**, 400—455).—The equilibria between carbon dioxide, carbonic acid, and carbonate and hydrogen carbonate ions in aqueous solutions of different acidity were investigated in detail. Buffer solutions of formates, acetates, cacodylates, phosphates, borates, and carbonates with their respective acids were used to give solutions of known p_H value. To these were added solutions of carbonic acid, and, after a measured interval, excess of dimethylamine; the latter combines with carbonate or carbonic acid to form a carbonate, and with molecular carbon dioxide (CO_2) to form a carbamate, the relative amounts of the two being determined. In some cases corrections have to be applied owing to variation of the p_H value during the experiment, but the original must be consulted for these. Carbon dioxide is hydrated in two ways, represented by the equations (1) $CO_2+H_2O=H_2CO_3$, and (2) $CO_2+OH'=HCO_3'$. These reactions take place simultaneously, but for values of $p_H<8$ the hydration is almost entirely due to reaction (1), whilst for values of $p_H>10$ reaction (2) predominates. Between these limits the two reactions take place with comparable velocity, but the agreement between calculated and experimental values is not good, owing possibly to side reactions with the (borate) buffer solution. The velocity coefficients of the reactions (1) and (2) are respectively 0·0013 and 405 at 0° and 0·011 and 1740 at 18°. Dehydration occurs by the reversal of reactions (1) and (2), reaction (1) predominating in acid solutions. The values of the dehydration velocity coefficients at 0° and 18° are $k_{H_2CO_3}$, 1·16 and 7·1, and $k_{HCO_3'}$, $10^{-5\cdot59}$ and $10^{-4\cdot52}$, respectively. The total velocity of dehydration varies with the acidity and is a complex function, as the proportions of the initial carbonate existing as H_2CO_3, HCO_3', and CO_3'' vary greatly with the acidity. In strongly acid solution the time taken to reach equilibrium is about 1 sec. and 1/7 sec. at 0° and 18°; with decreasing acidity these times rise to a maximum at p_H 8, being 700 secs. and 80 secs. at the same temperatures, whilst for $p_H>9$ the times decrease regularly. At equilibrium, in solutions from p_H 0 to p_H 4·5, less than 2% of the total dissolved carbon dioxide is in the form of carbonic acid or carbonate or hydrogen carbonate ion; in alkaline solutions (p_H 12 to 15) almost the whole exists as carbonate (CO_3'') ion. The values of the first and second dissociation constants of carbonic acid are determined as 2×10^{-4} and $10^{-10\cdot5}$ respectively at 0°. In reaction (1) above, the equilibrium constant $K_{\text{hydrate}}=a_{H_2CO_3}/a_{CO_2}$ is 1/891 at 0°, and 1/646 at 18°. The solutions of carbon dioxide used varied from 0·2 to 0·5 *M*. W. H.-R.

Condition of Methyl-orange in its Transition Interval. I. M. KOLTHOFF (*Rec. trav. chim.*, 1925, **44**, 68—74).—Bjerrum's theory of salt-like double ions is applied to the case of methyl-orange, and the colour change thus represented:

$$\underset{\text{red}}{\text{'HNMe}_2\text{RSO}_3'} + \text{OH}' \rightleftharpoons \underset{\text{yellow}}{\text{NMe}_2\text{RSO}_3'} + \text{H}_2\text{O}.$$

Methyl-orange fulfils the criteria for a basic indicator (cf. A., 1922, ii, 156; 1923, ii, 330) and the dissociation constant of the base is of the same order as that of dimethylaminoazobenzene. The sulphonic acid group behaves as a very strong acid. F. M. H.

Condition of Methyl-red in its Transition Interval. I. M. KOLTHOFF (*Rec. trav. chim.*, 1925, **44**, 75—81).—By means of partition experiments with the aqueous solution and light petroleum near the isoelectric point (p_H 3·9) of *o*-methyl-red (dimethylamino-azobenzene-*o*-carboxylic acid), it is found that at 15° $k_b = 2{\cdot}5 \cdot 10^{-12}$ and $k_a = 9 \cdot 10^{-6}$. According to Bjerrum's theory (A., 1923, i, 444), the red double ion $\text{'HNMe}_2\text{RCO}_2'$ forms with acids $\text{'HNMe}_2\text{RCO}_2\text{H}$ and with bases $\text{NMe}_2\text{RCO}_2'$. At p_H 4—6, *o*-methyl-red behaves as a base, k_b $7 \cdot 10^{-10}$, k_a $2{\cdot}5 \cdot 10^{-3}$. Similarly, the behaviour of *p*-methyl-red is best explained by the theory of double ions, and for it are found k_b $10^{-10{\cdot}5}$ and k_a $10^{-3{\cdot}3}$. F. M. H.

Cryoscopic Measurements with Nitrobenzene. III. Equilibrium in Nitrobenzene Solution. F. S. BROWN (*J. Chem. Soc.*, 1925, **127**, 345—348; cf. this vol., ii, 32).—The dissociation of naphthalene picrate and of naphthalene-trinitrotoluene have been investigated by cryoscopic measurements of their solutions in moist nitrobenzene in the presence of partially dehydrated Glauber's salt. The dissociation obeys the law of mass action. The free energy of formation of naphthalene picrate at 3° is calculated as 2083 cal. per mol. in agreement with values obtained by Brönsted (A., 1912, ii, 20) from *E.M.F.* measurements. W. H.-R.

Deliquescence of Salts. K. SCHERINGA (*Pharm. Weekblad*, 1925, **62**, 185—190).—A solid salt becomes liquid on exposure by attraction of water from the air when the vapour pressure of its saturated solution, at the temperature prevailing, is less than 65% of the vapour pressure of water at that temperature, but remains dry if this figure is over 70%, the relative humidity of the atmosphere being usually about 65%. Tables showing this percentage pressure for various salts at various temperatures and pressures are given. S. I. L.

Lithium. III. Lithium Hydride. G. F. HÜTTIG and A. KRAJEWSKI (*Z. anorg. Chem.*, 1925, **141**, 133—160; cf. A., 1924, ii, 756).—The dissociation pressure of lithium hydride has been measured at various temperatures. The hydride was prepared by a modification of Moers' method (A., 1921, ii, 200), the maximum yield being obtained at 750°. Hydrogen attacks the molten lithium at temperatures above 400°, yielding a product which contains 98·7%

of the hydrogen required for the formula LiH. Sublimation is accompanied by decomposition, the hydrogen not recombining with the lithium, and the hydride is extremely unstable in air. As the percentage of hydrogen in the sample increases so the pressure increases, an extremely rapid increase occurring as the hydrogen content approaches that required for the composition LiH; this behaviour is similar to that observed with magnesium halide–ammonia systems investigated by Biltz and Hüttig (A., 1922, ii, 59), and is said to afford additional evidence that lithium hydride is a true compound. A difference of 0·02% in the hydrogen content doubles the pressure. The period required for the attainment of a constant pressure value varies very largely for different investigations and different temperatures and the experimental results are broadly represented by two typical curves, one for high temperatures and the other for low temperatures. The values for the dissociation pressure of a solid phase of composition $LiH_{0·987}$ are, at temperatures of 150°, 170°, and 190°, p(mm.)=0·05, 0·11, and 0·34, respectively. At the ordinary temperature (23·5°) the observed pressure was 0·023 mm., which shows a large discrepancy from the value ($4·57\times10^{-22}$ mm. at 13°) calculated by Moers (*loc. cit.*) from the heat of formation and specific heat data. If a preparation which has been decomposed at high temperature is left for a time at the ordinary temperature and then again heated at the higher temperature the hydrogen pressure measured is greater than that recorded when the heating is uninterrupted. With a solid phase containing a large excess of metallic lithium no extremely small dissociation pressures are obtained such as are required on thermochemical grounds. In explanation, it is suggested that the hydrogen ion eliminated is freely mobile and diffuses throughout the system, producing a homogeneous phase. The calculated heat of the reaction is also in good agreement with the experimental value obtained by Gunz, $2Li+1·00H_2=2LiH+43,200$ cals. Arbitrary extrapolation of the value of the dissociation pressure to that of pure lithium hydride yields a value greater than 1 atm. From the experimental p/t value the heat of reaction is calculated by use of the Nernst equation, and certain X-ray spectroscopic measurements are recorded. In pure lithium hydride, the arrangement of the lithium ion is a face-centred cubic lattice and the distance between the middle points of the lithium and hydrogen ions is calculated to be $2·00\times10^{-8}$ cm. The energy liberated by the combination of metallic lithium with gaseous hydrogen ($2Li+H_2=2LiH$) at absolute zero is calculated to be U_0=40,775 cals., whilst that for the reaction of two atoms of lithium with 1 mol. of hydrogen to produce 2 mols. of lithium hydride is practically zero. J. W. B.

Alpha Phase Boundary in the Copper-Zinc System. R. Genders and G. L. Bailey (Inst. Metals, Mar., 1925; advance copy, 9 pp.).—The α phase boundary in the copper–zinc system is a straight line perpendicular to the axis of composition up to 450° at 61% Cu; above this temperature it inclines in a slightly curved line to meet the solidus at about 906° and 67·5% Cu. Alloys containing 61—

63% Cu consist of pure α at the ordinary temperature, but on heating above 450° this is progressively transformed into β until above 800° the change is complete. [Cf. *B.*, 1925, 246.] A. R. P.

Equilibrium Diagram of the Aluminium–Zinc System. T. ISHIHARA (Inst. Metals, Mar., 1925; advance copy, 17 pp.).—According to measurements of the electrical conductivity the solubility of aluminium in solid zinc falls from 1% at the m. p. to 0·3% at 20°, whilst the solubility of zinc in solid aluminium is 22·5% at 20°, 30% at 280°, and 60% at 440°. The eutectic contains 5% Al and melts at 380°, the peritectic line at 440° extends from 13% to 41% Al and the eutectoid line at 280° from 0·3% to 65% Al. The eutectoid contains 21% Al and is formed by the decomposition of the unstable β phase, which appears to consist of a solid solution of an unknown compound in α, into $\beta+\gamma$. In alloys containing β a transformation similar to the A2 transformation in iron takes place at 340—360°. [Cf. *B.*, 1925, 246.] A. R. P.

Ternary System Molybdenum–Nickel–Silicon. PFAUTSCH (*Z. Metallk.*, 1925, **17**, 53—56).—Besides the binary compounds $MoSi_3$, $MoSi_2$, MoNi, Ni_2Si, Ni_3Si_2, and NiSi, the system molybdenum–nickel–silicon contains two ternary compounds Ni_3Mo_2Si and Ni_4MoSi_2. The former is stable at all temperatures below 2100°, when it melts unchanged, but the latter decomposes below 850° as follows: $2Ni_4MoSi_2=Ni_3Mo_2Si+Ni_3Si_2+Ni_2Si$. The silicide, NiSi, forms a eutectic with the stable ternary compound. All the alloys in this system with the exception of those rich in nickel and consisting of homogeneous mixed crystals are very hard and brittle. [Cf. *B.*, 1925, 247.] A. R. P.

Ternary System Chromium–Nickel–Molybdenum. E. SIEDSCHLAG (*Z. Metallk.*, 1925, **17**, 53—56).—No ternary compounds are formed in this system, but there is evidence of the formation of a ternary eutectic containing between 5 and 10% Ni. The structure of the alloys rich in nickel consists of a homogeneous mixed crystal phase, but all other alloys contain two or three phases consisting of the compound MoNi, molybdenum containing small quantities of nickel and chromium in solid solution, and the homogeneous mixed crystal phase. The alloy containing 60% Ni, 20% Mo, and 20% Cr is only very slightly attacked by hot hydrochloric acid or by hot dilute sulphuric acid and unattacked by solutions of the alkali hydroxides. [Cf. *B.*, 1925, 247.] A. R. P.

Dissociation Equilibria of Compounds of Ferrous Salts with Nitric Oxide. W. MANCHOT [with H. HAUNSCHILD] (*Z. anorg. Chem.*, 1924, **140**, 22—36).—Old data (A., 1907, ii, 93) and some from new determinations are combined to obtain the equilibrium constant for the dissociation of the substance $FeSO_4,NO$. This compound is exothermic (11,900 cal.), and its dissociation increases with rise of temperature. No relationship exists between the ionisation and complex formation, but it is believed that addition

takes place in the first instance to the undissociated molecule. At higher temperatures oxidation occurs. L. J. H.

Equilibrium of the Reciprocal Salt System Sodium Chloride–Magnesium Sulphate with Reference to Natural Salt Solutions. N. S. KURNAKOV and S. F. SHEMTSCHUSHNI (*Z. anorg. Chem.*, 1924, **140**, 149—182).—The quaternary system H_2O–($Mg^{++}Na_2^{++}$)–($Cl_2^{--}SO_4^{--}$) was studied at 0° and 25°. At the lower temperature there are four solid phases, viz., NaCl, $Na_2SO_4,10H_2O$, $MgSO_4,7H_2O$, and $MgCl_2,6H_2O$. At 25°, the solid phases Na_2SO_4, $MgSO_4,6H_2O$, and astrakanite, $Na_2SO_4,MgSO_4,4H_2O$ are formed. Tables of data and projections of the space models for both temperatures are given.

The paths of crystallisation are discussed. L. J. H.

Heats of Solution and of Decomposition of Chlorine Dioxide. H. BOOTH and E. J. BOWEN (*J. Chem. Soc.*, 1925, **127**, 342—345).—Mixtures of chlorine dioxide and carbon dioxide were passed into water contained in a vacuum-jacketed calorimeter, and the rise in temperature was compared with that produced by the expenditure of a known amount of electrical energy. The heat of solution is 6600 ± 200 cal./mol. independent of the concentration of the solution produced. The heat of decomposition is 23,500 cal./mol., and was determined by sparking a mixture of chlorine dioxide and carbon dioxide in a vacuum-jacketed vessel containing a small thermocouple, the rise in temperature being compared with that produced by the expenditure of a known amount of electrical energy through a heating coil. The heat of dissociation of a molecule of chlorine dioxide is then calculated as $ClO_2=Cl+O_2-4000$ cals., the small energy change corresponding with two vibrational quanta. Since the gas is stable thermally, the energy of vibration is not sufficient to activate a molecule chemically but electronic activation is required. W. H.-R.

Graphitic Conduction in Conjugated Chains of Carbon Atoms. T. M. LOWRY (*Nature*, 1925, **115**, 376—377).—If the view is accepted that at each stage of an isomeric change involving migration of an atom the intermediate double bonds of the conjugated system are ionised, it is possible to explain the mechanism of such an action harmoniously with Armstrong's dictum that "chemical action is reversed electrolysis." The process, called "graphitic conduction," is analogous to metallic, and not to electrolytic conduction. A. A. E.

Conductivity Measurements of Very Dilute Solutions. H. REMY (*Z. Elektrochem.*, 1925, **31**, 88—95).—For conductivity measurements in very dilute solutions, the use of "ultra-pure" water can be avoided if the impurity in "conductivity water" be limited to the least practicable amount of carbonic acid the influence of which on the conductivity may be calculated on the basis of the law of mass action. A simple method is described for testing the compliance of a sample of water with this condition. The solubility

of a number of sparingly soluble oxides has been determined in this way by conductivity measurements and the results are in good agreement with those obtained by conductometric titration and (where possible) gravimetric analysis. N. H. H.

Velocity of the Hydrogen Ion in Gels under the Action of the Electric Current. N. ISGARISCHEV and A. POMERANZEVA (*Z. Elektrochem.*, 1925, **31**, 101).—An answer to the explanation offered by Liesegang (*ibid.*, 1924, **30**, 449) of the "inertia" of the hydrogen ion in gels, previously described by the authors (A., 1924, ii, 90). Experiment shows that there is no appreciable difference in the velocity of the hydrogen ion whether N- or $2N$-sulphuric acid be used. N. H. H.

Migration of Ions in Solid Electrolytes. C. TUBANDT and H. REINHOLD (*Z. Elektrochem.*, 1925, **31**, 84—88).—A reply to the suggestion of Le Blanc and Kröger (this vol., ii, 41) that the unidirectional ion migration in solid electrolytes found previously by the authors is a consequence of the prevailing experimental conditions. For a given substance, it is always the same ion which moves by diffusion and current conductance, irrespective of the conditions. N. H. H.

Diffusion Potential and Transport Number of Hydrochloric Acid in Concentrated Solution. S. R. CARTER and F. M. LEA (*J. Chem. Soc.*, 1925, **127**, 487—494).—The diffusion potentials between N-hydrochloric acid and solutions of concentration from 1·0—11·5N have been investigated. The usual diffusion potential formula requires correction for the vapour pressure of the solutions, and for the variation of transport numbers between solutions of widely differing concentration. If ϵ' is the observed potential of a cell with transport of the type

$$(\mathrm{Pt})\mathrm{H_2}|\mathrm{HCl}(C_2)|\mathrm{HCl}(C_1)|\mathrm{H_2}(\mathrm{Pt}),$$

and E' that of a cell without transport of the type

$$(\mathrm{Pt})\mathrm{H_2}|\mathrm{HCl}(C_2),\mathrm{HgCl}|\mathrm{Hg}|\mathrm{HgCl},\mathrm{HCl}(C_1)|\mathrm{H_2}(\mathrm{Pt}),$$

the diffusion potential π can be expressed by the relation

$$\pi = E' - \epsilon' + RT/4F \,.\log\,(b-c)/(b-c')$$

where b is the barometric pressure, c and c' are the vapour pressures of the dilute and concentrated solutions, respectively. By means of this formula the diffusion potentials between hydrochloric acid solutions have been calculated from observations on the above types of cells, and the results are satisfactorily confirmed by measurements on oxidation–reduction cells of the type

$$(\mathrm{Pt})|\mathrm{CuCl,CuCl_2};\ x\mathrm{N\text{-}HCl}|\mathrm{NHCl}|\mathrm{NKCl}|\mathrm{NKCl,HgCl}|\mathrm{Hg}$$

and a similar cell without transport. The values are, however, much higher than those calculated from conductivity–viscosity data assuming a constant transport number. The results confirm the equation of Dolezalek (A., 1898, ii, 421) for the calculation of the *E.M.F.* of a concentration cell from vapour-pressure measurements, and show that the calomel–mercury electrode is suitable as an anodically reversible electrode in concentrated hydrochloric acid.

W. H.-R.

Measurements in Series with the Gas Cell. E. WÖHLISCH (*Biochem. Z.*, 1924, **153**, 129—130).—A simple arrangement is described for rapidly connecting any one of a series of gas electrodes with a potassium chloride–calomel electrode. J. P.

Concentration Cells in Methyl Alcohol. II. Solutions containing Tetraethylammonium Iodide. J. GRANT (*Trans. Faraday Soc.*, 1924, **20**, 385—390; cf. A., 1924, i, 150).—Using ammonium iodide of different dilutions were made, and the electromotive forces measured at 25°. The transport numbers of the cation calculated from these results by the equation of Nernst are appreciably lower than those obtained by Carrara (A., 1903, ii, 708), using the direct method, but like the latter they increase with the dilution, and reach an approximately constant value of 0·280 at very great dilutions, and this may be taken as the true transport number when complex ions no longer exist. The form of the curves indicates that the term n_c in the Nernst equation does not really represent the value of the transport number for the mean dilution of the two solutions used. W. H.-R.

Overvoltage as a Function of Current Density and the Effects of Time, Temperature, Stirring, Pressure, Nature of Surface, and of a Superimposed Alternating Current. W. D. HARKINS and H. S. ADAMS (*J. Physical Chem.*, 1925, **29**, 205—219).—The overvoltage of hydrogen on mercury is proportional to the logarithm of the current density at 20°. No appreciable variation of the hydrogen overvoltage on mercury with the pressure (1/36—3 atm.) was found over a wide range of current density. For a range of temperature of 0—80°, the overvoltage is lowered about 2 millivolts per degree and all the curves exhibit considerable time hysteresis. The effect of rotating the cathode is to cause a decrease in the overvoltage on mercury, gold, polished and rough platinum. Stirring with gaseous hydrogen lowers the overvoltage on a tin cathode and subsequent rotation of the cathode has no further effect. When the current density is kept constant the overvoltage increases with time. Superposition of an alternating current (frequency 15—1800 and current density 1—200) lowers the overvoltage except on smooth or rough copper, on which the overvoltage is raised. The relation between the overvoltage and the current density was examined at 25° with cathodes of platinum, tungsten, molybdenum, monel metal, nickel, gold, silver, copper, tantalum, mercury, cadmium, and tin. A rough cathode gives a lower overvoltage than a smooth at the same apparent current density. Members of the same family of elements in the periodic system have nearly the same overvoltage. M. B. D.

Overvoltage and Surface Forces at the Lead Cathode. S. GLASSTONE (*Trans. Faraday Soc.*, 1925; advance proof).—The minimum overvoltage is said to be a measure of the free energy of the reaction $2H \longrightarrow H_2$, when the total concentration of gas at the

electrode is sufficient to overcome the capillary forces at the electrode and so permit bubble formation. The influence of the surface tension of the electrolyte on overvoltage has been examined. Mixtures of water with ethyl alcohol, methyl alcohol, acetic acid, *iso*butyl alcohol, *iso*amyl alcohol, and *iso*butyric acid were used containing sulphuric acid, also buffer solutions in ethyl alcohol and *N*-sodium hydroxide in ethyl alcohol. The addition of ethyl or methyl alcohol or acetic acid lowers the tension of the gas–electrolyte surface and also lowers the overvoltage. *iso*Amyl alcohol and *iso*butyric acid cause the overvoltage first to increase and then to decrease. L. L. B.

Electro-endosmosis. III. F. FAIRBROTHER and H. MASTIN (*J. Chem. Soc.*, 1925, **127**, 322—327; cf. J., 1924, **125**, 2319).—Using a diaphragm of carborundum powder, the influence of anions and cations on electro-endosmosis and on the difference of potential across the diaphragm have been investigated. Cations tend to annul the original negative charge of the carborundum in water; this effect increases with the valency of the cation, and, with ter- and quadri-valent ions the charge becomes positive and rises to a maximum at a concentration of about $N/4000$. In the case of $Al^{...}$ and $Th^{....}$ ions the sign of the charge is reversed at a concentration of a few micro-mols. per litre. With potassium salts in very low concentrations, the charge is slightly more negative than in water, but becomes less negative with increasing concentration. Anions have comparatively little effect. These results resemble those obtained by Kruyt (A., 1918, ii, 289) for the effects of cations on stream potentials in capillary tubes. W. H.-R.

Effect of Superposed Alternating Current on the Anodic Solution of Gold in Hydrochloric Acid. A. J. ALLMAND and V. S. PURI (*Trans. Faraday Soc.*, 1925; advance proof).—The experiments were made with a gold anode, a platinum cathode, and dilute hydrochloric acid as electrolyte. Without the alternating current the gold anode begins to dissolve at a certain potential, but on increasing the current density the anode becomes passive. By increasing the strength of hydrochloric acid, the potential range over which the gold remains active is increased. Further increase in anodic potential results in evolution of chlorine. Measurements were made of the effect of variation in the frequency, the A.C./D.C. ratio, the concentration of the electrolyte, and the temperature. Potential readings were first taken until chlorine was evolved. This gives the D.C. current density up to which gold remains active. Taking this current density as a standard, alternating currents in the ratio of 0·5, 1, and 2 were successively superposed, and potential readings with increasing D.C. were taken recording (*a*) anodic potentials, (*b*) D.C. current densities up to that at which gold is dissolved, (*c*) D.C. current densities at which chlorine is first evolved, and (*d*) cell voltages. The activity is defined as the limiting direct current density to which a gold cathode can be subjected without exhibiting passivity, and the percentage increase compared with the value when using direct current is found to increase with (1) increase in acid concentration,

(2) increase of temperature, (3) increase of the ratio A.C./D.C., and (4) decrease of frequency. The dissolution potential of gold is found to be lower (1) the higher the A.C./D.C. ratio, (2) the lower the frequency; and the potential of gold at current density at which dissolution ceases is lower the higher the frequency. Acid concentration and A.C./D.C. ratio have little effect on this value. The potential of initial chlorine evolution is lower (1) the greater the A.C./D.C. ratio, (2) the lower the acid concentration. The effect of frequency here is small. A theory is put forward to explain these results. L. L. B.

Effect of Superposed Alternating Current on the Polarisable Primary Cell Zinc–Sulphuric Acid–Carbon. I. Low Frequency Current. A. J. ALLMAND and V. S. PURI (*Proc. Roy. Soc.*, 1925, **A**, **107**, 126—137).—When an alternating current is superposed on the primary cell, amalgamated zinc–sulphuric acid–carbon, the delivery of direct current from the latter is increased. By studying the behaviour of each electrode separately, when an alternating current is passed through it alone by means of an auxiliary electrode, it has been shown that, contrary to Brown's conclusion (A., 1914, ii, 332), the influence of the alternating current, at least up to frequencies of about 400, is confined almost exclusively to the carbon electrode, a marked depolarisation of the hydrogen-ion discharge therefore taking place. The effect becomes relatively greater as the strength of the alternating current increases, but increase in periodicity reduces the influence. It is suggested that the oxygen discharged during the anodic pulse of the alternating current, by combining with or displacing the "active" hydrogen at the cathode, lowers the electrolytic solution pressure of the latter. The small effect on the zinc electrode is also in the direction of a depolarisation, indicating that, as the electrode behaves reversibly in the absence of an alternating current, the latter causes a dissolving zinc anode to act like a more electropositive metal. M. S. B.

Anodic Purification of Mercury. E. BRUMMER and S. VON NÁRAY-SZABÓ (*Z. Elektrochem.*, 1925, **31**, 95—97).—An apparatus is described in which mercury is purified electrolytically. A rotating cup containing the mercury forms the anode. It is constructed so as to stir the electrolyte, which is a solution of mercurous nitrate acidified with nitric acid. The cathode is of platinum. Base metals are thus dissolved out. The results of the purification are described. N. H. H.

Electrolytic Corrosion of Ferrous Metals. W. M. THORNTON and J. A. HARLE (*Trans. Faraday Soc.*, 1925; advance proof).—"Forced electrolytic corrosion" tests are described, in which the specimen is used as anode in a bath of dilute sulphuric acid. During test the anode is kept covered with a film of molecular oxygen. No appreciable amount of gas is given off, except with the rustless metals. By plotting loss of weight against ampère-hours, straight lines are obtained which indicate that there is no skin effect. A

table is given which shows that the alloys investigated fall into two groups. It appears that every ferrous alloy has a definite rate of corrosion if the conditions are kept constant, but it is probable that resistance to air corrosion will always be less than to anodic corrosion. L. L. B.

Electrolysis of Nitrobenzene with the Mercury Dropping Cathode. I. Reduction Potential of Nitrobenzene. II. Influence of the Cathodic Potential on the Adsorption of Nitrobenzene. M. SHIKATA (*Trans. Faraday Soc.*, 1925; advance proof).—I. Current–voltage curves for the reduction of nitrobenzene in hydrochloric acid, sodium hydroxide, and various salt solutions have been determined with the dropping mercury electrode. The concentration of the nitrobenzene was $4{\cdot}47\times10^{-4}$ and $4{\cdot}47\times10^{-5}$ mol./litre. The influence of hydrogen-ion concentration on the saturation current was investigated. In presence of nitrobenzene, deposition of hydrogen takes place at a much less negative cathodic polarisation. If the reduction proceeds according to the equation (1) $R{\cdot}NO_2+2H\rightarrow R{\cdot}NO+H_2O$, or (2) $R{\cdot}NO_2+4H\rightarrow R{\cdot}NH{\cdot}OH+H_2O$, the reduction potential from (1) is

$$\pi=-RT/2F\log_e p_H/[H^{\cdot}]=-RT/2F\log_e k'/[H^{\cdot}]^2C_{R\cdot NO_2},$$

$C_{R\cdot NO_2}$ being a constant under the experimental conditions. In hydrochloric acid solution the observed reduction potentials are in agreement with this formula, but in sodium hydroxide solution the reduction potentials are more positive. A theory is advanced to explain these results, involving the adsorption of the nitrobenzene at the mercury interface according to the well-known adsorption isotherm $C=aC_0^{1/m}$. Neutral salts exert a salting-out effect.

II. The current–potential curves indicate that the occurrence of a minimum is due to a desorption effect of the nitrobenzene on the mercury surface. From a consideration of electro-adsorption, the conclusion is reached that reducibility is favoured by increase in adsorption. In alkaline solution the oxygen of the nitro group appears to be attached more closely to the mercury surface and less firmly held in the nitrobenzene molecule. The possible utilisation of the observed facts in micro-analysis is pointed out. L. L. B.

Electrolysis of Solutions of Potassium Oxalate with a Tin Anode and an Electrometric Determination of the Constitution of the Complex Anions Formed. F. H. JEFFERY (*Trans. Faraday Soc.*, 1924, **20**, 392—401).—The electrolysis of 0·5—3*N*-solutions of potassium oxalate has been examined at 14—18°, using a tin anode. For currents of 0·4—0·01 amp. the tin dissolves first to form a complex anion according to the scheme,

$$Sn+2C_2O_4''-2\ominus=\{Sn(C_2O_4)_2\}'',$$

and the substance $K_2Sn(C_2O_4)_2,H_2O$ has been isolated. At this stage no gas is evolved, but after a time, which depends on the current density and the concentration of the anolyte, the current suddenly drops. At this point, the anode is covered with a fine black deposit of tin, and if this is not removed, oxygen begins to be evolved; if the electrolysis is continued the whole of the stannous complex undergoes anodic oxidation with the production of stannic

complex ions of the type $\{Sn(C_2O_4)_3\}''$; a solid substance derived from quadrivalent tin is formed which may be either $Sn(C_2O_4)_2$ or $K_2Sn(C_2O_4)_3$. Up to this point, no tin is deposited on the cathode. The anode potential remains constant over a wide range of current densities if the surface is kept free from finely-divided metal and from products of electrolysis, but if these accumulate the potential may rise to 9 volts referred the hydrogen electrode as zero, the current being 0·1 amp. The change from complex stannous ion formation to that of anodic oxidation is very rapid. A method for the determination of the composition of complex ions by measurements of potential, viscosity, and resistance is described, for details of which the original must be consulted. W. H.-R.

Electro-deposition of Manganese. II. A. J. ALLMAND and A. N. CAMPBELL (*Trans. Faraday Soc.*, 1924, **20**, 379—384; cf. A., 1924, ii, 555).—The best conditions for the deposition of pure manganese consist in the electrolysis of a solution containing manganous and ammonium sulphates separated by a diaphragm from the anode solution, which contains ammonium sulphate. The hydrogen-ion concentration is kept at 10^{-6} to 10^{-8} by the addition of sulphuric acid or ammonia during the electrolysis. The temperature should be 30° and the current density at the cathode from 10 to 15 amp./dm.^{2}; under these conditions a current efficiency of 30 to 35% can be obtained with a rotating cathode. If an ebonite burnisher is pressed very lightly against the rotating cathode, the character of the deposit is much improved whilst the efficiency may rise to as much as 54%. No advantage is gained by superposing an alternating current on the direct current, or by using the chloride instead of the sulphate. Electrolytic manganese contains considerable quantities of dissolved hydrogen, but is still brittle when the latter is removed. W. H.-R.

Potentiometric Investigation of the Reduction of Permanganate by Ferrous Ion and Iodine Ion. E. MÜLLER and H. MÖLLERING (*Z. anorg. Chem.*, 1924, **141**, 111—118).—The reactions between permanganate and ferrous sulphate, and permanganate and potassium iodide, in sulphuric and hydrochloric acid solutions, have been studied potentiometrically. For the former reaction in sulphuric acid solution, $MnO_4' + 5Fe^{\cdot\cdot} + 8H^{\cdot} = Mn^{\cdot\cdot} + 5Fe^{\cdot\cdot\cdot} + 4H_2O$, the end-point potential e_u is +0·65 volt if the permanganate is added to the iron solution, and +0·76 volt if the ferrous salt is added to the permanganate solution. In hydrochloric acid solution, e_u is +0·67 volt (permanganate added to iron), or +0·66 volt (iron added to permanganate). In sulphuric acid solution the second reaction is complicated by a secondary reaction resulting in the formation of iodate, and in hydrochloric acid solution, by the formation of iodine chloride. L. L. B.

Kinetics and Mechanism of Reaction of the Reduction of Ferric Salts by Thiosulphate in Weakly Acid Solution. J. HOLLUTA and A. MARTINI (*Z. anorg. Chem.*, 1924, **140**, 206—226).—The velocity of reduction of ferric chloride by sodium thiosulphate

in the presence of dilute hydrochloric acid was studied. No consistent velocity constant could be obtained on any assumption as to the order of the reaction, principally owing to the accelerating influence of the iron in acid solution. In neutral solution, excess of ferric chloride retards the reaction, as does excess of thiosulphate in both neutral and acid solutions. Neutral salts retard the reaction. The facts are explained on the assumption that the reaction takes place in two stages, a preliminary (rapid) equilibrium $Fe^{\cdots}+2HS_2O_3'=[Fe(S_2O_3)_2]'+2H^{\cdot}$ being followed by the slow reaction $[Fe(S_2O_3)_2]'+Fe^{\cdots}=2Fe^{\cdot\cdot}+S_4O_6''$. The influence of neutral salts and the retarding influence of excess of ferric chloride in very low acid concentration are then in accord with Brönsted's theory (A., 1922, ii, 699). L. J. H.

Occurrence of Iodine in Nature. IV. Evolution of Elementary Iodine from Sea Water. T. VON FELLENBERG (*Biochem. Z.*, 1924, **152**, 132—134).—The rate of loss of iodine from sea-water (from Capri and Isle of Wight) has been determined. Lighting conditions have little effect on the rate of loss, which is chiefly dependent on the access of air, and surface exposed. J. P.

Reactions between Solid Phases. IV. J. A. HEDVALL and J. HEUBERGER (*Z. anorg. Chem.*, 1924, **140**, 243—252).—A reply to the criticism of Balareff (A., 1924, ii, 611). Further experiments are described showing that reaction does occur between substances that have been carefully dried, although the presence of water may slightly lower the temperature at which reaction begins and facilitates its completion. The suggestion that surface melting occurs is examined and rejected. L. J. H.

Influence of Emulsoids on the Rate of Dissolution of Zinc in Solutions of Lead, Nickel, and Copper Salts. J. N. FRIEND and J. S. TIDMUS (Inst. Metals, Mar., 1925; advance copy, 7 pp.).—Agar reduces the rate of dissolution of metallic zinc in solutions of lead acetate according to the logarithmic law; the rate is increased by an increase of temperature or by a rise in the concentration of the lead salt. The percentage retardation of dissolution of zinc in solutions of copper sulphate containing small quantities of agar is reduced by a rise in temperature above 15°, contrary to the usual behaviour. Sucrose retards the dissolution of zinc in nickel sulphate solutions considerably, but has little action in the case of copper sulphate or lead acetate solutions. [Cf. *B.*, 1925, 246.] A. R. P.

Some Metallic Couples Decomposing Water at the Ordinary Temperature. E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1925, **127**, 495—496).—Very active metallic couples are obtained by placing clean magnesium sheet in a 2% ammonium chloride solution containing 0·2% of crystallised nickel chloride, ferrous sulphate, or cobalt chloride. The resulting deposits of copper are of very fine texture and very adherent and the couples decompose water vigorously for a few minutes, then more slowly, the hydrogen

evolution continuing for several hours, especially in the presence of 0·1% of ammonium chloride. A. R. P.

Kinetics of the Oxidation of Thiocarbamide by Charcoal. H. FREUNDLICH and A. H. FISCHER (*Z. physikal. Chem.*, 1925, **114**, 413—429; cf. A., 1916, ii, 238).—The oxidation of thiocarbamide in solution by blood charcoal is similar to the oxidation of phenylthiocarbamide under the same conditions, and is regarded as following the equation $2CS(NH_2)_2+O_2=C_2H_4N_4S+2H_2O+S$. The course of the reaction was followed by manometric measurement of the velocity of oxygen absorption, but in some cases the decrease of thiocarbamide concentration was followed by titration. In the first stages, the reaction is an adsorption catalysis. The velocity depends on the quantity of thiocarbamide adsorbed by the charcoal, and follows the equation (i) $dz/dt=k(a/q+sa)$, where dz is the amount of oxygen adsorbed in the time dt, a the adsorbed quantity of thiocarbamide, and q and s are constants. The velocity also depends on the quantity of oxygen adsorbed on the surface, and the kinetics of the reaction can be explained by supposing that the two substances replace one another. If $dz/dt=kab$, where b is the adsorbed oxygen, and assuming that $b=1/q+sa$, the equation (i) is obtained. The influence of oxygen pressure on the velocity of the reaction is given by the equation $dz/dt=kp^{1/n}$. The temperature coefficient is 1·62 for 10°, and is in keeping with the Arrhenius formula. The reaction products are preferentially adsorbed by the charcoal, owing to the fact that they drive out both the oxygen and the thiocarbamide. Urethane also checks the reaction, and the retardation increases with rise in the homologous series. Hydrocyanic acid has a retarding influence only at low concentrations of thiocarbamide, at which the hydrocyanic acid and thiocarbamide adsorption were of the same order of magnitude. L. L. B.

Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air. III. W. P. JORISSEN and J. C. MEUWISSEN (*Rec. trav. chim.*, 1925, **44**, 132—140; cf. A., 1924, i, 253; this vol., ii, 53).—The effect of the vapours of carbon tetrachloride, di- and tri-chloroethylene, tetrachloroethylene, and tetra- and penta-chloroethane, on the explosion limits of pure methane, carbon monoxide, acetylene, and hydrogen has been investigated. In every instance, there is a fall in the lower explosion limit with di- and tri-chloroethylene, whilst in the case of hydrogen, a similar effect is also produced by tetrachloroethylene and tetra- and penta-chloroethane. [Cf. *B.*, 1925, 234.] F. M. H.

Catalysis and the Inversion of Sucrose by Acetic Acid. E. SAILLARD (*Mon. Sci.*, 1925, **15**, 10—12).—The effect of the addition of organic and inorganic salts on the rate of inversion of sucrose by acetic acid is studied. Potassium acetate and sodium formate entirely prevent the inversion and sodium sulphate exerts a retarding influence. Sodium chloride and nitrate, magnesium chloride and sulphate accelerate the reaction. The non-inversion of the sucrose

precipitated from beet molasses by glacial acetic acid may hence be ascribed to the anticatalytic influence of the organic salts present. W. E. E.

[Negative] Catalysis. H. W. UNDERWOOD, jun. (*Proc. Nat. Acad. Sci.*, 1925, **11**, 78—80).—The so-called stabilisers employed in the preservation of otherwise unstable substances form molecular compounds with the substance preserved and are thus true negative catalysts. Ether, phenol, resorcinol, and benzene are stabilisers for chloroform, and evidence of molecular compound formation is available for each of these substances. In examining 25 compounds, no serious contradiction to the molecular compound theory was found. Fugitive dyes may be protected against the action of light by treatment of the dyed wool or cotton with dilute solutions of phenol or resorcinol. J. S. C.

Catalysis of Hydroxylamine. A. KURTENACKER and F. WENGEFELD (*Z. anorg. Chem.*, 1924, **140**, 301—319).—Investigations of the action of various substances on the decomposition of hydroxylamine are described. Molybdic acid has no action in alkaline solution; it acts catalytically in acid solution, ammonia, nitrogen, nitrous and nitric oxides being formed. The results with vanadic acid confirm those previously published (A., 1924, ii, 250). Copper sulphate in acid solutions yields mainly nitrous and nitric oxides, with small quantities of nitrogen; in strongly alkaline solutions nitrous oxide is the main product. Ferric hydroxide produces nitrous oxide and ammonia, catalytically, in alkaline solutions. The decomposition of hot alkaline hydroxylamine solutions yields nitrous oxide, ammonia, and nitrogen, but no nitric oxide. The results are explained by assuming a rapid oxidation and reduction of the catalyst by the hydroxylamine, which is itself reduced to ammonia in the former process. Quadrivalent vanadium, quinquevalent molybdenum, and bivalent iron are shown to reduce hydroxylamine to ammonia, in support of this explanation. The formation of nitric oxide is explained by assuming the reduced catalyst to be peroxidised and so able to oxidise some hydroxylamine more energetically. Previously published results of other workers are cited in support of the theory. S. K. T.

Reaction Velocity of Oxygen with Solutions of Inorganic Salts. I. Oxidation of Nitrites. II. Catalytic Oxidation of Arsenites. W. REINDERS and S. I. VLES (*Rec. trav. chim.*, 1925, **44**, 1—28, 29—46).—I. Pure sodium nitrite (from which carbon dioxide must be excluded, since it gives rise to nitrous acid and nitrous oxide) is not oxidised in neutral or alkaline solution. Oxidation of a dilute solution by oxygen in presence of nitric acid is carried out in a closed thermostat, with stirring so rapid that a saturated solution of oxygen results; the initial relative reaction velocity is determined from measurements of the consumption of oxygen. When sodium nitrite is present in large excess, the velocity is independent of its concentration, but it increases with the quantity of nitric acid which is converted into nitrous acid,

and the reaction is bimolecular as regards the latter; no simple relationship exists between reaction velocity and oxygen concentration. The mechanism of the reaction is considered to consist in the oxidation of free nitrous acid to nitric oxide, nitrogen peroxide, and water, followed by oxidation of nitric oxide to nitrogen peroxide; this reacts with water to form nitric oxide and nitric acid, which yields sodium nitrate and nitrous acid. The detection of nitric oxide, the concentration of which is determined for various mixtures of sodium nitrite and nitric acid, confirms the theory, as also does the effect of temperature changes. Potassium nitrite behaves like sodium nitrite. All strong acids produce the same effect, and salts have no catalytic influence, the accelerating action of iron and aluminium salts being due to their hydrolysis.

II. Oxidation of pure sodium or potassium arsenite by free oxygen only occurs in alkaline solution in presence of a catalyst. If a copper salt is used for this purpose, a complex of unknown composition is formed and the order of the reaction with regard to it lies between 1 and 2. The reaction velocity is proportional to the arsenite-ion concentration and depends on the hydroxyl-ion concentration, reaching a maximum with a 0·5 *N*-solution of potassium hydroxide. It is unaffected by various inorganic salts, but retarded by glycerol and other substances which form complexes with copper salts in presence of alkalis. Since alteration of the oxygen pressure has little influence, the measured velocity cannot be that of direct oxidation of arsenite to arsenate. It is suggested that oxidation takes place in two stages: (*a*) Cu″ complex + $AsO_2' \rightarrow$ Cu′ complex + AsO_3, which is shown to be a reaction of the same order of velocity as the measured oxidation of arsenites, (*b*) Cu′ complex + $O_2 \rightarrow$ Cu″ complex, which is a very rapid reaction. Certain other metallic salts do not behave like copper, since they do not form reducible complexes at such alkalinity that the arsenite is incompletely hydrolysed.

Carbon catalyses the oxidation of arsenite to arsenate. This reaction is proportional to the arsenite-ion concentration, to that of potassium hydroxide, and to the quantity of carbon, but is little influenced by the oxygen concentration. It is suggested that (*a*) the oxygen is adsorbed by the carbon and thus activated, this being a rapid reaction, and (*b*) the activated oxygen gradually converts the arsenite into arsenate. F. M. H.

Periodic Dissolution of Metals. E. S. Hedges and J. E. Myers (*J. Chem. Soc.*, 1925, 127, 445—449; cf. A., 1924, ii, 325).—The dissolution of magnesium in acetic, sulphuric, nitric, or orthophosphoric acid in the presence of an activating agent shows periodicity. In these and the previously described periodic reactions activation can be produced by touching the dissolving metal with electrically deposited copper, or by first dipping the magnesium into solutions of copper or ferrous sulphate. Regularity in the periodicity is favoured by uniformity of the surface of the activating metal, whilst the frequency increases with decreasing amounts of the activating agents. Ordinary copper is inactive, but can be

activated by electrolytic or chemical deposition and also by cold-rolling; the activation is associated with an unstable, close-grained, and possibly amorphous structure. "Naturally active" vessels (*loc. cit.*) can be produced by leaving glass tubes to soak for long periods in a mixture of colloidal platinum and gelatin in hydrochloric acid. W. H.-R.

Union of Hydrogen and Oxygen in Presence of Silver and Gold. D. L. CHAPMAN, J. E. RAMSBOTTOM, and C. G. TROTMAN (*Proc. Roy. Soc.*, 1925, **A**, **107**, 92—100).—The catalytic action of metallic gold and silver on the reaction between hydrogen and oxygen is prevented by the presence of a film of oxide on the surface of the metal. If this be removed the metal is as active as if previously heated in hydrogen. The Bone and Wheeler effect (A., 1906, ii, 434), therefore, can apparently be simply explained by the removal of inhibiting oxygen by hydrogen instead of activation by adsorbed hydrogen. Hydrogen and oxygen will combine, even at ordinary temperature, in the presence of a condensed silver film. M. S. B.

Catalytic Decomposition of Hydrogen Peroxide Solution by Animal Charcoal: the Production of Highly Active Charcoals. J. B. FIRTH and F. S. WATSON (*Trans. Faraday Soc.*, 1924, **20**, 370—377; cf. A., 1924, ii, 542).—Crude animal charcoal dried at 120° is comparatively inactive towards hydrogen peroxide, but its activity can be slightly increased by heating in a vacuum or treatment with iodine. The catalytic activity of the charcoal purified with hydrochloric acid is greater than that of the crude material and can be greatly increased by heating in a vacuum at 600—900°, and still more so by sorption of iodine from solution followed by complete removal of the iodine and further heating in a vacuum. The increased activity is accompanied by an increase in bulk, although repeated treatment with iodine increases the volume but not the catalytic activity. On the other hand, after four treatments with iodine, the charcoal produces a vigorous oxidation of alcohol with the formation of aldehyde. Small quantities of mineral matter increase the activity owing to their action as a spacing agent, whilst larger quantities retard it, since the carbon particles tend to be covered and protected. W. H.-R.

Comparison between the Homogeneous Thermal Decomposition of Nitrous Oxide and its Heterogenous Catalytic Decomposition on the Surface of Platinum. C. N. HINSHELWOOD and C. R. PRICHARD (*J. Chem. Soc.*, 1925, **127**, 327—336).—The heterogeneous thermal decomposition of nitrous oxide on the surface of a heated platinum wire between 600° and 1200° is retarded by the presence of oxygen and proceeds at a relatively faster rate at low than at high pressures. The velocity of the reaction is represented by the equation $-d[N_2O]/dt=k[N_2O]/(1+b[O_2])$, and the heat of activation in the catalytic reaction is 32,500 cal. per g.-mol. This reaction is unimolecular, whereas the homogeneous

thermal decomposition of nitrous oxide is bimolecular and its heat of activation is much greater; the platinum surface in the heterogeneous reaction acts as an acceptor for atomic oxygen, the nitrous oxide probably giving its oxygen atom to the platinum, thereby forming a retarding film of atomic oxygen. A. R. P.

Catalytic Activity of Copper. V. Comparison of the Rates of Dehydrogenation of Various Alcohols. W. G. PALMER and F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, **A**, **107**, 255—269; cf. A., 1924, ii, 843).—Measurements of the rates of dehydrogenation of certain alcohols by supported copper films have led to the conclusion that the reaction is direct, as stated by Sabatier, and that there is no intermediate formation of ethylene and water, as suggested by Ipatiev. The primary alcohols, ethyl, propyl, butyl, *iso*butyl, and *iso*amyl, show equal rates of dehydrogenation and the same temperature coefficients. It is therefore inferred that reaction occurs in a unimolecular adsorption film covering the surface of the copper, the common radical $\cdot CH_2 \cdot OH$ being in contact with the surface, whilst the hydrocarbon chains are perpendicular to it. With *iso*propyl alcohol, the velocity was five times that of the others. Rapid poisoning of the catalyst occurred with one sample of *iso*propyl alcohol and with *iso*butyl and *iso*amyl alcohols. From a study of the decay curves a theory of poisoning has been developed, and on the basis of this a poisoning correction has been applied to the results with *iso*butyl and *iso*amyl alcohols, which are then seen to be identical in activity with ethyl alcohol. N. H. H.

Catalytic Action of Copper. VI. Reproducibility of the Catalyst, and of the Periodic Change in its Activity, and the Activation of the Catalyst by Alternate Oxidation and Reduction. F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, **A**, **107**, 270—279).—The reproducibility of the catalyst is attributed to the persistence of the granular structure throughout oxidation and reduction, assisted by the fireclay support and by standardising the conditions of oxidation. Chemical reaction occurs only when the alcohol molecule is adsorbed over a characteristic arrangement of copper atoms termed a reaction centre. The catalyst surface exposes many crystal faces as well as some amorphous material. There is a large variation in the number of atom centres lying beneath one adsorbed alcohol molecule on various faces of the crystal; it is thus probable that the density of reaction centres varies also. The periodic variation in activity may be explained as due to a periodic predomination of more active planes in the surface. The activity is controlled by at least two factors: the value of the heat of activation and the reaction centre density. If the latter is of the same order for all the types of faces exposed, then the heat of activation plays the greater part in deciding the activity of the surface. The variation of the temperature coefficient in the opposite sense to the activity is thus explained. N. H. H.

Catalytic Action of Copper. VII. Effect of Pressure on the Rate of Dehydrogenation of Alcohols. F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, **A**, **107**, 279—286).—The validity of the

assumption that reaction occurs in a unimolecular film covering the surface of the copper has been demonstrated by measuring the rate of dehydrogenation of ethyl and butyl alcohols under pressures ranging from 10 to 140 cm. of mercury, when the velocity of reaction was found to be independent of the pressure. The observations show further that the mean life of a molecule in the activated layer does not alter appreciably under the conditions studied.

N. H. H.

Mechanism of Kolbe's Electrosynthesis. R. A. GIBSON (*J. Chem. Soc.*, 1925, **127**, 475—486).—The production of trichloromethyl trichloroacetate by the electrolysis of a normal solution of trichloroacetic acid is independent of the current density at the anode within wide limits. No formation of ester occurs until the polished platinum or iridium anode acquires a potential of 2·35 volts, at which point a marked decrease occurs in the amount of free oxygen evolved, but this critical potential does not represent the discharging potential of the trichloroacetate ion. The reaction is not determined solely by the anode potential, but the nature and state of the anode are important factors; thus no ester formation takes place at anode potentials of 3 volts when anodes of gold or of platinum or glass are used. The synthesis is not due to the union of discharged anions, as suggested by Crum Brown and Walker (A., 1891, 1192, 1193), but to direct oxidation by the oxygen developed at the anode (cf. Kolbe, *Annalen*, 1849, **69**, 279), according to the reactions (*a*) $R{\cdot}CO_2H+R'{\cdot}CO_2H+O=RR'+2CO_2+H_2O$, or (*b*) $R{\cdot}CO_2H+R'{\cdot}CO_2H+O=R{\cdot}CO_2R'+CO_2+H_2O$, or (*c*) $R{\cdot}CO_2H+O=R{\cdot}OH+CO_2$. Peculiarities are noted in the behaviour of platinum anodes which have been polarised for many hours at a low potential. These are due to the existence of α- and β-forms of platinum; the former has a limited oxidising power but accelerates the reaction $O+O\longrightarrow O_2$, whilst the latter has high oxidising power and retards the same reaction. The α-form is produced by prolonged polarisation.

W. H.-R.

Reactions in the Lead Accumulator. A. LOTTERMOSER and M. GRÜTZNER (*Z. anorg. Chem.*, 1924, **140**, 93—115).—The potential of each plate separately has been determined during charge and discharge at varying current strengths and with acid of different density, and from this the separate capacities of the plates are considered. The theory of Dolezalek completely accounts for the observed results. The capacity of the accumulator is the less the more rapidly it is discharged, mainly owing to incomplete diffusion of acid into the porous layer. This effect is far more apparent at the peroxide than at the lead plate. The capacity is also greatest for the concentration of acid which has the greatest conductivity (*d* 1·19). The recovery curves after charge and discharge are also given.

L. J. H.

Electrolysis of some Tin Alloys. R. KREMANN and P. G. VON REHENBURG (*Z. anorg. Chem.*, 1924, **140**, 1—21).—In continuation of previous work (A., 1924, ii, 723, 724) the electrolytic conductivity

of fused lead–tin, tin-bismuth, and antimony–tin alloys was studied. In each case the electrolytic effect increases to a limit with increasing current density. The maximum electrolytic effect is obtained with equimolecular mixtures. In each case the tin goes to the cathode in accordance with its "conductance capacity" as defined by Benedicks (*Jahrb. Radioaktiv.*, 1916, **13**, 381). [See *B.*, 1925, 211.]

L. J. H.

Electrolysis of Molten Amalgams of Lead, Tin, and Bismuth. R. KREMANN and A. KAPAUN [with BUDAN] (*Z. anorg. Chem.*, 1924, **140**, 183—205; cf. preceding abstract).—In the electrolysis of amalgams of lead, tin, and bismuth, the lead, tin, and mercury, respectively, migrate to the cathode in agreement with the rule that the component having the greater conductance capacity should do so. In the case of the lead amalgam, considerable diffusion occurred after the alloy had become solid (at the ordinary temperature). The general rules previously reported were all followed, although the limiting value of the electrolysis effect (with increasing current density) was not quite reached. [See *B.*, 1925, 211.]

L. J. H.

Photographic Reversal. H. ARENS (*Z. physikal. Chem.*, 1925, **114**, 337—386).—Three types of photographic reversal are described. The first type (solarisation) is caused by the continued action of the same kind of energy, and in place of the Lüppo-Cramer theory, which is shown to have little experimental support, another is advanced, involving the coagulation of the silver of the grain surface. By means of this theory, a number of phenomena are explained. The second type of reversal is that caused by the superposition of different kinds of energy. The Villard-effect (white light $\longrightarrow$ Röntgen rays) and the Clayden-effect (spark light $\longrightarrow$ white light) are closely similar, and can be traced to solarisation. The Herschel effect (red light $\longrightarrow$ white light) is shown to be dependent on the presence of potassium bromide, bromine ions or molecules, and is supposed to be due to the desensitising action of potassium bromide for red light. The third type of reversal is that due to addition of the image substance (desensitisation). This phenomenon is classed by the author with the Herschel effect, and regarded as being due to the oxidation by light of the silver of the grain surface, in presence of bromine molecules or ions. [Cf. *B.*, 1925, 266.]

L. L. B.

Photocatalytic Effect of Neutral Salts. G. BERGER (*Rec. trav. chim.*, 1925, **44**, 47—67).—The decomposition of uranyl formate in formic acid solution, $U^{VI}O_2(HCO_2)_2+3H{\cdot}CO_2H=U^{IV}(HCO_2)_4+CO_2+2H_2O$, was followed by determining the decrease in acidity, and for this ionic reaction the influence of neutral salts is large. The salt effect is small for the non-ionic transformation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid, observed in dilute acetone solution. The magnitudes of the salt effects are in good agreement with the activity theory which Brönsted postulated for dark reactions (A., 1922, ii, 699), whence it seems that these photocatalytic

reactions are identical. The influence of neutral salts is also studied in the case of the decomposition in light of a weakly acid solution of each of 9 complex cobalt salts. Here the matter is more complicated and the activity theory can be applied only qualitatively; with high salt concentrations, a secondary effect is superimposed, which, according to the positive or negative charge of the light-sensitive complex, is retarding or accelerating.

F. M. H.

Realisation of Chemical Reactions in Compressors. M. BEUTZKUS (*Compt. rend.*, 1925, **180**, 429—431; cf. this vol., ii, 215).—The conditions obtaining in Diesel gas engine cylinders are recommended as providing a general method for the promoting of chemical reaction in gaseous systems. J. S. C.

Mercury Helide. J. J. MANLEY (*Nature*, 1925, **115**, 337; cf. this vol., ii, 57).—The simplest formula for mercury helide is HgHe. A. A. E.

Higher Oxides of Silver. I. Ag_2O_3. F. JIRSA (*Chem. Listy*, 1925, **19**, 3—9).—Higher oxides of silver are formed by the energetic oxidation of metallic silver or of silver salts, and contain either the monoxide, Ag_2O_2, alone or the sesquioxide, Ag_2O_3, together with the monoxide and varying amounts of the silver salt from which they are prepared. The higher oxide does not appear to be capable of separate existence and is easily decomposed by heating the compounds containing it to temperatures just below 100°; for example, $Ag_7NO_{11}=3Ag_2O_2+AgNO_3+O_2$. By extracting the product of this reaction with boiling water the oxide, Ag_2O_2, remains insoluble in an almost pure state. This oxide catalytically accelerates the decomposition of the sesquioxide. A. R. P.

Beryllium. I. Beryllium Sulphate and its Hydrates. F. KRAUSS and H. GERLACH (*Z. anorg. Chem.*, 1924, **140**, 61—80).—Beryllium sulphate tetrahydrate may be crystallised from slightly acid solution. On heating, any smaller proportion of water may be obtained, but vapour-pressure measurements indicate that only the tetra- and di-hydrates, and possibly the monohydrate, exist as pure substances. The anhydrous salt may be prepared either by dissolving beryllium oxide in concentrated sulphuric acid, and washing off the excess acid with absolute alcohol, or by heating the tetrahydrate at 400° for 1 hr. Loss of sulphur trioxide does not occur until the temperature is raised to 580°. The hexa- and hepta-hydrates, although frequently referred to in the literature, do not exist. L. J. H.

Kinetic Studies on Solid Metals. Decomposition of the Compound Al_2Zn_3. W. FRAENKEL and W. GOEZ (*Z. Metallk.*, 1925, **17**, 12—21).—The compound Al_2Zn_3 is stable only above 256°; at lower temperatures it decomposes into its elements with evolution of heat and contraction in volume. A specimen quenched from 400° in water at 0° soon attains a temperature of 40° or more when removed from the water, whilst its volume is reduced by

0·33%. Calorimetric measurements of the rate of rise of temperature and dilatometric measurements of the volume change show that the decomposition is strictly a unimolecular action. [Cf. *B.*, 1925, 175.] A. R. P.

Double Chromates of the Rare Earths and Alkali Metals. I. Double Chromates of Lanthanum and Potassium. G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 416—420).—Investigation of the isotherm for 25° of the system $La_2(CrO_4)_3$–K_2CrO_4–H_2O indicates the existence of hydrated *double chromates* with the components in the molecular proportions 1 : 1 : 2, 1 : 3 : 2, 1 : 4 : 2, 1 : 4·5 : 2, and 1 : 5 : 2. T. H. P.

Double Sulphates of Rare Earth and Alkali Metals. II. Neodymium and Potassium Sulphates. F. ZAMBONINI and V. CAGLIOTI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 385—389).—The various double neodymium potassium sulphates are described. [Cf. this vol., ii, 222.] T. H. P.

Mechanism of the Reaction in the Reduction of Titanium Tetrachloride with Hydrogen and the Behaviour of the Reduction Products in a Vacuum. R. SCHMIDT (*Ber.*, 1925, **58**, [*B*], 400—404; cf. A., 1923, ii, 769).—Titanium dichloride, almost free from oxygen, is obtained by the thermal decomposition of titanium trichloride in a carbon tube at temperatures not greatly exceeding 600°; if glass or quartz tubes are used oxygen is abstracted from the silica with consequent production of oxygenated compounds. At 600°/0·02 mm., titanium dichloride is slowly volatile, but the volatilised dichloride is decomposed and deposited in the colder parts of the tube as the trichloride mixed with small amounts of the tetrachloride. The effect is due to decomposition of the dichloride into titanium and the tetrachloride and reaction of the latter with unchanged dichloride to give trichloride. Confirmation is afforded of the previous view (*loc. cit.*) that reduction of titanium tetrachloride by hydrogen is not direct, but that three reactions, $TiCl_4+H_2=TiCl_2+2HCl$; $TiCl_2+TiCl_4=2TiCl_3$; $2TiCl_3+2HCl=2TiCl_4+H_2$, may proceed simultaneously. H. W.

Acid Properties of Ammonium Salts in Liquid Ammonia. F. W. BERGSTROM (*J. Physical Chem.*, 1925, **29**, 160—165).—Ammonium salts in liquid ammonia behave as acids and react with most of the elements above hydrogen in the electropotential series as it is known in water. By treating various elements with ammonium salts in liquid ammonia the following ammonates have been prepared: LaI_3,xNH_3, CeI_3,7·5—8NH_3, $CeBr_3$,7·5—8NH_3, $Fe(NO_3)_2$,0·6—0·4NH_3. M. B. D.

Action of Nitric Acid on Metals. N. R. DHAR (*J. Physical Chem.*, 1925, **29**, 142—159; cf. A., 1922, ii, 756; 1924, ii, 486).—The action of nitric acid on copper, silver, mercury, and bismuth gives only nitrous acid and hyponitrous acid and not hydroxylamine, hydrazine, or ammonia, which are formed by hydrogenation of nitric acid. These four metals can only take oxygen away from nitric

acid and cannot add hydrogen to it. Nitrogen is formed by decomposition of hyponitrous acid and nitric oxide from the decomposition of nitrous acid. M. B. D.

Experiments with a Hot and Cold Quartz Tube. H. STAUDINGER and W. KREIS (*Helv. Chim. Acta*, 1925, **8**, 71—74).—A number of unsuccessful attempts were made to isolate unstable substances such as solid unimolecular NO_2, red tellurium, S_2, and SO by the sudden cooling of gases from 1000° to −190°. G. M. B.

Hydrolytic Decomposition of Phosphorus Trichloride. A. D. MITCHELL (*J. Chem. Soc.*, 1925, **127**, 336—342).—When phosphorus trichloride is hydrolysed by water the solution produced has much stronger reducing properties when first formed than has a normally produced solution of phosphorous acid; its acidity is 98% of the theoretical at first and gradually increases during ½ hr. to the maximum, probably owing to the intermediate formation and gradual decomposition of an oxychloride. The duration of increased reducing power is greater than can be attributed to the formation of the oxychloride, and is most probably due to the presence of the active tautomeric form of phosphorous acid, $P(OH)_3$, which is slowly converted into the normal form $HPO(OH)_2$. A. R. P.

Oxidation of Tervalent Chromium by Silver Oxide in Alkaline Solution. F. HANS (*Z. anorg. Chem.*, 1924, **140**, 337—338).—The quantitative oxidation of chromic salts in alkaline solution by silver oxide is shown to proceed equally well when the latter is replaced by silver nitrate, chloride, carbonate, or thiocyanate. Silver bromide and iodide are too insoluble to react. S. K. T.

Tellurium Suboxide. A. DAMIENS (*Compt. rend.*, 1924, **179**, 829—831).—Attempts to repeat the preparation of tellurium suboxide as described by Divers and Shimoze (T., 1883, **43**, 319) did not corroborate their results. The reactions $Te+SO_3 \longrightarrow TeSO_3$ and $TeSO_3 \longrightarrow TeO+SO_2$ are incomplete when pure tellurium is used, and the resulting substance, described as suboxide, was found to be a mixture of tellurium and tellurium dioxide. H. J. E.

Occurrence of Iodine in Nature. V. Iodine Content of Air. T. VON FELLENBERG (*Biochem. Z.*, 1924, **152**, 135—140).—Elementary iodine is present in dew, and is demonstrable in larger amounts just above the ground than at higher levels of the atmosphere as the dew evaporates. J. P.

Iron and Oxygen. F. S. TRITTON and D. HANSON (*J. Iron and Steel Inst.*, 1924, **110**, 90—121).—The purest electrolytic iron that could be obtained by electrolysis of ferrous sodium chloride solutions contained 0·08% of oxygen and melted at 1535°. Molten iron will retain oxide equivalent to 0·21% of oxygen in solution at 1530°; further quantities of iron oxide simply float on the surface of the metal. At the ordinary temperature, the oxygen–iron solid solution contains 0·05% O. The oxide in equilibrium with molten

iron at high temperatures melts at 1370°. The chief effect of oxygen in iron is to increase the grain size, with a corresponding decrease in the resistance of the metal to shock, and to reduce its ductility. Oxygen has no influence on the temperatures of the transformation points. A. R. P.

Action of Iron on Copper at High Temperatures. P. SIEBE (*Z. Metallk.*, 1925, **17**, 19—21).—Iron has no action on pure electrolytic copper at any temperature below 1100°, but ordinary "tough pitch" copper which contains cuprous oxide is rendered brittle and porous by heating in contact with iron at temperatures above 750°. This is due to the reducing action of the hydrogen and carbon monoxide in the iron; the action of the hydrogen is the greater as it readily diffuses into hot copper, whereas carbon monoxide has only a superficial action. [Cf. *B.*, 1925, 175.] A. R. P.

Effects of Impurities on Copper. II. Effect of Iron on Copper. D. HANSON and (MISS) G. W. FORD (*J. Inst. Metals*, 1924, **32**, 335—361).—The solubility of iron in solid copper is 4% at 1100° and less than 0·2% at 750°, below which temperature the solubility changes only very slightly. The large change in solubility at about 800° is ascribed to the transition γ-iron $\longrightarrow$ α-iron. Addition of iron up to 0·2% rapidly lowers the electrical conductivity of copper; with higher percentages heat treatment has a large influence. The ductility of copper is unimpaired by the presence of iron, which also acts as a deoxidiser. [Cf. *B.*, 1924, 833.] S. K. T.

Preparation of Crystalline Compounds of Ferrous Salts and Nitric Oxide. III. W. MANCHOT and E. LINCKH (*Z. anorg. Chem.*, 1924, **140**, 37—46; cf. A., 1914, ii, 567).—Ferrous selenate behaves like ferrous sulphate in absorbing nitric oxide and a similar ring test may be made with ferrous selenate and concentrated selenic acid. The combination is similar to that in the case of ferrous sulphate (cf. ii, 298), giving an equilibrium constant on the assumption that the combining ratio is 1 : 1. The crystalline compound may be prepared by saturating a concentrated aqueous solution of ferrous selenate ($FeSeO_4,5H_2O$) with nitric oxide in the presence of a little concentrated selenic acid. On adding a large excess of absolute alcohol, also saturated with nitric oxide, with cooling in a freezing mixture, brownish-black crystals appear after some hours. The crystals are unstable, losing nitric oxide when kept in air, but apparently the formula is $FeSeO_4,NO,4H_2O$. L. J. H.

Action of Ammonia on Aqueous Solutions of Ferrous Salts. E. WEITZ and H. MÜLLER (*Ber.*, 1925, **58**, [*B*], 363—375).—If gaseous ammonia is slowly passed into a sufficiently concentrated solution of a ferrous salt in the presence of a suitable quantity (2—5 mol.) of the corresponding ammonium salt in the absence of air, greenish-white ferrous hydroxide is precipitated initially; this slowly passes into solution and is replaced by the complex salt, which rapidly separates in the crystalline form as the passage

of the gas is continued. In this manner, ferrous chloride, bromide, iodide, nitrate, and perchlorate are converted into the corresponding hexammineferrous *salts*, $[Fe(NH_3)_6]X_2$. Ferrous sulphate does not give a hexammine compound, but, according to the quantity of ammonium sulphate, either *aquopentammineferrous sulphate*, $[Fe(NH_3)_5H_2O]SO_4$, or an additive *compound* of this substance and ammonium sulphate, $[Fe(NH_3)_5H_2O]SO_4,(NH_4)_2SO_4$. Ferrous acetate does not yield a crystalline hexammine by reason of its ready solubility and, on this account, solutions of ferrous acetate, ammonium acetate, and ammonia are well adapted to the preparation of sparingly soluble hexammine salts by double decomposition with potassium bromide or iodide or ammonium perchlorate. Since the hexammines lose ammonia readily and quantitatively when heated in a current of an indifferent gas, a means is provided of preparing anhydrous ferrous halides. The crystalline hexammines and their solutions have the pale green colour of the hexaaquo salts. Like the salts prepared in the dry way, the white colour of which is due to their finer state of division, they are unstable towards air and moisture. In consequence of the ready oxidisability of ferrous iron the hexammineferrous salts of powerfully oxidising acids, such as chloric, bromic, chromic, and permanganic acids, are incapable of existence; the solution of hexammineferrous acetate gives a precipitate of ferric hydroxide with the alkali or ammonium salts of these acids. The nitrate and perchlorate are stable at the atmospheric temperature, but when warmed in solution or suspension give a black precipitate of ferrosoferric oxide; the perchlorate ion is reduced to chloride, nitrate ion mainly to nitrous oxide. Hexammineferrous nitrite appears to exist in solution.

The inability of ferrous solutions containing ammonium salts to give a precipitate of ferrous hydroxide with ammonia is attributed to the depression of the concentration of ferrous ions in consequence of ammine formation and of hydroxyl ions by repression of the dissociation of ammonium hydroxide to such an extent that the solubility product of ferrous hydroxide is not attained. The precipitability of ferrous hydroxide depends to some extent on the anion present in the solution; its formation is most readily repressed in the case of the sulphate, whereas with perchlorate some separation occurs even when ammonium perchlorate and ferrous salt are present in the molecular ratio, 30 : 1.

Manganous salts behave very similarly to ferrous salts. Magnesium salts yield crystalline ammines in strongly ammoniacal solution, whereas in more dilute solution complex formation is less in evidence. H. W.

Cuprous Hydroxide. P. Klason (*Svensk Kem. Tidskr.*, **36**, 202—203; from *Chem. Zentr.*, 1924, ii, 2741).—Cuprous hydroxide, CuOH, is obtained practically pure by the interaction of cuprous iodide with sodium hydroxide. The exclusion of air is not essential. The precipitate is insoluble in ammonia, and is oxidised to the blue cupric state only on prolonged keeping. R. B.

Crystalline Cuprous Bromide. D. B. Briggs (*J. Chem. Soc.*, 1925, **127**, 496).—The residual liquid in the distilling flask used for the preparation of ethyl bromide from ethyl alcohol, bromine, and red phosphorus, after filtration gave a dark green solution and, on boiling, a white, crystalline precipitate of cuprous bromide when treated with copper sulphate. Under the same conditions, the residual liquid from the preparation of ethyl iodide yielded cuprous iodide. A. R. P.

Preparation of Selenic Acid. W. Manchot and A. Wirz-müller (*Z. anorg. Chem.*, 1924, **140**, 47—51).—Selenic acid may be prepared entirely free from selenious acid by the anodic oxidation of the latter. The best results were obtained with a cathode of platinum, an anode of platinum covered with lead peroxide and surrounded by a porous pot, 5*N*-nitric acid as catholyte and concentrated selenious acid as anolyte, low current density, and low temperature; 1·7 amp.-hrs. were required per g. of selenium dioxide (theoretical 0·48) and the yield was about 80% of the theoretical. L. J. H.

Ultra-balance. F. Holtz and W. H. F. Kuhlmann (*Ber.*, 1925, **58**, [*B*], 266—268).—By placing in front of the rider scale which carries the 5 mg. rider a second, short scale carrying a 0·5 mg. rider an ultra-balance is constructed which is sensitive to 5×10^{-8} g. with a maximal load of 20 g. The balance is figured in the original. H. W.

Ebullioscopic Apparatus. W. Swientoslawski, and W. Romer (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, 59—62).—The modified apparatus previously described (A., 1924, ii, 469) is altered by the introduction of a short glass-tube sleeve to surround the thermometer bulb. This improved apparatus admits of the determination of the b. p. with an accuracy of $\pm0{\cdot}0015°$. When making ebullioscopic measurements, two such instruments should be used, so that the b. p. of the solvent and solution may be determined simultaneously. T. H. P.

Electrolyte-free, Water-soluble Proteins. I. Electro-dialysis. W. Pauli (*Biochem. Z.*, 1924, **152**, 355—359).—The general principles of electro-dialysis are discussed, and an apparatus having parchment or collodion membranes, which may be used for the purification of water-insoluble proteins, is described. J. P.

Laboratory Apparatus for High-temperature Nitrations. C. Kranz and R. Kopecky (*Z. ges. Schiess- u. Sprengstoffw.*, 1925, **20**, 25—26).—A flask is fitted with a cap carrying three tubulures for, respectively, thermometer, stirrer, and reflux condenser. The joint between the flask and the cap is either packed with asbestos or sealed with an appropriate liquid. The other joints are made acid-proof in a similar manner. W. A. S.

Laboratory Apparatus. F. A. Wiggers (*Ind. Eng. Chem.*, 1925, **17**, 141).—A device for saving supernatant fluids consists of a separating funnel, closed at the top, with a tap on its stem, and

having an inlet pipette for the liquid and an attachment for the vacuum pump. A distilling apparatus consists of a flask encased in an outer closed flask containing water, the latter provided with an inlet, a thermometer holder, and a safety valve. [Cf. *B.*, 1925, 268.] D. G. H.

Apparatus for Concentrating Specially Sensitive Solutions. H. SCHMALFUSS and K. KALLE (*J. pr. Chem.*, 1925, [ii], **109**, 153—157).—A modification of the Schulze-Tollens apparatus (A., 1892, 1386) is described, in which an automatic regulator allows of continuous evaporation for prolonged periods without attention. The solution to be evaporated is placed in a flask *A* and the whole apparatus is evacuated. From *A*, the solution is siphoned into a counterpoised flask, *B*, until the increased weight in *B* operates a regulating lever which shuts off the vacuum from *B*, closes the siphon, and admits carbon dioxide at atmospheric pressure to *B*. The solution is thereby lifted to the top of an evaporating coil down which it is allowed to drip slowly in a vacuum, the coil being maintained at a suitable temperature. The vapours pass off through a condenser and are collected. The concentrated liquid drips back into *A*. The operation continues until, owing to the diminished weight in *B*, the lever shuts off the carbon dioxide, opens the vacuum cock, and releases the siphon, when the cycle commences again. The whole apparatus can be placed in a thermostat and operated at constant temperature. The apparatus will evaporate 3 litres to 100 c.c. at 40° in two days. R. B.

Mineralogical Chemistry.

Radioactive Methods for the Age Determination of Minerals. G. KIRSCH (*Tsch. Min. Mitt.*, 1924, **36**, 147—156).—The trustworthiness of the method of determining the age of minerals from the lead (radium-*G*)/uranium ratio is discussed. It is necessary to know the atomic weight of the lead present in order to distinguish between primary lead and radium-*G*; and further, it is found that in specimens for which this has been determined the composition varies from piece to piece. New estimates, in millions of years, are: for bröggerite from Moss, Norway, 895; pitchblende from Jáchymov, Bohemia, 207; uraninite from Morogoro, East Africa, 605; pitchblende from Katanga, Belgian Congo, 550. From the published data for thorianite from Ceylon, the half life-period for thorium is calculated as $T=(1{\cdot}65\pm0{\cdot}05)\times10^{10}$ years, and the age of the thorianite estimated at about 150 million years. The genetic relationship between uranium and thorium is discussed, and for thorium uranium is calculated $T=63{\cdot}2\times10^{6}$ or $62{\cdot}6\times10^{6}$ years. L. J. S.

Occurrence of Iodine in Nature. VII. Iodine Content of Rocks, Geological Formations, and Minerals, and Conditions for the Accumulation of Iodine in Earths. T. VON FELLENBERG (*Biochem. Z.*, 1924, **152**, 153—171).—Iodine is present in rocks and sedimentary deposits in amounts considerably greater than in organic products. It occurs partly in acid-soluble and partly in acid-insoluble form, and is but slightly extracted by water. No relation between iodine content and given geological formations appears to exist. The same mineral from different sources generally contains the same amount of iodine, but chemically similar and mineralogically different specimens (*e.g.*, quartz) often contain very different amounts of iodine. The iodine present in weathered rocks, and still more so in the earths derived from these rocks, is greater than in the original unweathered rock. The accumulation of iodine is more evident in acid than in basic rocks and earths.

J. P.

Occurrence of Iodine in Nature. VIII. Evolution of Elementary Iodine from Earths. T. VON FELLENBERG, H. GEILINGER, and K. SCHWEIZER (*Biochem. Z.*, 1924, **152**, 172—184).—In the presence of oxygen earths and rocks liberate elementary iodine from added alkali iodide. The action is catalytic and is specially marked if ferric oxide and alkaline-earth carbonates be present. Ferrous iron is much less catalytically active. Earth treated with manure liberates less iodine than untreated earth. The smaller the catalytic activity an earth possesses the greater is its power of accumulating iodine. Earths of low catalytic power are found in districts relatively free from goitre and *vice versa*.

J. P.

Merrillite and Chlorapatite in Stony Meteorites. E. V. SHANNON and E. S. LARSEN (*Amer. J. Sci.*, 1925, [v], **9**, 250—260).—A calcium phosphate sparingly present (a few hundredths of 1%) in certain meteoric stones was provisionally referred to francolite by Merrill in 1917, and was called merrillite by Wherry in the same year. In order to isolate sufficient material for analysis, 0·5—1 kg. samples of the material were crushed and sieved and separated by means of an electromagnet and heavy liquids. From the Allegan meteorite 35 mg. of merrillite were isolated, and from the New Concord meteorite 58 mg. of merrillite (I) and 42 mg. of chlorapatite (II), which yielded:

	P_2O_5.	CaO.	Na_2O.	Cl.	F.	CO_2.	Insol.	Sp. gr.
I.	35·21	44·10	16·42	trace	nil	nil	4·27	3·10
II.	36·06	52·40	—	4·87	nil	—	5·29	3·20

This and two other analyses give for merrillite the formula $3CaO,Na_2O,P_2O_5$. It is distinct from any known terrestrial mineral, and it does not belong to the apatite group, although it is optically uniaxial and negative (ω=1·623, ϵ=1·620). A search for merrillite amongst the apatite isolated from 25 samples of rocks and iron ores was unsuccessful.

L. J. S.

Cordierite from Madras, India. M. S. KRISHNAN (*Min. Mag.*, 1924, **20**, 248—251).—Cordierite of a deep violet colour and *d* 2·598 from a garnet-sillimanite-cordierite-gneiss in the Madura district, Madras, gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	MnO.	H_2O.	Total.
48·37	29·22	2·20	7·07	9·54	1·92	0·42	1·84	100·58

It is unusual in often being optically positive. The optic axial angle in four crystals was 2V=81° to 84° over the positive bisectrix, whilst in another crystal 2V=85° over the negative bisectrix. This variation in the optic axial angle is probably due to the isomorphous replacement of magnesia by ferrous oxide. The violet colour of the mineral is to be attributed to manganese rather than to iron.

L. J. S.

Calcio-Ancylite and accompanying Minerals from the Chibine Mountains [Russian Lapland]. G. P. TSCHERNIK (*Bull. Acad. Sci. Russie*, 1923, **17**, 81—94).—This mineral, *d* 3·82, has the composition:

Ce_2O_3.	Y_2O_3.	SrO.	CaO.	BaO.	Fe_2O_3.	Al_2O_3.
37·81	0·59	9·69	3·49	1·27	0·32	0·65

Na_2O+K_2O.	SiO_2.	CO_2.	H_2O.	Impurities.	Total.
0·39	1·15	22·70	4·44	17·8	100·32

If the impurities, and the iron, aluminium, alkali metals, and silica, which appear to be derived from natrolite or other admixtures, are left out of account, the formula of the mineral is calculated to be $5\{(Ce,Y)_2O_3,3CO_3\},7\{(Sr,Ca,Ba)O,CO_2\},10H_2O$. The only other published analysis of ancylite was made by Mauzelius (*Z. Kryst.*, 1901, **34**, 649) on a specimen from Narsarsuk in Southern Greenland, and indicated the formula $4Ce(OH)CO_3,3SrCO_3,3H_2O$. The mineral investigated by the author has evidently been subjected to the action of an alkaline solution rich in calcium, barium, and iron.

The matrix containing the calcio-ancylite contained also (i) grains of violet-red yttrocerite, $2\{(Ce,Y)_2F_6\},18CaF_2,3H_2O$, *d* 3·61, hardness 4, and (ii) crusts of snow-white, porcelain-like material, *d* 2·86, hardness above 5, and of composition corresponding with the formula $2(Ce,Y,Al)_2O_3,2(Ca,Fe'',K_2,Na_2)O,5(Si,Ti)O_2,8H_2O$, which resembles that of the zeolites in structure. T. H. P.

Manganese-bearing River Pebbles. E. DITTLER (*Tsch. Min. Mitt.*, 1924, **36**, 164—169).—"Shiny pebbles" from the bed of the Vistula have a thin (1—2 mm.) black coating of iron and manganese hydroxides, the smooth surface having a metallic lustre. Analysis of a sandstone pebble gave: insoluble in hydrochloric acid (quartz grains) 90·84, Mn_2O_3 (and MnO_2) 1·14, Fe_2O_3 3·67, H_2O 4·19%; micro-sections show the presence of psilomelane and limonite as the cementing material of the sand grains. Pebbles of mangandolomite from the Enns in Upper Austria show a dull black skin 1—2 mm. in thickness. Analyses of the inner

and outer portions show that manganese hydroxide has accumulated on the exterior at the expense of manganese carbonate. Experiments were made on the adsorption of manganese from a solution of manganese hydrogen carbonate by quartz sand and other materials. Quartz sand took up 51·74% of the manganese from the solution, kaolin 68·73, compact limestone 72·90, marl 78·53, and precipitated chalk 96·53% (in the last case there being probably also chemical replacement). It is suggested that in the case of the "shiny pebbles" the manganese was taken up from the river water. L. J. S.

New Mineral Analyses. E. DITTLER (*Tsch. Min. Mitt.*, 1924, **36**, 213—216).—*Talc from Sirwan, Armenia.*—A compact, pale yellowish-green mineral, thought to be "agalmatolite" gave *d* 2·832, *n* 1·554, and, on material dried at 110°, the results under I. The molecular ratios $H_2O : RO : SiO_2 = 1 : 2·5 : 3$ differ somewhat from those of talc.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	NiO.	MgO.	CaO.	H_2O.	Total.
I.	59·44	0·24	trace	1·51	0·12	0·02	31·11	1·85	5·80	100·09

Damourite from Mt. Lyell, Tasmania.—Pale greenish material translucent at the edges and consisting of a compact aggregate of fine scales has *d* 2·872; from analysis II (mean of two) is calculated: muscovite ($KH_2Al_3Si_3O_{12}$) 98·07, fayalite (Fe_2SiO_4) 1·93 mol.-%.

Felspars from Lower Austria.—These are from a felspar quarry in pegmatite between Krems and Gföhl. Microcline-perthite, *d* 2·558, showing enclosed spindles of albite, gave III, corresponding with orthoclase 68·10, albite 31·90 mol.-%. Albite, *d* 2·625, as bluish-white cleavages, gave IV, corresponding with albite 98·14, orthoclase 1·86 mol.-%.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	K_2O.	Na_2O.	H_2O (−110°).	H_2O (+110°).	Total.
II.	43·37	39·03	0·40	1·41	—	10·98	0·75	0·76	3·80	100·50
III.	64·20	20·55	0·14	—	trace	11·26	3·48	—	0·28	99·91
IV.	66·80	20·94	—	—	trace	0·34	11·91	—	0·10	100·09

L. J. S.

Composition of the River and Lake Waters of the United States. F. W. CLARKE (*U.S. Geol. Survey, Prof. Paper*, 135, 1924, 198 pp.).

Analytical Chemistry.

Logarithmic Tables for Volumetric Analysis. E. J. KRAUS (*Chem.-Ztg.*, 1925, 49, 145).—The author recommends the construction of special tables giving only the essential figures required, *e.g.*, the logarithms of numbers increasing by 0·05 corresponding with burette readings and the factors and their logarithms cor-

responding with different titres of a definite weight of the standard substance. A. R. P.

Qualitative "Drop-analysis" of the Elements in Groups I to III. N. A. TANANAEV (*Z. anorg. Chem.*, 1924, **140**, 320—334).—A method is given for the qualitative analysis of solutions containing the nitrates of most of the metals occurring in the first three analytical groups. The reactions, which are carried out on one drop of solution, are arranged so that the tests for any one metal are, as a rule, not masked by the presence of the other metals. A modified scheme is also described in which a preliminary separation into groups is carried out by precipitating all the metals as sulphides and successively treating the precipitate with acids of different concentration. S. K. T.

Collodion Ultra-filtration Membrane for Physico-chemical Analysis of Solutions. E. FOUARD (*Ann. Chim. Analyt.*, 1925, [ii], **7**, 33—34).—A diaphragm of collodion is capable of acting as a retainer not only of micro-organisms but also of colloidal, protein, pectic, cellulosic, starch, and tannic aggregates. It may be rendered rigid and resistant to a pressure of 40 atm. by being deposited on a framework of fine mesh wire (1—2 mm.) surrounding an artificial silk envelope, which in its turn covers an enamelled metal tube uniformly pierced by small holes. [Cf. *B.*, 1925, 268.] D. G. H.

Rapid Determination of Solid Matter in Liquids. C. B. VON BÖRNEGG (*Chem.-Ztg.*, 1925, **49**, 185).—The evaporation of a small quantity of the liquid is accelerated by means of a filter-paper which is held vertical, with its lower edge in the liquid, by means of a wire passing through a hole pierced in the upper portion. The liquid must not ascend as high as the hole. The filter-paper is weighed in with the containing dish both before and after evaporation. [Cf. *B.*, 1925, May 1.] S. K. T.

Detection of Gaseous Poisons in Blood. E. KOHN-ABREST.—(See i, 451.)

Quantitative Chemical Analysis by Means of *X*-Ray Spectrum. D. COSTER and Y. NISHINA (*Chem. News*, 1925, **130**, 149—152).—The method of determining the proportion of a metal in a mixture of oxides containing it by adding a known weight of another oxide until the intensity of one of its lines in the *X*-ray spectrum coincides with that of the corresponding line in the spectrum of the metal the proportion of which is required, sometimes gives false results owing to the presence of other elements. This defect in the process may be remedied by determining in an artificial mixture of the same substances in known proportions the concentration of added element necessary to make the intensity of any one of its lines equal to that of any near one of the lines of the element the proportion of which is sought. In this way a factor is obtained which is used in calculating the proportion of the desired element in the original mixture from the data obtained by testing this mixture in the same way as the standard. For

example, in the determination of hafnia in zirconium materials the intensity of the $L\beta_1$ line of hafnium is compared with that of the $L\beta_2$ line of lutecium, and in the determination of zirconium in hafnium compounds the $L\alpha$ line of zirconium is compared with the $L\beta_1$ line of yttrium. A. R. P.

Spectrophotometric Determination of Hydrogen-ion Concentrations and of the Apparent Dissociation Constants of Indicators. II. Thymol-blue. III. Bromocresol-green. W. C. HOLMES and E. F. SNYDER (*J. Amer. Chem. Soc.*, 1925, **47**, 221—226, 226—229).—II. The dissociation curve of thymol-blue in alkaline solution conforms with the theoretical dissociation curve over a range of less than 10% and more than 90% dissociation. In the acid range the dissociation of the indicator remains normal up to the mid-point, beyond which dissociation is retarded. The average values obtained for the apparent dissociation constant, K, were 8·91 in the alkaline range and 1·5 in the acid range.

III. The apparent dissociation constant of bromocresol-green was found to be 4·68 in a relatively pure sample, 4·65 and 4·69 in commercial samples. The dissociation curve in the alkaline range conformed with the theoretical formula between 10% and 90% dissociation. G. S. W.

Rational Notation for the Expression of the Reaction of Solutions. D. GIRIBALDO (*Anal. Fis. Quím.*, 1924, **22**, 555—572).—The disadvantages of the Sörensen (p_H) method of expressing the reaction of solutions are discussed. The author proposes $\log [H]/[OH]$ as an expression for reaction. By this means, neutrality is expressed by zero. Comparative figures are given for different acids and also for certain physiological fluids. G. W. R.

Antimony Electrode as an Indicator for Hydrogen Ions and its Application in Potentiometric Titrations of Acids and Bases. I. M. KOLTHOFF and B. D. HARTONG (*Rec. trav. chim.*, 1925, **44**, 113—120).—The potential of the antimony electrode, as used in presence of a little antimony oxide, changes with p_H, but its rate of change at p_H 1—5 differs from that at $p_H > 9$. The use of an antimony electrode in neutralisation reactions is described, whilst it may be employed where the hydrogen electrode cannot, in determining free acid in the presence of oxidising agents. F. M. H.

Colorimetric Determination of Hydrogen-ion Concentration in Soils. H. NIKLAS and A. HOCK (*Z. angew. Chem.*, 1925, **38**, 150—151).—Either Michaelis' nitrophenol series or Clark's series of indicators may be used for p_H determinations in soils. The results agree well with those obtained electrometrically. W. A. S.

Borax as a Standardising Agent for Acids and Bases. M. G. MELLON and V. N. MORRIS (*Ind. Eng. Chem.*, 1925, **17**, 145—146).—Borax is shown to be a suitable standardising reagent for

both hydrochloric and sulphuric acids, and sodium, potassium, and barium hydroxides, and if suitably recrystallised appears to have no disadvantages. Indicators of suitable p_H range are methyl-orange for the acids and phenolphthalein for the bases. [Cf. *B.*, 1925, 269.] D. G. H.

Determination of the Acidity of Mineral Soils. G. HAGER.—(See i, 489.)

Determination of Free Acid of Gastric Juice. H. SAHLI.—(See i, 458.)

Test for Chlorine in the Presence of Bromine, Iodine, etc. M. DIMITROFF (*Z. anorg. Chem.*, 1924, **140**, 253—260).—The substance is oxidised by potassium permanganate in acid solution in a flask so fitted that air can be passed through the solution during the process and passed, together with the halogens evolved, out into a solution containing one or two drops of 0·1*N*-ammonium bromide in 10 c.c. of 2*N*-sulphuric acid. Here any chlorine from the original substance replaces bromine in the solution. One to two drops of sodium bromate are now added while air (now pure) is still passed through. The bromide is oxidised and the bromine passes off whilst the chloride remains unaffected; thus a precipitate with silver nitrate indicates chlorine in the original substance.

L. J. H.

Determination of Chlorides in Blood. C. BENGUEREL.—(See i, 455.)

Determination of Chlorides and Sulphates in Expressed Plant Tissue Fluids. R. A. GORTNER and W. F. HOFFMAN.—(See i, 455.)

Sensitive Reaction for Copper and Bromine. K. SCHERINGA (*Pharm. Weekblad*, 1925, **62**, 173—174).—The solution is evaporated to dryness and the residue damped with sulphuric acid containing a trace of a bromide or a copper salt. Formation of copper bromide occurs with a deep violet coloration. The test will detect 0·0005 mg. of sodium bromide or of a copper salt; it is very suitable for the detection of bromine in organic materials.

S. I. L.

Detection of Minute Quantities of Bromine [in Blood]. H. BERNHARDT and H. UCKO.—(See i, 454.)

Colorimetric Determination of Oxygen. W. W. EFIMOFF.—(See i, 481.)

Determination of Dissolved Oxygen. J. N. FRIEND (*Chem. News*, 1925, **130**, 163—164).—When using Winkler's method for determining dissolved oxygen, introduction of air may be avoided by using a 250-c.c. flask closed by the stem of a tap funnel, which is a capillary glass tube accurately fitting the neck of the flask, so that when the stopper is inserted a space of about 2 c.c. is left above the 250-c.c. mark. The addition of the manganese chloride

solution after introduction of the sodium hydroxide and potassium iodide solution fills the capillary tube on insertion of the stopper, and at the end of the reaction the hydrochloric acid is put in the funnel, the tap opened, and the stopper gradually withdrawn. [Cf. *B.*, 1925, May 1.] D. G. H.

Determination of Oxygen in Pure Iron. T. E. Rooney (*J. Iron and Steel Inst.*, 1924, **110**, 122—128).—For the determination of oxygen in iron by heating the metal in hydrogen and weighing the water formed, it is essential to use extremely fine millings of the metal as the depth of penetration of the hydrogen is only about 0·5 mm. even after prolonged heating at 1200°. This temperature is necessary in order to effect complete removal of the oxygen, and is best obtained by using an alundum tube electric furnace wound with platinum strip and capable of giving a temperature of 1300°. A calcium chloride bulb for the absorption of the water is preferable to a sulphuric acid tube. Care should be taken not to allow the temperature to rise much above 1200° as high results will be obtained owing to reduction of the silica boat by hydrogen in the presence of iron to form iron silicide. Consistent results, usually a little lower than those obtained by the above method, may be obtained by heating a mixture of the iron millings with three times their weight of an alloy of 60% Sn and 40% Sb at 950—1000° in a stream of hydrogen. In all cases a blank test should be carried out and the appropriate deduction made. A. R. P.

Determination of Sulphide, Polysulphide, and Thiosulphate Sulphur in Solutions of Alkali and Alkaline-earth Sulphides. E. Schulek (*Z. anal. Chem.*, 1925, **65**, 352—358).—The solution to be analysed is allowed to fall into a boiling solution of boric acid and potassium cyanide free from air and the evolved hydrogen sulphide is collected in potassium hydroxide and hydrogen peroxide, the sulphate formed being determined as usual. The residual liquid in the distilling flask contains thiocyanate from the polysulphide sulphur, and undecomposed thiosulphate; it is divided into two parts in one of which the thiosulphate is determined iodometrically, and in the other the thiocyanate by treatment with bromine, removal of excess of the latter with phenol, and titration of the bromocyanogen with thiosulphate, after addition of potassium iodide. [Cf. *B.*, 1925, 241.] A. R. P.

Preparation of Nessler's Solution. H. D. Richmond (*Analyst*, 1925, **50**, 67).—The precipitate obtained on mixing aqueous solutions of potassium iodide (17·5 g. in 100 c.c.) and mercuric chloride (15 g. in 300 c.c.) is washed by decantation and dissolved in potassium iodide solution (17·5 g. in 100 c.c.), a few drops of mercuric chloride added until a permanent red precipitate appears, and then water to 500 c.c. Aqueous sodium hydroxide (105 g. in 300 c.c.) is added at 0°, and the mixture diluted to 1 litre. The clear portion is sensitive immediately after preparation.
D. G. H.

Tromsdorff Reagent for Nitrites. A. COQUILLAT (*Anal. Fis. Quim.*, 1924, 22, 523—544).—Directions are given for the preparation of a more sensitive and stable modification of the Tromsdorff reagent for nitrites. The delicacy of the reaction is increased by the presence of dissolved oxygen. [See *B.*, 1925, 261.]

G. W. R.

Separation of Phosphoric Acid in Qualitative Analysis by means of Basic Bismuth Nitrate. A. KESCHAN (*Z. anal. Chem.*, 1925, 65, 346—351).—The solubility of bismuth phosphate in dilute nitric acid is proportional to the concentration of acid up to 0·4*N*, but is considerably increased in the presence of halogen acids. For the separation of phosphoric acid from a solution to be tested for metals of groups III, IV, and V the slightly acid solution is treated with hydrazine hydrochloride to reduce ferric salts to ferrous, then with solid bismuth oxynitrate which removes the halogen ions first, then phosphoric acid. The precipitate filters readily and the filtrate will contain less than 1 mg. of phosphoric anhydride per litre.

A. R. P.

Determination of Lipoid Phosphorus in Cereal Products. O. S. RASK and I. K. PHELPS (*Ind. Eng. Chem.*, 1925, 17, 189—190).—Since the ammoniacal method extracts all the lipoids, the phospholipins will be included and may be computed by a determination of total phosphorus in the extract. The result is higher than by direct determination. [Cf. *B.*, 1925, 224.]

D. G. H.

Salts of Cupferron. V. AUGER, L. LAFONTAINE, and C. CASPAR (*Compt. rend.*, 1925, 180, 376—378).—The preparation, appearance, and solubilities of the following cupferron salts are described: (*a*) salts precipitated by hydrogen sulphide (generally in acid solution): silver, decomp. 130°, lead, m. p. 147°, mercurous, decomp. 215°, mercuric, decomp. 160°, bismuth, m. p. 170° (decomp.), cadmium, m. p. 245° (decomp.), stannous, m. p. 138°, stannic, m. p. 180° (decomp.), antimony, decomp. 112°, also $[Ph{\cdot}N(NO)O]MoO_3$, decomp. 165°, and $[Ph{\cdot}N(NO)O]_2MoO_3$, m. p. 139° (decomp.); (*b*) ammonium sulphide group: cerous, ceric, chromic, indium, m. p. 90°, cobaltic, m. p. 116° (decomp.), cobaltous, m. p. 162° (decomp.), nickel, decomp. 200°, zinc, m. p. 138°; (*c*) alkaline-earth group: barium ($+3H_2O$), decomp. 245°, strontium ($+2H_2O$), decomp. 290°, calcium ($+2H_2O$), decomp. 275°.

F. M. H.

Electrolytic Separation of Copper, Antimony, Lead, and Tin. A. LASSIEUR (*Compt. rend.*, 1924, 179, 827—829; cf. this vol., ii, 159).—Lead and tin are deposited together from hydrochloric acid solution and cannot be separated by variation of the cathode potential. On adding hydrofluoric acid, stannic salts form a complex which does not yield tin on electrolysis; after deposition of lead, tin may then be determined in the resulting solution. In depositing copper and antimony in presence of lead by the method already described, tin is reduced to the stannous

form. This should be oxidised by means of hydrogen peroxide before separating the lead. H. J. E.

Complex-chemical Methods for the Volumetric Determination of Acidity, Basicity, and Aluminium Content of Aluminium Solutions. F. FEIGL and G. KRAUSS (*Ber.*, 1925, 58, [*B*], 398—400).—The solution is treated with a suitable excess of alkali oxalate with which the aluminium salt reacts: $AlCl_3+3K_2C_2O_4=K_3[Al(C_2O_4)_3]+3KCl$, whereby the acid formed by hydrolysis of the aluminium salt is converted into neutral products. "Residual acidity" is determined by addition of potassium iodide–potassium iodate and titration of the liberated iodine. Aluminium is determined from the difference between "residual" and "total" acidity determined iodometrically. For the determination of basicity (*e.g.*, in basic aluminium acetate), the total acid is determined, after which a measured excess of 0·1*N*-hydrochloric acid is added and the experiment finished as in the determination of "residual" acid. The difference between the found and added acid indicates the amount of base which is liberated by formation of the complex. H. W.

Separation of Iron and Aluminium from Manganese and Magnesium and from Phosphoric Acid by Means of Sulphosalicylic Acid. L. MOSER and A. BRUKL [and, in part, I. VÉN] (*Ber.*, 1925, 58, [*B*], 380—385; cf. A., 1923, ii, 438).—Manganese is separated from ferric iron by precipitation with disodium hydrogen phosphate in a solution containing ammonium chloride and sufficient sulphosalicylic acid, ammonia being finally added in slight excess. The precipitated manganese ammonium phosphate is weighed as the pyrophosphate, whilst iron is precipitated in the filtrate by hydrogen sulphide and finally weighed as ferric oxide.

Iron and manganese are separated from aluminium by precipitation with hydrogen sulphide in ammoniacal solution in the presence of sulphosalicylic acid (cf. Moser, *loc. cit.*); the precipitated sulphides are dissolved and iron and manganese are separated as described above.

Magnesium may be determined in the presence of iron and aluminium by rapidly adding a solution of diammonium hydrogen phosphate to a boiling solution of the salts (chloride, sulphate, or nitrate) in the presence of ammonium chloride, sulphosalicylic acid, and an excess of ammonia; the solution is boiled for a few minutes, treated with one-third of its volume of concentrated ammonia, and kept at the atmospheric temperature for a few hours, after which the magnesium ammonium phosphate is treated in the usual manner. Precipitates formed in neutral solution contain aluminium. The method is applicable to the determination of magnesium in the presence of a large excess of aluminium.

Phosphate is determined in the presence of iron and aluminium by precipitation with magnesia mixture in boiling ammoniacal solution containing ammonium chloride and sulphosalicylic acid. Iron is precipitated from the filtrate by ammonium sulphide.

Aluminium is determined from the difference in weight of the oxides. [Cf. *B.*, 1925, 269.] H. W.

Separation of Aluminium from Calcium by Means of Hexamethylenetetramine. (MRS.) C. KOLLO and N. GEORGIAN (*Bul. Soc. Chim. România*, 1924, 6, 111—112).—Owing to the absorption of carbon dioxide by ammonia solution and the consequent formation of ammonium carbonate, calcium is sometimes precipitated to some extent with aluminium. Replacement of the ammonia by hexamethylenetetramine, which decomposes with formation of ammonia when boiled with the salt solution, yields results of far greater accuracy. [Cf. *B.*, 1925, 192.]

T. H. P.

Volumetric Determination of Manganese. B. N. ANGELESCU (*Bul. Soc. Chim. România*, 1924, 6, 109—110).—In presence of alcohol, potassium chromate precipitates manganous salts quantitatively as manganous chromate, $MnCrO_4,2H_2O$, the excess of the known amount of potassium chromate taken being then determinable by titration with sodium thiosulphate. The method gives accurate results. [Cf. *B.*, 1925, 192.] T. H. P.

Use of Oxalenediuramidoxime in the Detection and Determination of Nickel. F. FEIGL and A. CHRISTIANI-KRONWALD (*Z. anal. Chem.*, 1925, 65, 341—345).—Oxalenediamidoxime (Zinkeisen, A., 1890, 122) functions as an oxime and as an ammonia derivative with nickel salts, forming the compounds,

$$Ni(C_2H_5O_2N_4)_2,2H_2O$$

and $Ni(C_2H_6O_2N_4)_3Cl_2$; cobalt salts yield a sparingly soluble derivative of the first type, so that this reagent is useless for separating these elements. If, however, two $NH_2{\cdot}CO{\cdot}$ groups are introduced into the molecule, the acidic properties of the compound so formed, oxalenediuramidoxime (Zinkeisen, *loc. cit.*), become more pronounced and the basic properties entirely suppressed, so that compounds of the first type only are formed with nickel salts. Oxalenediuramidoxime in ammoniacal solution produces a visible precipitate in ammoniacal nickel solutions containing more than 1 part of the metal in 150,000 parts. The precipitate is orange-yellow, crystalline, slightly soluble in hot water, but insoluble in cold water or ammonia, and contains 19·92% Ni when dried at 110—130°; it may be used for the gravimetric determination of nickel and for the separation of nickel from cobalt. [Cf. *B.*, 1925, 269.] A. R. P.

Colorimetric Determination of Molybdenum. H. TER MEULEN (*Chem. Weekblad*, 1925, 22, 80—81).—The dark red colour of ammonium thiomolybdate, $(NH_4)_2MoS_4$, allows of colorimetric titration. The comparison solution is one of ammonium molybdate, to which an equal volume of ammonia is added, and hydrogen sulphide passed in. The method is rapid and fairly accurate, and not affected by alkalis. Vanadium and tungsten interfere.

S. I. L.

Oxidimetric Titration of Uranium. O. KOBLIC (*Chem. Listy*, 1925, 19, 1—3).—When salts of sexavalent uranium are reduced with the usual metallic reducing agents the greater part of the uranium is converted into the quadrivalent form, but there is always a certain amount of a derivative of a lower oxide produced. Lead, in the presence of hydrochloric acid, quantitatively reduces uranyl chloride to uranium tetrachloride, which, after addition of manganese sulphate and sulphuric acid, may be titrated with permanganate with good results. [Cf. *B.*, 1925, 270.]

A. R. P.

Volumetric Determination of Sugar by Schoorl's Process. C. VAN DER HOEVEN (*Chem. Weekblad*, 1925, 22, 79—80; cf. this vol., ii, 74).—The statement of van den Hout, Neeteson, and van Scherpenberg that the concentration of the Fehling's solution influences the result is confirmed; the effect can be compensated by altering the time of boiling. S. I. L.

Sugar Analysis by Fehling's Method. P. KLASON (*Svensk Kem. Tidskr.*, 36, 195—202; from *Chem. Zentr.*, 1924, ii, 2798).—A critical study of Fehling's method for the determination of sugars. The conversion of the cuprous into cupric oxide is best effected in a silica crucible. R. B.

Micro-determination of Blood-sugar. C. J. DIAZ and B. S. CUENCA.—(See i, 453.)

Comparison of certain Chemical Methods for the Determination of Dextrose. A. IONESCU and (MLLE.) E. SPIRESCU (*Bul. Soc. Chim. România*, 1924, 6, 101—108).—The methods of Fehling, Bertrand, and Lehmann give good results in the determination of dextrose in liquids containing 0·1—1% of the sugar, but they are more difficult to operate than the ferricyanide method (cf. Ionescu and Vargolici, A., 1921, ii, 283), which furnishes equally exact results. This last method yields accurate results also with solutions such as cerebro-spinal fluid, containing between 0·05% and 0·1% of the sugar, and is easier to apply than the Folin and Wu (A., 1920, ii, 337) and the Fontès and Thivolle methods (A., 1921, ii, 563), although these are capable of affording satisfactory results. T. H. P.

Determination of Dextrose in presence of Sucrose in Organic Liquids. M. BUFANO.—(See i, 453.)

Influence of Hydrogen-ion Concentration on the Colorimetric Determination of Pyrogallol and Pyrocatechol Derivatives. S. GLASSTONE (*Analyst*, 1925, 50, 49—53).—The violet colorations produced by certain phenolic compounds with Mitchell's ferrous tartrate reagent are seen only between certain definite p_H limits which even vary between different substances of the same group. The addition of 5—10 c.c. of 10% ammonium acetate solution to the usual reaction quantities, together with a little ammonia solution in the case of pyrocatechol derivatives, usually ensures the development of maximum colours. [Cf. *B.*, 1925, 226.]

D. G. H.

Gravimetric Micro-determination of Cholesterol. T. TOMINAGA.—(See i, 453.)

Determination of Cyanates in Blood. E. G. MONTGOMERY.—(See i, 455.)

Application of Sodium Hyposulphite in Qualitative Organic Analysis. E. CLARK (*Chem. News*, 1925, **130**, 132—133).—The reduction of aromatic nitro compounds in qualitative analysis is effected in the presence of alkali by solid sodium hyposulphite, the excess of which is removed by boiling with excess of concentrated hydrochloric acid. S. K. T.

Colour Standards for Use in the Determination of Glyoxalines. G. HUNTER (*Biochem. J.*, 1925, **19**, 42—46).—Commercial Congo-red and methyl-orange must be purified before use as artificial standards in colorimetric work. Details are given for the preparation of a colour standard made from pure Congo-red and methyl-orange suitable for the determination of histidine or carnosine. S. S. Z.

Determination of Lipoids in Blood Serum. S. MINOVICI and (MISS) M. ILIESCO.—(See i, 452.)

Determination of Lecithin in Blood. A. GRIGAUT.—(See i, 453.)

Detection of Urobilin and Urobilinogen in Urine. C. BENGUEREL.—(See i, 460.)

Determination of Methæmoglobin in the Presence of its Cleavage Products. J. B. CONANT and L. F. FIESER.—(See i, 456.)

Detection of Chlorophyll Degradation Products in Urine. M. HOFSTETTER.—(See i, 460.)

Enzymic Hydrolysis of Proteins. III. Determination of Peptic and Tryptic Digestion of Caseinogen. P. RONA and H. KLEINMANN.—(See i, 473.)

Source of Error in the Use of Lintner's Starch Solution for determining Diastatic Power. W. SYNIEWSKI.—(See i, 470.)

Determination of Diastase in Fæces. W. FRANK and F. DOLESCHALL.—(See i, 461.)

Determination of Lipase in Body Fluids and in Tissues. P. RONA and A. LASNITZKI.—(See i, 471.)

Standards for the Colorimetric Determination of Trypsin. J. A. SMORODINZEV and A. N. ADOVA.—(See i, 473.)

Chemical Analysis of Soil. K. K. GEDROIZ.—(See i, 489.)

General, Physical, and Inorganic Chemistry.

Continuous Hydrogen Spectrum. A. CARST (*Ann. Physik*, 1924, [iv], 75, 665—672).—The continuous ultra-violet hydrogen spectrum found by Stark (A., 1917, ii, 281; 1918, ii, 141) in the canal rays, and ascribed by him to an atomic quantum pair, has been examined. The spectrum is found when the hydrogen or nitrogen canal rays pass into hydrogen, but not when hydrogen canal rays pass into nitrogen, and it coincides with the Geissler tube spectrum. The starting point is in the visible spectrum and changes with the pressure. The spectrum appears to be due to the hydrogen molecule and has nothing to do with the Bohr continuous spectrum, which is probably only obtained if the higher members of the Balmer series are excited at the same time. M. S. B.

Excitation of the Secondary Spectrum of Hydrogen by Electron Impacts. O. S. DUFFENDACK (*Astrophys. J.*, 1924, 60, 122—132).—Practically the entire secondary spectrum of hydrogen was developed below the ionisation potential of 16 volts. The spectrum is apparently due to the neutral molecule, and its excitation is not intimately connected with the dissociation of the molecule. Support is afforded for the existence of a characteristic ultra-violet spectrum due to the molecule the initial state of which is identical with the final state of the molecule after the emission of the secondary lines. A. A. E.

Spectrum of Nitrogen. T. R. MERTON and J. G. PILLEY (*Proc. Roy. Soc.*, 1925, A, 107, 411—422).—The nitrogen arc spectrum can be obtained free from the band or spark spectrum by passing a weak condensed discharge through helium at a pressure of about 30 mm. of mercury and adding a little nitrogen to the gas by heating alumina which has been soaked in sodium azide solution. Argon will not serve the same purpose. The explanation offered is that the resonance potential of helium is 20·4 volts and that of argon 11·5 volts; the value for the arc spectrum of nitrogen may lie between these. The spark spectrum requiring more than 20·4 volts will not be produced, because the helium will act as a " safety valve " for the energy. The small partial pressure of the nitrogen will favour the existence of atoms. A table of wave-lengths of the lines in the arc spectrum is given.

From a study of the spectrum of the light excited by electronic impact it was deduced that as the energy of impact increased there was direct transition from the negative band spectrum to the spark spectrum, indicating that the nitrogen molecule did not break up into neutral atoms but into ions. E. B. L.

Spontaneous Reversal of Rays in the Neon Spectrum. H. BUISSON and C. JAUSSERAN (*Compt. rend.*, 1924, 180, 505—507). —Many of the fine lines in the spectrum of neon which were pro-

posed as standards of wave-length measurements have previously been shown (Pérard, *ibid.*, 1923, **176**, 375) to consist of doublets; and this is now shown, by means of interference effects with silvered slides, to be due to the spontaneous reversal of several of the rays. The phenomenon is shown to the greatest extent by the line 6402, where a separation of 0·060 Å. occurs with a current of 3 milliamps. These observations render the use of the neon lines as a wave-length standard inadvisable. J. W. B.

Spark Spectrum of Neon. L. Bloch, E. Bloch, and G. Déjardin (*Compt. rend.*, 1925, **180**, 731—733).—The method previously described (A., 1924, ii, 286) has been applied to the examination of the first order spark spectrum of neon. About 250 lines are recorded in the region 4900—2700 Å. The values given are accurate to within 0·05 Å. J. S. C.

First Spark Spectra of Zinc and Cadmium. G. von Salis (*Ann. Physik*, 1925, [iv], **76**, 145—162).—The first spark spectra, Zn II and Cd II, of zinc and cadmium, respectively, have been examined photographically, the discharge taking place in a tube in which the vapour of the metal itself formed the carrier, the metal being vaporised from a hollow cathode. The Ritz formula has been applied. For every term value the effective quantum number, n^*, and the nuclear charge number, p^*, have been determined. The relation of the chief quantum numbers, n, to the term values is in agreement with the standard given by Bohr (A., 1923, ii, 679), who foretold a penetration of the p-orbit. The d-orbit is also penetrated. The tables given are so arranged that the term values of zinc and cadmium, and the quantities n^*, p^*, and $(n - n^*)$ may be easily compared. M. S. B.

Spark Spectrum of Mercury in the Extreme Red. J. Laffay (*Compt. rend.*, 1925, **180**, 823—825).—The spark spectrum of mercury was not hitherto known on the red side of 600 $\mu\mu$. About 70 new lines extending to 800 $\mu\mu$ have been found by using panchromatic plates and a grating spectrograph of high dispersion. The mercury arc lines in the same region are given for comparison. R. A. M.

Spectrum of Potassium Excited during its Spontaneous Combination with Chlorine. L. A. Ramdas (*Nature*, 1925, **115**, 533—534).—Spectrum photographs of potassium spontaneously burning in chlorine at the ordinary pressure show a strong emission band extending from 7200 to 6150 Å., many arc lines, and the enhanced lines 4466, 4388, 4307, 4220, and 4115 Å. The excitation of the enhanced lines in the absence of any external electrical forces is accounted for by the electron affinity of the chlorine atom, together with the temperature attained by the potassium vapour. A. A. E.

Regularities in the Arc Spectrum of Cobalt. F. M. Walters, jun. (*J. Washington Acad. Sci.*, 1924, **17**, 407).—An extension of

previous work (A., 1923, ii, 519) on the arc spectra of elements of group VIII. Eighty-eight lines of the arc spectrum of cobalt have been classified into twelve multiplets in the quartet system resulting from the combination of two *P*-levels, two *D*-levels, three *F*-levels and one *G*-level. Whilst the terms found previously for the arc spectrum of iron belong to systems of odd permanent multiplicity, those found for cobalt belong to even systems. In addition to the quartet terms, there is evidence for the existence of a doublet or sextet system. The separations of the sub-levels of the quartet system of cobalt are on the average four to five times larger than the corresponding separations of the sub-levels of the quintet system terms in iron. A. E. M.

Regularities in the Arc Spectrum of Nickel. F. M. WALTERS (*J. Washington Acad. Sci.*, 1925, **15**, 88—100).—A preliminary analysis of the arc spectrum of nickel in which 345 lines are classified. The distribution of the inner quantum numbers indicates that the spectrum consists of singlets and triplets. The spectroscopic alternation law holds in the triad Fe, Co, Ni. F. G. T.

Vacuum-arc Spectrum of Titanium. H. CREW (*Astrophys. J.*, 1924, **60**, 108—121).—Measurements of the vacuum-arc spectrum of titanium between 6366·382 Å. and 3653·499 Å. revealed 78 new lines. Practically no impurity was found in cast titanium. Temperature regulation by the toluene control was made more frequent by wrapping a portion of the heating coil directly on the bulb. A. A. E.

Spectrometric Methods of Investigation of the Infra-red. H. WITT (*Z. Physik*, 1924, **28**, 236—248).—The construction of sensitive bolometers and thermopiles for infra-red spectrometry is given in detail. In the course of testing the apparatus, measurements of the infra-red absorption of water-vapour were obtained. S. B.

Spectroscopy in the Infra-red Region of the Spectrum. A. TROWBRIDGE (*J. Franklin Inst.*, 1925, **199**, 343—352).—A review of advances in the technique and of the treatment of series and band spectra in the infra-red region. F. G. T.

Intensity Measurements in the Ultra-violet. H. B. DORGELO (*Z. Physik*, 1925, **31**, 827—835).—An extension of a method already published (*ibid.*, 1923, **13**, 206; A., 1924, ii, 282) for determining the relative intensities of the components of multiplets. The relative intensities are found by comparing the densities of photographs taken through screens of graduated transparency. Screens transparent to 2200 Å. were prepared by coating quartz plates with films of platinum. The relative intensities of the spark doublets of the first and second subsidiary series of calcium were measured; the ratio depends on the current, but it is concluded that it would be 2 : 1 if self-reversal were prevented; for the multiplet 3181, 3179, 3158, the ratio is 11 : 100 : 54. E. B. L.

Exact Measurements of Spectral Frequencies in the Region between Light and *X*-Rays (L_{III}-Discontinuities of Cl, S, P, Si, Al). F. HOLWECK (*Compt. rend.*, 1925, **180**, 658—661; cf. *ibid.*, 1925, **180**, 266).—By the absorption method previously described, the critical potentials for the levels L_{III} L_{II} have been found for the elements of atomic number 13—18, as follow: argon, 246·5, chlorine 203, sulphur 163, phosphorus 128, silicon 98, and aluminium 68 volts, with a probable error of ± 1 to ± 2. These results, which fit excellently on a Moseley diagram, are compared with other determinations in the same region. G. M. B.

Relative Intensities of Fluorescent and Scattered *X*-Rays. G. L. CLARK and W. DUANE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 173—175; cf. A., 1924, ii, 368, 369).—The scattered and tertiary radiation due to tungsten *X*-rays falling upon chemical elements of atomic weights near that of molybdenum are extremely weak as compared with the fluorescent radiation. The scattered radiation from these heavy elements is much weaker than that from light elements. F. G. T.

Total Intensity of Scattered *X*-Radiation. O. K. DE FOE and W. W. NIPPER (*Nature*, 1925, **115**, 607).

Spectroscopic Evidence of *J*-Transformation of *X*-Rays. S. R. KHASTGIR and W. H. WATSON (*Nature*, 1925, **115**, 604—605).—Deviations from the simple relation between the atomic number of a radiator and the wave-lengths of its *X*-ray emission spectrum of *K*-series, occurring at $n = 52$ and $n = 56$, are ascribed to the *J*-transformation of *X*-radiation taking place in the crystal used for its analysis or in the anti-cathode or walls of the *X*-ray tube. A. A. E.

Soft *X*-Rays from Iron. C. H. THOMAS (*Physical Rev.*, 1925, [ii], **25**, 322—332).—When the ratio of the photo-electric current produced from a protected platinum semi-cylinder by soft *X*-radiation from a bombarded iron target to the thermionic bombarding current is plotted as a function of the exciting voltage, breaks appear corresponding with the radiation potentials, 7·3, 14·1, 16·5, 24·3, 28·8, 34·3, 48·0, 51·3, 62·0, 75·3, 82·7, 94·8, 112·2, 131·8, 158·5, 181·6, 192·0, 221·3, 277·4, 288·6, 303·7, 331·0, and 639·0(?) volts, and the ionisation potentials, 11·1, 19·4, 41·2, 54·6, 103·5, 169·4, 228·1, 704·3, and 818·5 volts. The ionisation potentials at 818·5, 704·3, and 54·6 volts are identified with the lines L_I, L_{III}, and M_{III}. A. A. E.

Absorption Spectrum of Oxygen in the Extreme Ultra-violet. E. SCHMIDT (*Z. Physik*, 1925, **31**, 475—487).—The band spectrum visible in photographs of the extreme ultra-violet taken with long exposures using a quartz mercury vapour lamp as the source of light has been previously regarded as a fluorescence spectrum from the atmosphere. The author shows that it is an absorption spectrum of the oxygen molecule, not of ozone. The absorption is quite different from what would be expected according

to Beer's law; it is much more intense for pure oxygen than for a column of air five times as long. Carbon dioxide is quite transparent in this region, 2000 to 1840 Å. E. B. L.

Absorption in Excited Neon. K. W. MEISSNER (*Ann. Physik*, 1925, [iv], 76, 124—144).—The secondary light absorption, shown by gases when under the influence of an electric discharge, depends on metastable states of the atom caused by the electrical disturbance. The relation between the intensity of the absorption lines and the strength of the current required to produce them gives indications as to the average life of these different states. The absorption spectrum of neon has been studied from this point of view, the intensity of the lines being examined photographically. Absorption in neon begins at a very low current density. The combinations with an s_2- or an s_4-term show feeble or zero absorption, but with the s_3-term, and especially with the s_5-term, the absorption is much stronger, the strongest absorption line being 6402 in the $p_9 s_5$ combination. This probably means that the s_2- and s_4-terms correspond with short-lived, and the other two with long-lived states. The dependence of absorption on the strength of the current in the absorption tube has been studied. It has also been found to depend on the strength of the current in the emission tube. The presence of impurities in the gas reduces the absorption. The intensity distribution in the lines is not the same in the emission as in the absorption tubes, the greater current density and higher temperature in the former giving a greater breadth of line. Further information on the period of duration of the excited states has been sought by sending one half-wave of the rectified alternating current through the emission tube, and the opposite one through the absorption tube. The light from the emission tube thus passes through the absorption tube during its dark period. No indication of even the strongly-absorbing s_5-term was obtained in 0·01 sec., but with suitable variation of frequency of the alternating current it may be possible to make the absorption lines persistent and thus determine the life-period of the state of excitation which produces them.

M. S. B.

Absorption of Excited Neon. P. JORDAN (*Z. Physik*, 1925, 31, 877—881; cf. preceding abstract).—Of the lines $1s_i$—$2p_j$ absorbed by neon excited by the passage of a weak direct current, the members $1s_2$ and $1s_4$ are only slightly absorbed, if at all, whilst $1s_3$ and $1s_5$ are strongly absorbed. The positive neon ion exists in two conditions the neutralisation of which should lead to a triplet-quintet and a singlet-triplet system, respectively. A consideration of the term-multiplicities in the light of Stoner's theory of the distribution of electrons among the different energy levels leads to the conclusion that the ground term is a p term of inner quantum number $\frac{1}{2}$, and that $1s_3$ and $1s_5$ must be metastable.

E. B. L.

Absorption of Magnesium Vapour. A. L. NARAYAN, D. GUNNAIYA, and K. R. RAO (*Astrophys. J.*, 1924, 60, 204—205).—The magnesium line 4571 Å. ($1s$—$2p_2$) has been obtained as an

absorption line. The line 2852 Å., but not 4571 A., increased in width with rise of temperature. A. A. E.

Absorption Spectrum of Aluminium. K. MAJUMDER and N. K. SWE (*Nature*, 1925, **115**, 459).—No aluminium lines were obtained below 1500°. At 1520°, the pair, 3961, 3944, appear reversed; at 1650°, the leading members of $2p_1$—*md* appear reversed, but the higher members require a somewhat higher temperature. Gallium is present in ordinary aluminium. A. A. E.

Absorption Spectrum of the Neutral and Ionised Cadmium Atom in the Spark Discharge under Water. H. STÜCKLEN (*Z. Physik*, 1924, **30**, 24—39).—By sparking between cadmium electrodes under water, both absorption and emission spectra against a background of a continuous spectrum can be obtained, the proportion of lines in the two varying with the frequency, voltage, and electrode diameter. The absorption lines are divisible into six groups. From the sequence in which these groups appear conclusions may be reached with regard to the states of excitation through which a neutral or ionised atom may pass. The group most easily obtained corresponds with the passage of the electron in the neutral atom from the normal 1*s*-orbit to the next higher one, 2*P*. The corresponding line for the ionised atom is less easily obtained. M. S. B.

Absorption Line of the Iodine Atom. C. FÜCHTBAUER, F. WAIBEL, and E. HOLM (*Z. Physik*, 1925, **31**, 523; cf. A., 1924, ii, 220).—Addendum to the paper (*ibid.*, 1924, **29**, 367) giving the exact value of the wave-length 2062·25 Å. in a vacuum. Other absorption lines are noted still further in the ultra-violet and a preliminary suggestion is made as to series terms. E. B. L.

Resonance Radiation from Thallium Vapour. A. L. NARAYAN and K. R. RAO (*Nature*, 1925, **115**, 534).—Further experimental confirmation of the view that $1\pi_2$ is the ground orbit of the valency electron of the thallium atom is afforded. A. A. E.

Broadening of Spectral Lines. III. J. HOLTSMARK and B. TRUMPY (*Z. Physik*, 1925, **31**, 803—812; cf. A., 1924, ii, 363).—Photographs of the arc spectra of lithium, silver, copper, and nickel were taken and the widening of the lines was measured by comparing the width of those which were broad with those which were not. The results agree with the values calculated from the Stark effect. The apparent reversal of the silver line, 4055, is explained as a splitting of the line by a peculiar type of Stark effect. For a current of five ampères the molecular electrical field is 12,600 volts per cm. E. B. L.

Excitation of Spectral Lines by Electron Impact. II. G. HERTZ and J. C. S. DE VISSER (*Z. Physik*, 1925, **31**, 470—474).—Neon was subjected to the bombardment of accelerated electrons in an apparatus previously described (A., 1924, ii, 283), and the intensity of the lines in the spectrum of the emitted radiation was

measured in a spectrometer by comparison with the light from a tungsten filament lamp which had been calibrated for different voltages in a Nutting spectrophotometer. Using the results to calculate the ionisation potential for neon, the value 21·6 volts was obtained, in good agreement with the result 21·5 volts obtained by the electrical method. E. B. L.

Relation between the Distribution of Electrons in the Atom into Sub-groups and the Complex Structure of Spectra. W. PAULI, jun. (*Z. Physik*, 1925, **31**, 765—783).—Development of a scheme of distribution of electrons in the atom to overcome the difficulties arising from the usual grouping referred to in a previous paper (this vol., ii, 251). A general classification of all the electrons in the atom is obtained through the principal quantum number n and two subsidiary quantum numbers k_1 and k_2, to which must be added another, m_1, in the presence of an external magnetic field. In conjunction with the work of Stoner (this vol., ii, 85) this leads to a grouping of electrons which satisfies the quantum conditions. E. B. L.

Metastable States in Low-voltage Mercury Arcs. M. MARSHALL (*Astrophys. J.*, 1924, **60**, 243—255).—Experiments with alternating and intermittent arcs indicate that the life of the two metastable forms of the mercury atom, $2p_1$ and $2p_3$, is about 1/22 and 1/170 second, respectively. The life of the latter, but not of the former, is reduced by the presence of carbon monoxide, carbon dioxide, nitrogen, water vapour, or hydrogen. A. A. E.

Fine Structures in the First Lithium Spark Spectrum. H. SCHÜLER (*Ann. Physik*, 1925, [iv], **76**, 292—298).—By means of the arrangement described by Lorenser (*Diss.*, Tübingen, 1913), the existence of fine structures in the three Li^+ lines, 5485, 2934, and 3714 Å., has been demonstrated. The intensities and wave-lengths of eleven components of the first, three of the second, and three of the third line are given. The theoretical significance of these results is discussed. M. S. B.

Auroral Green Line. J. C. MCLENNAN (*Nature*, 1925, **115**, 607).—The line at 5577 Å. can be obtained with a mixture of oxygen and excess of helium at the ordinary temperature; it probably originates from the oxygen. A. A. E.

Structure of the Mercury Line, 2536 Å. R. W. WOOD (*Nature*, 1925, **115**, 461).—The structure of the mercury line 2536 Å. observed by Nagaoka was that caused by the self-reversal of the true components. In the true structure now observed, there are five components of uniform intensity, four at sensibly equal intervals, the fifth having a slightly greater separation. The error was associated with the type of lamp employed. A. A. E.

Peculiarity of some Red Neon Lines. W. H. J. CHILDS (*Nature*, 1925, **115**, 572).—The value 6402·251 ±0·001 Å. is found for the wave-length of the reversal of the neon line 6402 Å. A. A. E.

Spectroscopic Shift Law. I. E. FUES (*Ann. Physik*, 1925, [iv], **76**, 299—316).—Theoretical. The relationship between the spectra due to similarly constructed atoms or ions, for example, neutral Li, Be^+, B^{++}, and C^{+++}, or neutral Na, Mg^+, Al^{++}, and Si^{+++}, is discussed. M. S. B.

Duration of the Quantic State $2p_2$ of the Mercury Atom. F. RASETTI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 223—225).—In view of the discordant values published for the mean duration of the mercury atom in the $2p_2$ state, the monochromatised light from a mercury lamp, immersed in cold water, was passed through the slit of a revolving disc on to mercury vapour contained in a quartz flask. Photographic examination revealed no trace of resonance in the mercury vapour even when the interval between excitation and observation was reduced to 5×10^{-5} sec. It is hence concluded that the $2p_2$ condition is not metastable at the ordinary temperature. At 200°, the resonance radiation begins to exhibit sensible duration, but the phenomenon is then complicated by the appearance of a green fluorescence, attributable to a molecule Hg_2, formed by the shock between an excited and a normal atom and possessed of a long life. The spectrum of the green luminescence observed when mercury is shaken in an evacuated vessel at about 200° shows, besides a continuous band reaching from the yellow to the violet, also the more intense of the mercury lines, such as 5790, 5769, 5460, 4358 Å., and, less strongly, 2536 Å. This excitation is evidently analogous to electrification by friction. T. H. P.

Intensity of Multiple Lines. E. FERMI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 120—124).—A theoretical interpretation is suggested for the empirical rules governing the intensities of the components of multiple lines. T. H. P.

Intensities of Components in the Zeeman Effect. L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1924, **28**, 135—141).—A theoretical paper, giving a generalisation of the rules already described (cf. A., 1924, ii, 433) for the calculation of the intensities of multiplets, which make it possible to predict the intensities of the components in the Zeeman effect. A preliminary announcement is made of experimental verifications of the theory. S. B.

Zeeman Effect in Multiplets of Higher Grade. A. LANDÉ (*Ann. Physik*, 1925, [iv], **76**, 273—283).—The regularities of the splitting factor g in the Zeeman effect are discussed. Not all the g-values of the higher grades are rational and constant with increasing sequence number, but the g-values of the terms with common K and J values, the impulse quantum number, and inner quantum number, respectively, add up to rational and constant g-totals which all obey a general law. Two methods for the calculation of g are given. The first depends on the branching principle (Landé and Heisenberg, A., 1924, ii, 710) and the permanence of the g-sum in the passage from a weak to a strong field (Pauli, *Z. Physik*, 1923, **16**, 155). The second method rests on a conjecture not yet verified that limiting values of g for higher sequence numbers are the "ideal"

g-values in a weak field, the latter being determined by the first method. As a result, it appears evident that a simple and uniform scheme governs the structure and Zeeman effect of the multiplets. The details of the scheme give clear evidence of the inadequacy of the theoretical principles based on quanta, for coupled systems. M. S. B.

Zeeman Effect of Neon. E. Back (*Ann. Physik*, 1925, [iv], **76**, 317—332).—Very exact determinations have been made of the splitting up by a magnetic field of the neon lines $1s_i$—$2p_i$ and also of the term separation factor g and the inner quantum number j deduced from them. The g-values are found to be rational numbers which can all be reduced to Runge fractions with a denominator of 30. They are thus in agreement with Landé's theory (see preceding abstract). M. S. B.

Paschen-Back Effect. C. Runge (*Ann. Physik*, 1925, [iv], **76**, 266—272).—A theoretical paper in which it is shown that Sommerfeld's interpretation (*Z. Physik*, 1922, **8**, 269) of Voigt's theory of the Paschen-Back effect for the pairs of lines s-p_1 and s-p_2 is not in agreement with the facts, as is shown by Kent's work (*Astrophys. J.*, 1914, **40**, 337) on the splitting up of the lithium line 6708 by a magnetic field. Kent's observation of the behaviour of component 7, however, cannot be reconciled with the author's views on the term resolution of spectral lines. M. S. B.

New Spectrum Apparatus, Monochromator, and Quartz Spectrograph with Crossed Prisms to Secure Highest Spectral Purity in the Region 200 $\mu\mu$ to 2 μ. C. Leiss (*Z. Physik*, 1925, **31**, 488—495).—The instrument is designed to give great range and adaptability with purity of spectral lines and without clumsiness. E. B. L.

New Type of Electric Discharge. Streamer Discharge. I. Langmuir, C. G. Found, and A. F. Dittmer (*Science*, 1924, **60**, 392—394).

Cathode Fall, Current Density, and Dark Space in Mixtures of Gases which do not React Chemically. A. Günther-Schulze (*Z. Physik*, 1924, **28**, 129—134).—The cathode fall, current density, and dark space in the discharge through binary mixtures of the inert gases with each other and with hydrogen have been measured. From inflexions in the curves connecting cathode fall with gas composition it is inferred that in the electric discharge the inert gases probably have the power of forming temporary compounds. S. B.

Processes in the Vacuum Mercury Arc. A. Günther-Schulze (*Z. Physik*, 1925, **31**, 509—513).—The fall of potential round the anode and cathode is discussed and the energy changes are calculated. The cathode fall of potential is not very different from the ionisation potential and about half the current is carried by electrons. Previous results obtained by using probe electrodes gave values much

too low. At the anode, previous results obtained by calculation from the intensity of the radiation caused by the heating were much too high, as the energy of neutralisation of the electrons had not been considered. E. B. L.

Pseudo-high Vacuum. A. GÜNTHER-SCHULZE (*Z. Physik*, 1925, **31**, 606—616).—After prolonged use, a Wehnelt high-voltage rectifier behaves as though the vacuum had become too high for the discharge to pass, although there is plenty of argon present. The explanation is that the electrostatic charge on the walls of the bulb deflects the electric field between the electrodes and prevents the discharge. At first a film of moisture on the surface provides a leak, but this is removed in time by a deposit from the disintegrating cathode. E. B. L.

Simple Kinetic Derivation of the Ionisation and Vapour Pressure Equations. R. BECKER (*Z. Physik*, 1924, **28**, 256—260).—The theory of equilibrium in a thermally ionised gas and of the process of evaporation are considered, and are shown to submit to analogous mathematical treatment. S. B.

Excitation and Ionisation Potentials of the Noble Gases. G. HERTZ and R. K. KLOPPERS (*Z. Physik*, 1925, **31**, 463—469).—The method employed was that of the impact of electrons accelerated by a known potential; the gases examined were argon, krypton, and xenon. As impurities could not be removed from the two last-named by cooling in liquid air, solid carbon dioxide in alcohol was used and traces of impurities may have been present. The electrons were emitted from a nickel cathode coated with barium oxide and heated by a fine tungsten wire, the advantage of the arrangement being that there was no fall of potential along the cathode itself. The ionisation potentials found were: argon 15·4, krypton 13·3, xenon 11·5 volts; the values found for the excitation potentials do not indicate the passage of the atom from its normal state into a definite stationary state of higher energy but an average value, corresponding with terms of the spectral series which lie close together. The lowest values found were: argon 11·5, krypton 9·9, xenon 8·3 volts. E. B. L.

Work of Escape of Positive Ions. A. GÜNTHER-SCHULZE (*Z. Physik*, 1925, **31**, 507—508).—The values are obtained by taking the algebraic sum of the energies necessary to eject both positive ions and negative electrons from the surface of a metal, the ionisation potential of the gaseous atom of the metal and its latent heat of vaporisation, and equating this sum to zero. The result of this cyclic process is to show that the energy necessary to remove a positive ion is two or three times as great as is required to eject an electron and about the same as the ionisation energy for the gaseous metal. E. B. L.

Series Spectra of the Stripped Atoms of Phosphorus (P V), Sulphur (S VI), and Chlorine (Cl VII). I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **25**, 295—305).—More accurate values have been obtained for the $(3p_2-3p_1)$,

($3s-3p_2$), and ($3p_1-3d$) terms of Al III, Si IV, P V, and S VI, leading to the determination of 18 series lines of P V, 11 series lines of S VI, and the first doublet of the principal series of Cl VII, as already predicted (cf. A., 1924, ii, 710). Both the regular and the irregular doublet laws of X-ray spectra appear to hold also throughout the field of optics. When values of $\sqrt{\nu/R}$ for the stripped atom levels are plotted as a function of atomic number, approximately straight lines are obtained (Moseley's law). The general similarity of the stripped atoms of sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine is demonstrated, but the D doublets deviate from their calculated position, that of sodium to the greatest extent. Ionisation potentials of P V and S VI are computed to be 64·7 and 87·6 volts, respectively. A. A. E.

Influence of Radiation on Ionisation Equilibrium. J. Woltjer, jun. (*Nature*, 1925, **115**, 534).—An alternative method of arriving at the results of Saha and Swe (this vol., ii, 254) is based on a formulation of the conditions required for a stationary state by means of probability laws governing the elementary processes involved. A. A. E.

Total Ionisation produced in Air by Electrons of Various Energies. G. A. Anslow (*Science*, 1924, **60**, 432—433).—An experimental verification of Bohr's theory of ionisation as corrected by Fowler. A. A. E.

Thermionic Work-functions and Photo-electric Thresholds of the Alkali Metals. O. W. Richardson and A. F. A. Young (*Proc. Roy. Soc.*, 1925, **A**, **107**, 377—410).—Both sodium and potassium show more than one value for the thermionic work function and for the photo-electric threshold. Photo-electric currents soon reach the saturation value, but thermionic currents do not. The authors suggest that the surface of the metal is not uniform, but that there are small patches associated with the lower value of the work function. A photo-electric threshold has been found for potassium at about $\lambda=10{,}000$ Å. by exposing the metal to a luminous discharge in hydrogen or a trace of water vapour, the suggestion being that this encourages the growth of the patches. E. B. L.

Photo-electric Primary Current in Sodium Chloride Crystals. B. Gudden and R. Pohl (*Z. Physik*, 1925, **31**, 651—665; cf. A., 1921, ii, 145).—Rock-salt crystals coloured yellow by X-rays were exposed alternately to mercury radiation 405 and 436 $\mu\mu$, and to infra-red radiation from an arc lamp, and the photo-electric current measured by a string galvanometer. Current–time curves are given for great and for small light intensity for temperatures between 30° and 130°. The primary current is caused by the electrons detached by the high-frequency light moving towards the anode; the reverse, positive current is due to the return of the electrons under the influence of the infra-red radiation or thermal agitation. Below 40°, heat does not produce the positive current; above 100°, it reaches its full value. Differences in the

behaviour of rock-salt and diamond are due to the electrons in the former penetrating only a small distance. In agreement with Lenard's theory of phosphorescence, there is a correspondence between the intensity of phosphorescence and the positive portion of the primary current. E. B. L.

Photo-electric Properties of Thin Films of Alkali Metals. H. E. IVES (*Astrophys. J.*, 1924, 60, 209—230).—Thin films of sodium, potassium, rubidium, and cæsium, spontaneously deposited on clean metal surfaces in a vacuum, exhibit a selective photo-electric effect. The selective characteristic depends on the thickness of the film. The effect is ascribed to a particular orientation of the atoms completely covering the surface. A. A. E.

Normal and Selective Photo-electric Effects in the Alkali Metals and their Alloys. H. E. IVES and A. L. JOHNSRUD (*Astrophys. J.*, 1924, 60, 231—242; cf. preceding abstract).—The selective photo-electric effect observed in the case of an alloy of sodium and potassium is not exhibited by the pure bulk metals, nor by other alloys of alkali metals. A. A. E.

Selective Photo-electric Effect on Metallic Films Prepared in Various Ways. F. GROSS (*Z. Physik*, 1925, 31, 637—646).—The photo-electric behaviour of various kinds of copper, bismuth, and silver films towards the mercury radiation, 254 $\mu\mu$, was studied. A selective effect was found for a copper film evaporated in a vacuum from an alloy of copper and molybdenum but smaller than that obtained from a film spluttered from a copper cathode in hydrogen. A film prepared in a high vacuum by evaporation of copper in a magnesium crucible showed only the normal effect. The selective effect is attributed to the dissolved gases in the metal. Bismuth films exhibited no selective effect. A definite conclusion was not reached for silver. Copper films retain their photo-electric sensitivity; those of silver and bismuth lose it in time. E. B. L.

Mechanism of the Photo-electric Primary Current in Crystals. B. GUDDEN and R. POHL (*Z. Physik*, 1924, 30, 14—23; cf. *ibid.*, 1921, 6, 248).—The absorption of light by diamond has been examined in different portions of the spectrum by the amount of positive and negative electricity liberated. For the same amount of light energy, the negative primary current constantly decreases with the increase in wave-length. If the diamond be previously illuminated with light of wave-length 436 $\mu\mu$, the absorption of light of wave-length greater than 540 $\mu\mu$ is increased, as shown by the increased current, and this increase becomes relatively greater as the infra-red end of the spectrum is approached. This excess current is ascribed to the positive charges stored up during the preliminary illumination with light of short wave-length. Previous disturbance of the crystal lattice by the presence of positive charges, therefore, appears to extend the absorption of light by the diamond towards the long-wave region. It is probable that the mechanism of the primary positive current consists in the

passage of electrons between positive ions and neutral atoms made possible by increased temperature vibrations of the molecules due to absorption of infra-red radiations. By continued illumination with blue light, a gradually increasing fraction of the positive charges takes part in the primary current, so that less than the equivalent quantity is obtained by subsequent treatment with infra-red rays. When equilibrium is reached between the positive charges formed and those displaced to the cathode, the current reaches a stationary state when its value may be greater or less than at first. The latter happens when the lowering of field-strength through the presence of the positive charges outweighs the increase due to the spontaneously flowing positive constituent of the primary current. M. S. B.

"Phenomenology" of the Richardson Effect. D. REICHINSTEIN (*Z. Elektrochem.*, 1925, **31**, 124—135).—A discussion of current theories of electron emission in vacuum tubes of the thermionic valve type. Richardson's equation connecting saturation current with temperature requires the immediate establishment of the equilibrium between the filament and the electron vapour, but this is contrary to experience. A "phenomenological" description of the electron emission is therefore necessary. The probable results of such an interpretation are indicated and lines of research suggested. In particular, it would be of interest to study the behaviour of the grid electrode at the temperature of liquid air. N. H. H.

Study under Reduced Pressure of the Radiations Emitted by Bodies of High Resistance traversed by an Electric Current. G. REBOUL (*Compt. rend.*, 1925, **180**, 916—919; cf. A., 1924, ii, 578).—The coefficients of absorption of the radiations emitted by conductors of high resistance traversed by an electric current, by air, carbon dioxide, and hydrogen have been investigated at various reduced pressures. The radiations traverse a layer of gas to enter an ionisation chamber, their intensity being estimated from the magnitude of the ionisation current. The nature of the results obtained indicates that these radiations form a continuous spectrum, successive wave-lengths differing only by a very small fraction of an Å. J. S. C.

Electron Emission from Tungsten, Molybdenum, and Tantalum. S. DUSHMAN, H. N. ROWE, J. EWALD, and C. A. KIDNER (*Physical Rev.*, 1925, [ii], **25**, 338—360).—The equation $I=AT^2e^{-b_0/T}$ holds in the case of tungsten; the accuracy of results with tantalum and molybdenum is not so great. In the former, but not the latter case, the value of A is approximately the same as that for tungsten. A. A. E.

Various Magnetic States of an Ion. G. FOEX (*Compt. rend.*, 1925, **180**, 919—921).—Specimens of the same salt often possess varying magnetic properties which appear to be connected with distinct structural differences in the paramagnetic ion which they contain. This diversity, which has already been examined for

salts in aqueous solution (*Ann. Physique*, 1921, **16**, 174) is now extended to crystalline salts. A specimen of ferrous ammonium sulphate has been prepared, corresponding with 26 magnetons and possessing a strong positive molecular field, there being in addition a sudden change in the direction of the temperature–coefficient of magnetisation curve at 100°. A specimen of the same salt examined by Jackson (*Phil. Trans.*, 1923, **A**, **224**, 1) corresponded with 27·5 magnetons, the molecular field being very weak and the influence of temperature quite normal.

Anhydrous cobalt sulphate has been shown to exist in two forms, the varieties having 25 and 24 magnetons, respectively, the respective magnetic fields being negative and feebly positive. J. S. C.

Isotope Effect in Band Spectra. II. Spectrum of Boron Monoxide. R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **25**, 259—294).—An extension of measurements of bands ascribed by Jevons (A., 1924, ii, 366, 438, 640) to boron nitride, but by the author (A., 1924, ii, 3, 294, 446, 640) to boron monoxide. The predicted vibrational isotope effect has been verified for both α and β systems; no indications were obtained of isotopes other than B^{10} and B^{11}. Equations are given representing the measured positions of all the heads of the bands. In view of the complete agreement between the experimental measurements and theoretical considerations, it is considered to be practically certain that the bands in question are due to boron monoxide. An indicated electronic isotope effect of unprecedented magnitude vanishes if the minimum values of the initial and final vibrational quantum numbers are assumed to be 0·5 instead of zero. Thus the existence of half-integral vibrational quantum numbers and a null-point vibrational energy of one half-quantum is probable. The rotational isotope effect is approximately confirmed. A new system of boron monoxide bands has been investigated, and the arc and active nitrogen spectra of boron monoxide have been compared. The possible analogy between BO and CN molecules and sodium atoms is discussed.

A. A. E.

Fundamental Atomic Weights. E. MOLES (*Anal. Fis. Quim.*, 1925, **23**, 39—75; *Z. physikal. Chem.*, 1925, **115**, 61—90).—The author discusses modern physico-chemical and chemical values for the atomic weights of hydrogen, chlorine, bromine, and silver, respectively. It is considered that there is no discordance between the values obtained for hydrogen, chlorine, and bromine by physico-chemical methods and those obtained by purely chemical methods, and the mean values are given as hydrogen, 1·00777; chlorine, 35·458; bromine, 79·918. The atomic weight of silver, according to the author, cannot be less than 107·880, but is somewhat greater than 107·882. G. W. R.

Redetermination of the Atomic Weight of Boron. H. V. A. BRISCOE and P. L. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 696—720).—The atomic weight of boron has been determined using samples of boron from widely-separated known sources in order to determine

whether the isotope ratio is always and everywhere the same. The value of the ratio $BCl_3 : 3Ag$ was determined, the actual method used consisting in breaking sealed bulbs containing boron trichloride under water and titrating the resulting solution with pure silver nitrate, the end-point being ascertained nephelometrically. The various refinements introduced and also the method for the isolation of boron trichloride in a state of purity are described in detail. Some evidence was obtained indicating a partial isotopic separation during the distillation of boron trichloride. The mean value of the atomic weight of boron from California was found to be 10·840 and that from boron from Tuscany and Asia Minor 10·820. These values indicate that a partial separation of the isotopes 10 and 11 has occurred in nature, the American boron containing 84% and the Eurasian boron 82% of the heavier isotope. Atomic weight determinations based on the analysis of fused borax are open to criticism. J. S. C.

Atomic Weight of Hafnium. Analysis of Hafnium Bromide. O. Hönigschmid and E. Zintl (*Ber.*, 1925, **58**, [*B*], 453—459).—Analysis of hafnium bromide, prepared by heating more highly-purified hafnium oxide with sugar charcoal in an atmosphere of nitrogen laden with bromine vapour (cf. this vol., ii, 174) gives the value 178·6 (±0·08) for the atomic weight of hafnium. The specimens of hafnium bromide are reconverted into the dioxide, which is found to contain 0·57 (±0·06)% and 0·16 (±0·02)% of zirconium dioxide, for which the necessary correction is applied. H. W.

Quantum Theory of Radioactive Process. II. A. Smekal (*Z. Physik*, 1924, **28**, 142—145; cf. A., 1924, ii, 717).—Meitner's views on the mechanism of the transformation of a disintegrating nucleus are in agreement with the author's quantum theory of the process. S. B.

Measurements of β-Rays associated with Scattered *X*-Rays. A. H. Compton and A. W. Simon (*Physical Rev.*, 1925, [ii], **25**, 306—313).—Stereoscopic photographs of β-ray tracks excited by strongly filtered *X*-rays in moist air confirm Wilson and Bothe's observations of *P* (longer) and *R* (shorter) tracks, and yield strong evidence that there is about one *R* track or recoil electron associated with each quantum of scattered radiation, and possessing, both in direction and magnitude, the vector difference of momentum between the incident and the scattered *X*-ray quantum. A. A. E.

β-Ray Spectrum of Thorium-*B*+*C*. W. Pohlmeyer (*Z. Physik*, 1924, 28, 216—230).—The β-ray spectrum of a mixture of thorium-*B*+*C* was obtained by magnetic resolution, and registered by the ionisation method. The results indicate that the continuous background present in β-ray spectra is due to secondary effects, the true β-ray spectrum being a simple "line" spectrum. S. B.

High-energy γ-Rays and their Photo-electric Effect. M. de Broglie (*Nature*, 1925, **115**, 461).—A correlation of the results of Black (this vol., ii, 177) with those of Thibaud (A., 1924, ii, 515, 717; this vol., ii 10, 85). A. A. E.

Homogeneity of Initial Velocities of α-Particles from Polonium. (MLLE.) I. CURIE (*Compt. rend.*, 1925, 180, 831—833; cf. A., 1923, ii, 207).—Geiger (A., 1910, ii, 473) claimed an accuracy of 0·5% in verifying for radium-*C* the view that all α-particles are emitted at the same velocity by a radioelement (A., 1923, ii, 207).

The author criticises adversely Geiger's reasoning, but confirms his conclusion. She finds there is no evidence of initial differences in velocity for α-particles emitted by polonium. On the assumption of a uniform distribution of velocities between two extremes, the maximum difference is not greater than 0·3%. The alternative assumption of distribution about a velocity V according to the probability law $v=\gamma V$ results in a value for $\gamma<0{\cdot}15\%$ so that three-quarters of the α-particles have velocities differing by $<0{\cdot}3\%$.

R. A. M.

Number of Ions Produced by the α-Particle from Polonium. M. V. BIANU (*Bull. Acad. Sci. Roumaine*, 1924, 9, [5—6], 37—39).—The method employed was to determine total ionisation due to the α-particles and the charge of an α-particle in the same apparatus, current being measured by the quartz-piezo electrometer. The number of ions per α-particle was found to be $1{\cdot}58\,.\,10^5$, in agreement with $1{\cdot}62\,.\,10^5$ (Geiger) and $1{\cdot}64\,.\,10^5$ (Taylor). A. S. R.

Effect of the Sun on Radioactivity. (MLLE.) S. MARACINEANU (*Bull. Acad. Sci. Roumaine*, 1924, 9, [3—4], 1—11).—Preliminary experiments. Peculiar changes in the radioactive properties of actinium-*B*, polonium, and of lead, detected principally by the effects produced on a photographic plate, are ascribed to the sun's rays. The magnetic field, cold, pressure, and friction are found to excite lead. Ionised water is necessary for the effects to be produced. A. S. R.

Disintegration of Atomic Nuclei. (SIR) E. RUTHERFORD (*Nature*, 1925, 115, 493—494).—A discussion of the results of Blackett (this vol., ii, 256), Harkins and Ryan (A., 1923, ii, 601, 720), Akiyama (A., 1924, ii, 814), and Pettersson and Kirsch (*Physikal. Z.*, 1924, 25, 588) on the branched tracks observed on collision between α-particles and nuclei. A. A. E.

Electrical Explosion of Tungsten Wires. H. V. A. BRISCOE, P. L. ROBINSON, and G. E. STEPHENSON (*J. Chem. Soc.*, 1925, 127, 240—247).—Anderson (*Astrophys. J.*, 1920, 51, 37) has shown that, by the passage of heavy high-tension discharges through thin metallic wires temperatures are momentarily attained which are much higher than can be reached by any other known means. Experiments by Wendt and Irion (A., 1922, ii, 773) appear to indicate that, when a fine tungsten wire is exploded by this method, helium is produced. These conclusions have been tested by passing the high-tension discharge between molybdenum electrodes, connected by a fine tungsten wire, in an evacuated bulb, and then examining the residual gas spectroscopically on passing an induction coil discharge between a supplementary electrode and one of

the main electrodes. Some mercury and hydrogen lines were observed, but no trace of the yellow helium line. These results confirm the recent work of other investigators (cf. Smith, *Proc. Nat. Acad. Science*, 1924, **10**, 4; Harkins and Allison, A., 1924, ii, 407). M. S. B.

Theory of the Electron. H. REISSNER (*Z. Physik*, 1925, **31**, 844—865).—A theory of point charges exhibiting the properties of the electron and of the proton is developed mathematically on the basis of Einstein's field equations of the point charge. The solution with unchanged Maxwellian energy tensor gives incorrect values for the mass of the positive and negative charges, making them equal and much too great. The introduction of an additional member of the energy tensor contributing only at the charge-point, with the help of three universal constants, leads to the correct value of the positive and negative charges and of the difference in mass of the two kinds of charge. E. B. L.

Statistical Investigations on the Sub-electron. H. DAECKE (*Z. Physik*, 1925, **31**, 552—575).—Mathematical treatment of independent series of results in which the values of e were less than $4{\cdot}77\times10^{-10}$. If the sub-electron is defined as $(m/n).e$, in which $m<n$ and n is not large, then the assumption of a sub-electron is more probable than any other deduction. E. B. L.

Static Model for Helium. H. S. ALLEN (*Proc. Roy. Soc. Edin.*, 1924, **44**, 116—128).—By assuming the existence of a quantum force as postulated by Langmuir (*Physical Rev.*, 1921, [ii], **18**, 104) acting along the line joining two charged particles, static models have been deduced for the ionised helium atom, the neutral helium atom, and the helium molecule. The introduction of three quantum numbers renders the models adjustable by the choice of these numbers. The results obtained for the atom are in agreement with the original model of Bohr, but are not in agreement with the experimentally determined ionisation potential. For the molecule, the moment of inertia obtained is of the same order of magnitude as that determined by Curtis from the band spectrum. A. E. M.

Relative Sizes of the Kernels of Ten Electrons of Sodium, Magnesium, Aluminium, and Silicon. L. A. TURNER (*Astrophys. J.*, 1924, **60**, 81—86).—From optical data, the relative sizes of the ten-electron-kernels of neutral sodium, singly ionised magnesium, doubly ionised aluminium, and trebly ionised silicon have been computed as $1:0{\cdot}740:0{\cdot}575:0{\cdot}472$. Thus the effective nuclear charge for the outer orbits of the kernel is equal to the true nuclear charge less an unvarying screening constant which is approximately that predicted from the L X-ray term values. A. A. E.

Emission Spectrum of Water Vapour. W. W. WATSON (*Astrophys. J.*, 1924, **60**, 145—158).—Accurate wave-lengths have been determined for all the lines of the band 2811 Å., and every

line has been assigned to a parabolic series. Fifteen new lines of a band at 3021 Å., which form a single parabolic series, have also been measured. Analysis of the series for the bands 2811 Å. and 3064 Å. indicates that they are due to hydroxyl ions. A. A. E.

Ultra-violet Emission Spectra of the Halogens. E. B. LUDLAM and W. WEST (*Proc. Roy. Soc. Edin.*, 1924, **44**, 185—196).—Examination of the emission spectra of chlorine, bromine, and iodine excited in silica tubes by means of the Tesla discharge shows that their most prominent features are two continuous bands rising sharply on the long wave side with a displacement of corresponding features to the less refrangible side with increase of atomic weight. The long wave limits of the first continuous band are 3200 Å. for chlorine, 3700 Å. for bromine, and 4800 Å. for iodine. The corresponding energies calculated from the frequencies of the long wave limits are 89·1, 77·0, and 96·6 cals., respectively. These values do not hold for any conceivable chemical reactions, and it is suggested that the first continuous band is of molecular origin. The long wave limits of the second continuous bands are 2650, 2950, and 3450 Å., respectively, and the corresponding calculated energies are 107·3, 96·6, and 82·3 cals. These values are in agreement with the electron affinities calculated on the lattice theory, and it is suggested that the second continuous band is the electron affinity spectrum. In addition, iodine shows a sharp line spectrum the first member of which is at 2061 Å. This is suggested as the principal line series of iodine. The corresponding hydrides showed the same features together with the hydrogen spectrum. A. E. M.

Visible Radiation from Niobium Oxide. E. L. NICHOLS (*Physical Rev.*, 1925, [ii], **25**, 376—385).—When niobium oxide, Nb_2O_5, is gradually introduced into a hydrogen flame, it glows with a pale greenish-blue colour when in the oxidising portion, but in the reducing region the colour changes abruptly to deep red. The former phase is selective with luminescence bands superposed on the radiation due to temperature, whilst the latter resembles that of a black body and is due to the formation of the oxide Nb_2O_4, which is black at the temperature of incandescence. The formation of similar black suboxides was observed in the cases of titanium and tantalum. A. A. E.

Negative Nitrogen Band Spectrum. M. FASSBENDER (*Z. Physik*, 1924, **20**, 73—92).—An extensive examination of the negative nitrogen band spectrum has been made, precautions being taken to reduce to a minimum intensity the bands of the second positive nitrogen group, which overlaps it in the violet and ultra-violet. Seven of the twenty bands observed have been measured and arranged in series. *P* and *R* branches, zero lines, and intensity distribution have been determined. M. S. B.

Vibration–Rotation Spectrum of Gaseous Ammonia at 3 μ. B. J. SPENCE (*J. Opt. Soc. Amer.*, 1925, **10**, 127—132).—The ammonia band at 3 μ is double, with serrated branches unequally distributed about a central branch. This is in disagreement with

the theory of Lenz for the points of maximum absorption for diatomic molecules, but agrees with the views of Kratzer that for larger periods of oscillation the vibrations are non-harmonic, and that the moment of inertia of the molecule is not constant. The prominence of the central branch indicates that many ammonia molecules exist in the rotationless state. A doubly branched, faint, harmonic band at approximately 1·5 μ was observed. F. G. T.

Structure of a Class of Band Spectra. R. MECKE (*Z. Physik*, 1925, **31**, 709—712).—The band spectra of molecules having identical constituent atoms exhibit anomalies in the intensities of the individual lines. According to an earlier paper (this vol., ii, 259), the total impulse of a molecule is made up of two components, the nuclear impulse and the electron impulse. The observed anomalies can now be accounted for by assuming the electron impulse of the diatomic molecule of an element to be subdivided unsymmetrically into two components, one to each atom. It is concluded that the series of strong lines in the band is emitted only by an electron of one atom, the remaining portion by an electron of the other atom. These spectra are analogous to a series of infra-red bands exhibited by all compounds containing a carbon–hydrogen linkage. E. B. L.

Fulcher Hydrogen Bands. W. E. CURTIS (*Proc. Roy. Soc.*, 1925, **A**, **107**, 570—587).—A theoretical discussion of existing data indicating that the bands are due to simultaneous rotation and vibration changes in the " excited " molecule. The unique structure of the system is accounted for by the nuclear vibrations within the hydrogen molecule being very nearly simple harmonic.
E. B. L.

Infra-red Absorption Spectra of Alcohols. J. LECOMTE (*Compt. rend.*, 1925, **180**, 825—827).—Monohydric alcohols absorb strongly in the regions 3—3·5 μ and 6·85—8 μ. They transmit freely in the intermediate region. Sharp maxima are found at 2·98—3·08, 3·42—3·50, 3·42—3·50, 6·85—6·93 for all alcohols. The secondary alcohols show an additional band at 7·70 which is shifted to 7·90 for the tertiary alcohols. There is little difference between straight chain and branched chain members of the series. Between 3·5 and 6·85 there are feeble bands irregularly distributed. The higher homologues are exceptional, since they absorb strongly between 5·8 and 6·15. Polyhydric alcohols, glycerol, and glycols absorb similarly, but two of the feeble secondary bands disappear. The maxima for 26 alcohols are given correct to $\pm$0·02 μ.
R. A. M.

Photographic Method for Absorption Spectra in the Ultra-violet. W. CROSS (*Z. Elektrochem.*, 1924, **30**, 18—20).—To overcome the difficulties in the determination of absorption spectra due to changes in the intensity of the arc light, a method of comparing the spectra of two solutions simultaneously by means of a " dual " spectrograph is described. Some measurements of the absorption spectra of copper solutions at concentrations 0·01,

0·001, and 0·0001 *N* are given, and the deviations of the observed data from Beer's law discussed. H. T.

Absorption of Light by Ammonia. G. LANDSBERG and A. PREDWODITELEFF (*Z. Physik*, 1925, **31**, 544—551).—Light from the spark between metallic electrodes was passed through mixtures of air and ammonia, then through a quartz spectrograph and the intensity in the region 1858 to 2195 Å. determined by means of a photo-electric cell. Absorption coefficients are given and also a photograph; the maximum absorption is at 1935 Å. There is no apparent deviation from Beer's law. E. B. L.

Series in Absorption Spectrum of Water Vapour. H. WITT (*Z. Physik*, 1924, **28**, 249—255).—In the region between 20 and 170 μ, the absorption spectrum of water vapour can be represented by two series of the form $\nu=a(n+\frac{1}{2})$, where a has the values 16·83 and 24·55. In the region 6500—9000 Å., the lines fall into three series, which may be correlated with the three principal moments of inertia of the triatomic molecule. From the spacing of the water bands in the ultra-violet, in comparison with the above, it is inferred that they probably originate from an OH molecule, or ion. S. B.

Mutability of the Absorption Spectra of Non-polar Compounds and Halochromism of Unsaturated Ketones. II. G. SCHEIBE [with G. RÖSSLER and F. BACKENKÖHLER] (*Ber.*, 1925, **58**, [*B*], 586—601; cf. A., 1924, ii, 712).—The absorption curves of acetone in hexane, ethyl alcohol, water, calcium chloride solution, and aqueous ammonia have been determined together with the position of maximal absorption in mixtures of hexane with chloroform or ethyl alcohol, ethyl alcohol with carbon tetrachloride or water, and in calcium chloride solution. An attempt is made to correlate the results thus obtained with the dipolar character of the solvents, for which the dielectric constant is used as a rough index, Measurements are also recorded for ethyl iodide in hexane, carbon tetrachloride, alcohol, and water, iodoform in hexane, carbon tetrachloride, and alcohol, mesityl oxide in hexane, methyl alcohol, and calcium chloride solution, and phorone in hexane, carbon tetrachloride, ether, chloroform, ethyl and methyl alcohol, glacial acetic acid, water, and concentrated sulphuric acid. If the position of the absorption bands in almost indifferent media such as hexane and carbon tetrachloride be regarded as normal it is found that two classes of bands may be distinguished. One class is invariably displaced towards the ultra-violet by strongly dipolar solvents such as alcohol and water (carbonyl, CI chromophore), whereas the other class is displaced by the same solvents towards the red (ethylene chromophore). A new possibility is thus opened of disentangling complex absorption spectra and of assigning bands to definite groups of atoms. H. W.

Ultra-violet Absorption of Aqueous Potassium Permanganate Solutions. E. VITERBI (*Gazzetta*, 1925, 55, 127—135).—The ultra-violet absorption spectrum of aqueous potassium

permanganate solutions exhibits two wide principal bands, one between two minima at 4188·5 Å. and at about 2707 Å., respectively, and the other starting from 2707 Å. and extending towards the extreme ultra-violet. The first of these bands possesses seven or more striæ analogous to the eight present in the visible band; the order in which these are arranged according to their molecular absorption coefficients is the same in the two cases, the maximum coefficients being thus sensibly equal. Each of these two bands, as well as that in the extreme ultra-violet, shows in its less refractive part a band of less absorption not belonging to the system of striæ. The differences between the frequencies at the centres of two contiguous ultra-violet striæ are sensibly equal, not only to one another, but also to that shown by the visible striæ. These results, in conjunction with those obtained by Henri ("Études de Photochimie," 112 *et seq.*, 162 *et seq.*) for aromatic compounds, render it probable that the absorption spectrum of potassium permanganate contains an infra-red band of the frequency ν=about 22·1.

T. H. P.

Ultra-violet Absorption Spectra of Organic Compounds. VI. L. Marchlewski and A. Moroz (*Bull. Soc. chim.*, 1925, [iv], **37**, 404—412).—The ultra-violet absorption spectra of isatin (in alcoholic, aqueous, and in sodium hydroxide solution) and of acetylisatin (in alcoholic solution) and their extinction coefficients are given in tabular and in graphical form. Isatin in aqueous and alcoholic solution has bands at, approximately, 4170, 2940, and 2420 Å. (cf. Hartley and Dobbie, T., 1899, 75, 640), whilst acetylisatin has a completely different absorption spectrum (similar to that of isatin in sodium hydroxide solution) with bands at 3340 and 2660 Å. This is further evidence (cf. A., 1900, i, 100; 1901, i, 347; 1902, i, 646) that acetylisatin has the structure of *o*-acetamidobenzoylformic acid.

L. F. H.

Theory of Polarised Fluorescence. Influence of Viscosity. F. Perrin (*Compt. rend.*, 1925, **180**, 581—583).—The degree of polarisation of the light emitted by fluorescent solutions is small unless the solvent has a large viscosity. This is attributed to the influence of the viscous solvent in retarding any rotation of the molecules oriented in a certain position, during the interval of time between absorption and emission of light. This conception is developed mathematically on the assumption that the active agents in the fluorescent molecules are electronic orbits, and the degree of polarisation is shown to be of the form $0{\cdot}25\ \eta/\eta+s$, where s is a constant. The values calculated according to this theory are in good agreement with values which have been observed with solutions of erythrosin and rose-bengal in various alcohols.

G. M. B.

Fluorescence Spectra. III. Aromatic Amine Vapours. T. H. Nunan and J. K. Marsh (*J. Chem. Soc.*, 1924, **125**, 2123—2128).—Whilst previous study of the fluorescence spectra of the vapours of substances normally fluorescent in solution (A., 1924,

ii, 219) has shown that in many cases the vapour spectrum shows a number of fine lines not given in solution, the phenomena are only exhibited to a limited degree in the aromatic amine class. Of the toluidines, *p*-toluidine gives the most banded spectrum. The band interval is 42 Å. and extends from 3327 to 2966 Å. This band interval is practically the same as that previously recorded for *p*-cresol (A., 1924, ii, 219) and *p*-xylene (this vol., ii, 12).

A. E. M.

Glow of Phosphorus. H. J. Emeléus (*Nature*, 1925, **115**, 460—461).—The light from glowing phosphorus trioxide and from phosphine spontaneously burning in oxygen gives the same spectrum as that previously observed (Emeléus and Downey, this vol., ii, 89); the glow of phosphorus and of phosphorus trioxide are analogous, but not necessarily identical, processes. A. A. E.

Phosphorescence Properties of Rare Earths in Alkaline-earth Phosphors. II. R. Tomaschek (*Ann. Physik*, 1924, [iv], **75**, 561—597; cf. this vol., ii, 12).—Phosphors of the sulphides and oxides of the alkaline-earth metals with the rare earths, in particular samarium, have been studied with reference to the relative effects of the different alkaline-earth metals on the duration and intensity of the after-glow, the intensity, wave-lengths, and distances apart of the doublet lines of the emission spectra. The relation of these to the type atom (sulphur or oxygen) has also been studied. From the results conclusions are reached as to the structure of the centres of phosphorescence and the mechanism of phosphorescence phenomena. A large complex, held together in loose chemical combination, appears to be necessary, the centre of the complex being capable of taking up molecules of metallic compounds. Hence compounds showing subsidiary valencies, for example, the alkaline-earth sulphides and oxides, are necessary. The type atom acts as the bridging atom between the heavy metal or rare earth atom of the phosphorogen and the alkaline-earth atom. The differences in behaviour of the various alkaline-earths are intimately associated with the differences between the heats of formation of the different sulphides and oxides. The phosphorescence process probably takes place as follows: absorption of a light quantum by the centre; transference of energy to the bridging atom, resulting in the removal of an electron which then attaches itself to the complex in a new position of equilibrium; simultaneous change of the electron orbits of the heavy metal atom through change of the valency field of the type atom; thermal or optical disturbance of the new position of equilibrium of the photo-electric electron and return of the latter to its original position in the type atom, accompanied by a simultaneous reversal of the changes in the electron orbits of the heavy metal atom with the emission of light. The change in wave-length of the characteristic groups, in passing from one metal to another, can apparently be expressed as a function of the heats of formation and the dielectric constants of the compounds between the two alkaline-earth metals and the type atom, the heat of formation of the

phosphorogen, and certain factors depending on the electron orbits and on the structure of the complex. M. S. B.

Photo-electric and Phosphorogenic Effect. M. CURIE (*J. Chim. physique*, 1925, 22, 45—47).—From measurements of the fluorescence, phosphorescence, and photo-electric effect of calcium sulphide preparations containing various amounts of bismuth, it is found that whilst the photo-electric effect is dependent on the presence, although scarcely at all on the concentration, of the bismuth, fluorescence and phosphorescence are dependent on the bismuth concentration. It is suggested that a layer rich in bismuth on the surface of the calcium sulphide grains is responsible for the photo-electric effect, and that the luminescence effects are derived from the whole of the grains. F. G. T.

Electrical Conductivity and Hall Effect for Nickel Films. A. RIEDE (*Z. Physik*, 1924, 28, 177—215).—Nickel films have been prepared by cathodic spluttering in hydrogen. Their conductivity was found to be proportional to their cross-section even for the thinnest films. The Hall effect in such films is proportional to the field strength in weak magnetic fields, but approaches a limiting value in intense fields. The sign of the effect is negative. S. B.

Dielectric Constants and Absorption-coefficients of Glycerol. R. BOCK (*Z. Physik*, 1925, 31, 534—543).—The dielectric constants were determined at temperatures from −140° to 225°; the method was that of Drude using Lecher wires, but producing the short wave-length oscillations by means of a thermionic valve and measuring the intensity by means of a crystal detector in circuit with a string galvanometer. Waves of about 1 metre length were employed. There is a sudden rise in the dielectric constant, beginning at −15° and ending at 60°, the value rising from about 3 to 36; in this same temperature region, there is also a strong increase in absorption for these waves with a maximum at 22°. Theories based on earlier experimental results are shown to be valueless. E. B. L.

Dielectric Constant of Liquid Phosgene [Carbonyl Chloride]. H. SCHLUNDT and A. F. O. GERMANN (*J. Physical Chem.*, 1925, 29, 353—355).—The dielectric constant of liquid carbonyl chloride, measured by the method of Drude (A., 1897, ii, 438), is $4{\cdot}34 \pm 0{\cdot}04$ at 22° and 4·72 at 0°. This value is based on the constants given by Drude for benzene and solutions of acetone in benzene. M. B. D.

Alternation in Molecular Volume of the Normal Monobasic Fatty Acids. W. E. GARNER and E. A. RYDER (*J. Chem. Soc.*, 1925, 127, 720—729).—The molecular volumes of octoic, α-nonoic, decoic, α- and β-undecoic, and lauric acids have been determined. Whilst the values for the liquid state at 50° increase linearly by 16·8 c.c./g.-mol. for each CH_2 group added, those for the solid state alternate as the series is ascended. Calculations of the area of the cross-section of one molecule in the crystal show that this

value is independent of the acid, acids so far apart in the series as acetic and lauric having the same cross-sectional area. The alternation in molecular volume is due entirely to changes in the length of the chain as the number of carbon atoms is increased. The magnitude of the alternation is in agreement with views previously advanced (A., 1924, ii, 385) regarding the structures of these acids in the solid state. The area of cross-section of the unit cell, 23·8 sq. Å., is very large and indicates that the structure of the crystal must be very open. J. S. C.

Volume of the Water in the Hydrates of Calcium Sulphate. W. Biltz (*Z. anorg. Chem.*, 1925, **143**, 231—232).—From the determinations by Linck and Jung (A., 1924, ii, 758) of the densities of calcium sulphate and its hydrates, it is shown that the gradual (zeolithic) dehydration of the hemihydrate occurs without alteration of the molecular volume. The difference between the molecular volumes of the dihydrate and the α-anhydrite is 27·3, twice the molecular volume of water at 0° Abs. Hydration in stages is accompanied by increasing increments of molecular volume, as in the ammoniates. S. I. L.

Molecular Volume and Molecular Refraction. R. Lorenz and W. Herz (*Z. anorg. Chem.*, 1925, **142**, 80—82).—The expression $V_o=3M.R$ (where V_o is the zero point molecular volume and $M.R$ the molecular refractivity) is deduced for non-associated substances. Application of the formula shows that it is approximately true, even with associated substances such as water, ammonia, and methyl alcohol. N. H. H.

Variations in the Rotatory Power of Tartaric Acid as a Function of p_H. F. Vlès and E. Vellinger (*Compt. rend.*, 1925, **180**, 742—745).—The rotatory power of tartaric acid has been examined in its relation to the p_H value of the aqueous medium. The curve representing rotatory power as a function of p_H rises rapidly between p_H 2 and 5. Above p_H 5, the rotatory power is practically independent of the acidity of the solution until the medium becomes quite alkaline (p_H 13), when there is a falling off in value. It is found that the experimental numbers are in agreement with the assumption that, for each p_H value, the rotatory power is the sum of the effects due to the two tartrate ions and the undissociated acid molecule. The question as to the change in the space arrangements consequent on the removal of a hydrogen ion from a molecule of tartaric acid is considered. J. S. C.

Rotatory Dispersive Power of Organic Compounds. XV. Borneol, Camphor, and Camphorquinone. Origin of Complex and Anomalous Rotatory Dispersion. T. M. Lowry and J. O. Cutter (*J. Chem. Soc.*, 1925, **127**, 604—615).—The following equations represent satisfactorily the rotatory power of concentrated solutions of camphor in benzene (41 lines, λ 6708—3599), acetone (27 lines, λ 6708—3941), and *cyclo*hexane (18 lines, λ 6708—4358) at 20°, respectively; $[\alpha]=29{\cdot}384/(\lambda^2-0{\cdot}0872)-20{\cdot}138/(\lambda^2-0{\cdot}05428)$, $[\alpha]=18{\cdot}022/(\lambda^2-0{\cdot}09363)-7{\cdot}1324/\lambda^2$, and

$[\alpha]=20{\cdot}007/(\lambda^2-0{\cdot}09114)-9{\cdot}2255/\lambda^2$. The rotatory power of borneol in benzene at 20° (18 lines, λ 6708—4358) can be expressed by the equation $[\alpha]=9{\cdot}7866/(\lambda^2-0{\cdot}07442)-3{\cdot}2862/\lambda^2$, and the rotatory power of camphorquinone in the same solvent, also at 20° (9 lines, λ 6708—5461), by $[\alpha]=-13{\cdot}170/(\lambda^2-0{\cdot}022352)$. Although these equations are in the first instance empirical, they appear to have a real theoretical significance.

The general theory of the origin of anomalous rotatory dispersion is discussed and a summary is made of the methods of superposing opposite partial rotations. Evidence is put forward in favour of the view that optical activity is not to be regarded as a property of the total molecule, but rather that the optical effects are localised in certain of the groups present. J. S. C.

Action of Boric Acid on the Rotatory Power of Malic Acid and Malates. E. Darmois (*Compt. rend.*, 1925, **180**, 921—924).—The optical activities of solutions containing definite amounts of malic and boric acids and variable amounts of ammonia or sodium hydroxide have been determined. The results are interpreted in favour of the assumption of the existence of *l*- and *d*-complexes, the former being stable in solutions which are distinctly acid and are to be regarded as combinations of the acid salts of malic acid with boric acid. The *d*-complexes are considered to be complexes of neutral malates with boric acid, the magnitude of the rotatory dispersion pointing to the fact that they are considerably hydrolysed in aqueous solution. J. S. C.

Rotatory Powers of Fluoro Derivatives of Benzene and its Homologues as a Function of the Wave-length. F. Rizzi (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 124—126).—The curves representing the dependence of the optical rotation of fluorobenzene, fluorotoluene, fluoro-*m-s.*-, and fluoro-*m-as.*-xylenes on the wave-length exhibit a change in direction at approximately zero rotation, the rotation being dextro for red and lævo for violet light. T. H. P.

Effect of Reading Errors on the Rotatory Dispersion Constants. R. Rinderknecht (*Helv. Chim. Acta*, 1925, **8**, 179—184).—The constants $[\alpha]_F/[\alpha]_C$, λ_a, λ^2_o were determined from readings of the rotations for the *C*-, *D*-, *E*-, and *F*-lines of a Schmidt and Haensch polarimeter. The quotient $[\alpha]_F/[\alpha]_C$ was found untrustworthy in the first decimal place for rotations under 3—6° (*C*—*F*) on account of reading errors of ±0·02 for a 0·5 dm. tube. In the citronellal group, the characteristic wave-length λ_a is untrustworthy for rotations less than 5—10° (*C*—*F*) and quite untrustworthy for rotations less than 3—6°. The values of the constant λ^2_o are strongly affected by the assumed reading errors and become untrustworthy for rotations of about 10° in the citronellal group. For maximum readings the second decimals, for minimum readings the third decimals, are untrustworthy. A. C.

Transparence of Varieties of Glass in the Infra-red. F. Liana (*Compt. rend.*, 1925, **180**, 578—579).—A sheet of flint glass

15·6 mm. thick showing complete absorption at 3·19 μ was found to transmit 74% of light of wave-length 2·75 μ. G. M. B.

Electrostatic and Electrodynamic Significance of Electrons in the Crystallisation of the Elements of the Fourth Periodic Group. J. BECKENKAMP (*Z. anorg. Chem.*, 1925, **143**, 394—404).—A continuation of previous work (A., 1924, ii, 754), with special reference to carbon. It is considered that the two inner electrons in the atom of this element may be replaced by four half electrons rotating in planes parallel to the faces of a tetrahedron. Since the positive charge on the nucleus is greater than the total negative charge of the inner electrons, there will be outside these a surface of zero potential, and the points of intersection of the normals to the paths of the valency electrons with this surface are described as epicentres. Carbon has four epicentres arranged at the corners of a tetrahedron, and since the four inner electrons are also arranged tetrahedrally, the neutral surface is nearly spherical. Such atoms may combine in two ways, (1) the epicentres of one half of the atoms (*b*) lie on points opposite the epicentres of the other half of the atoms (*a*); all the atoms are then similarly oriented and the neutral surfaces of atoms (*a*) contain 8 electrons whilst those of atoms (*b*) contain 4; (2) the epicentres of atoms (*b*) are at three corners of an eicositetrahedron; with respect to their epicentres, the two sets of atoms are indirect mirror images and the neutral spheres of atoms (*a*) contain 7 electrons whilst those of atoms (*b*) contain 4. The first form corresponds with diamond (type α_2) and leads to four groups of six-membered rings the axes of which are parallel to the normals of a tetrahedron. The second form (somewhat distorted) corresponds with graphite (β_2) and the axial ratios thus calculated agree with those found by W. L. Bragg. The form α_2 is electrostatically stable, but β_2 is labile, whereas the second possible electrostatically stable arrangement of the epicentres, the rhombic dodecahedron, is unknown among elements. There must therefore be some other controlling force, and this is believed to be magnetic. The two forms of carbon are the arrangements which are most perfectly astatic; the eight valency electrons of the noble gases and of sodium chloride are also arranged astatically, and the thirty electrons in benzene are arranged in several astatic groups. In the elements of the iron–platinum group, the arrangement is not perfectly astatic. The rupture of an astatic group absorbs energy and its formation releases it; the tendency to form astatic groups is therefore a consequence of the second law of thermodynamics.

A benzene formula is proposed which contains the same six-membered ring, which, according to Bragg, is present in both diamond and graphite; this has the maximum possible symmetry and the carbon atoms are equivalent. A. G.

Rare Earths and the Magneton. B. CABRERA (*Compt. rend.*, 1925, **180**, 668—671).—Measurements of the magnetic properties of oxides or sulphates of the rare-earth metals are described and from the values of Curie's constant the following numbers n of Weiss magnetons are calculated for each element: La 0, Ce 11·89,

Pr 17·89, Nd 18·00, Sm 7·64 (?), Eu 17·92, Gd 40·07, Tb 47·92, Dy 52·25, Ho 52·00, Er 46·98, Tu 35·85, Yb 21·64, Lu 0. The diamagnetism of the atom itself of samarium is probably appreciable, whilst in the atom of gadolinium there are two magnetic states with 38 and 40 magnetons, respectively. The number n of magnetons when considered as a function of the atomic numbers of the elements falls on two curves, the first from $n=0$ for La to $n=0$ for Eu, and the second from $n=0$ for Sm to $n=0$ for Lu, but their superposition between Sm and Eu is hypothetical. The difficulties of finding a physical interpretation of these results are discussed. G. M. B.

Nature of Hydrogen Halides. A. HANTZSCH (*Ber.*, 1925, 58, [*B*], 612—641).—On account of the great optical similarity of HI with $C_nH_{2n+1}I$ and of HBr with $C_nH_{2n+1}Br$ and optical difference from the much more feebly absorbent salt solutions, the hydrogen halides are to be regarded as homopolar compounds and therefore as the inorganic, initial members of the series of alkyl derivatives for which $n=0$. This is established also for the transparent chlorides by a simple rule of boiling points. The quotient obtained by dividing the absolute boiling point of HCl, HBr, HI by 6 and of the boiling points of the corresponding methyl, ethyl, propyl, etc. derivatives by 8, 9, 10, etc., is almost constant. The gap between the hydrogen and methyl derivatives, "the carbon increment," is due to the tetrahedral configuration of the molecule which occurs here for the first time in the series. Accordingly, HCl, HBr, and HI are not appreciably associated; this is confirmed indirectly by the exceptional relationship of dimolar hydrogen fluoride to the alkyl fluorides which follow the rule.

In aqueous, alcoholic, and ethereal solution, HBr is optically identical with solutions of potassium and ammonium bromide in contrast to nitric acid, which in alcohol and ether is optically similar to its esters, and hence has the *pseudo* form, $O_2N{\cdot}OH$; the halogen acid is therefore present as the hydroxonium bromides, $Br[H_3O]$, $Br[H_2OEt]$, $Br[HOEt_2]$, in these solvents, which function as basic anhydrides. On account of its instability, this could be established for hydrogen iodide only in aqueous solution, and not at all for hydrogen chloride by reason of its transparency. The strength of HCl, HBr, and HI has been determined (1) from the rate of inversion of sucrose under the influence of the three acids in highly concentrated aqueous solution, (2) by indicators in non-aqueous solution, and (3) by the decomposition of ethyl diazoacetate in the presence of these acids in as many media as possible. According to the inversion method, the acidity, which is approximately equal in dilute solution, increases with increasing concentration of each acid and for all three acids in the sequence, $HCl<HBr<HI$. In non-aqueous solution, hydrogen bromide is much stronger than hydrogen chloride; in addition, the acidity is very greatly influenced by the nature of the solvent. This is also established by the indicator method by determining the limit of inactivation, *i.e.*, the dilution at which the intensely coloured indicator salt is transformed by solvolysis into acid and the less intensely coloured, free indicator.

Thus hydrogen chloride is inactive towards *p*-dimethylaminazobenzene in water at $n=0{\cdot}0005$, in ether at $n=0{\cdot}02$. A more accurate modification of the indicator method which depends on comparison of colour shows that hydrogen chloride becomes much more rapidly inactive with increasing dilution in ether than in water. The diazoacetate method gives corresponding but more important results. According to the nature of acid and solvent, the decomposition takes place in a different manner chemically and as a change of the first or second order, but invariably depends primarily on the addition of acid and ester to yield a diazonium salt, $CO_2Et{\cdot}CH_2{\cdot}N(:N){\cdot}X$; this, and not the subsequent decomposition of the diazonium salt, is the change which is measured. The "diazo constants," R_{N_2}, and the corresponding activities, $R_{N_2}:N$ (normality) are entirely concordant with the values obtained by the other two methods. With increasing concentration, hydrogen bromide decomposes the diazo ester invariably much more rapidly than hydrogen chloride. The activities of the two acids in non-ionising solvents are greater and more distinct from one another when the solvent is most completely saturated in character, and thus are at a maximum and almost independent of dilution in chloroform and tetrachloroethane. In unsaturated hydrocarbons such as toluene, the activities are less and decrease with increasing dilution owing to formation of compounds of the type $HCl(C_7H_8)_n$, which are in part already known and become more stable with increasing dilution. Accordingly, the homogeneous hydrogen halides are most active, hydrogen bromide being more active than the chloride. These great differences are practically obliterated by the levelling action of water in consequence of the optically established additive formation of hydroxonium compounds, $X[H_3O]$ or $X[H\ldots(OH_2)_n]$. All reactions of these strong acids in dilute aqueous solution do not depend primarily on simple additive salt formation but on distribution of the acid between two basic anhydrides, one of which is water.

Hydrogen chloride and bromide differ in their behaviour in ethereal solution. The latter, which is shown by optical analysis to be present as the salt, $Br[HOEt_2]$, retains almost the same high activity as in chloroform or tetrachloroethane, and this is nearly independent of the dilution. The salt, therefore, decomposes very readily into its components and appears almost as strongly acidic as hydrogen bromide, in contrast with nitric acid, which optically resembles the esters in ethereal solution and is readily inactivated chemically by ether. The other great difference, that hydrogen bromide is present in water as hydroxonium salt but is much less active in this solution and moderately rapidly attains a minimum of acidity with increasing dilution, is due to the attachment, not only of its hydrogen atom to the oxygen of the water, but also of the hydrogen of the latter to its bromine atom, and, further, to the formation of aquo salts, $[Br(H_2O)]$, $[(H_2O)_nH]$, which, in consequence of the great heat of solution of hydrogen bromide in water, are much more stable than the salt, $Br[HOEt_2]$, and with increasing dilution become richer in water and hence additionally stable.

Hydrogen chloride, on the other hand, at moderate dilution rapidly becomes inactive towards indicators and ethyl diazoacetate in ethereal solution; it appears, therefore, to exist solely as the etherate of the *pseudo*-acid, ClH . . . OEt_2, thus resembling nitric acid. In contrast with the levelling action of water, ether increases the difference in acidity between hydrogen chloride and bromide, which in chloroform are approximately in the ratio 1 : 2, whereas in ether the ratio becomes almost unmeasurable at great dilution.

Hydrogen iodide is the strongest halogen acid as judged by its ability to invert sucrose in aqueous solution. Its character could not be observed directly in non-aqueous solutions on account of their instability. Indirect evidence is afforded by the observations that, in alcohol and ether, certain reactions which depend on the primary formation of oxonium salts as intermediate products occur most rapidly in the presence of hydrogen iodide (corresponding with its greatest tendency towards salt formation) and most slowly in the presence of hydrogen chloride. The chief reactions are the esterification of the halogen acids, $EtOH+HX \rightleftharpoons [EtOH_2]X \rightleftharpoons EtX+H_2O$, and the production of ether from alcohol in consequence of the "catalytic" (actually salt-forming) action: $2[Et{\cdot}OH_2]X \rightleftharpoons [Et_2OH]X+[HOH_2]X$. The apparently catalytic ability of the halogen acids to loosen the bond between alkyl group and hydroxylic oxygen in alcohols depends on the production of oxonium cations or *pseudo*-oxonium halides, in which the central oxygen atom is combined directly with 3 or 4 other atoms with consequent weakening of the linking between alkyl and oxygen.

The strengths of the homopolar hydrogen halides increases in the order HF < HCl < HBr < HI, which is also the order of activity of their alkyl derivatives, MeF < MeCl < MeBr < MeI. This is due to the same cause in each case. In consequence of its great heat of formation, hydrogen fluoride is the most stable *pseudo*-acid and has the smallest tendency to permit salt formation, either by the replacement of hydrogen by metal or by additive production of onium halides; in methyl fluoride, the halogen atom is most firmly attached to the carbon. Precisely the reverse is true for hydrogen iodide (with a negative heat of formation) and its alkyl derivatives. The apparent gap between hydrogen fluoride and the other halogen acids is bridged to some extent by the observation that whereas hydrogen fluoride, as the weakest acid, has a much smaller tendency than hydrogen chloride to form hydroxonium halides with water, so also hydrogen chloride only partly yields diethylhydroxonium chloride with the weakest basic anhydride, ether, whereas the corresponding compound with hydrogen bromide is completely stable. H. W.

Possible Structure of the Hydrogen Halides. F. J. VON WISNIEWSKI (*Z. Physik*, 1925, **31**, 869—876).—A model consisting of a positive hydrogen ion and a negative halogen ion rotating round their common centre of gravity leads to impossible values of the ionisation potential. If it is assumed that the hydrides consist of a positive halogen ion and a positive hydrogen ion at rest in the

axis of the molecule, whilst two electrons rotate at the ends of a diameter in an orbit with plane perpendicular to the axis (as in the Bohr–Debye hydrogen molecule), the calculated ionisation potentials are near the observed values, and the calculated moments of inertia agree with those indicated by the rotation–vibration spectra.

E. B. L.

Internal Pressures produced by Chemical Affinity. T. W. RICHARDS (*J. Amer. Chem. Soc.*, 1925, 47, 731—742; cf. A., 1924, ii, 723).—Problems involved in attempts to calculate the enormous internal pressures determining the existence of chemical compounds are considered, a more exhaustive treatment being promised later. Some tentative results are recorded, which, although not very trustworthy, show that the chemical pressures are much greater than the cohesive pressures. The heat energy necessary for evaporation and thermal dissociation is probably of the same order as the work needed to overcome the cohesive and chemical pressures, respectively.

J. S. C.

Geometry of the Co-ordination Number. I. R. STRAUBEL (*Z. anorg. Chem.*, 1925, 142, 133—134).—A theoretical paper directed towards the quantitative treatment of the maximum co-ordination number, sought by Hüttig. Values are given for the radius of n equal spheres (where $n = 3$ to 12), representing co-ordinated atoms or groups, packed round a central sphere, representing the central atom, and touching it. The percentage of the surface of the central sphere "covered" by the planetary spheres is also calculated.

N. H. H.

Geometry of the Co-ordination Number. II. G. F. HÜTTIG (*Z. anorg. Chem.*, 1925, 142, 135—142).—From the results of Straubel (cf. preceding abstract), the theoretical relation between maximum co-ordination number and atomic volume has been worked out. By application of the figures to the ordinary atomic volume curve, the elements fall into areas each of which corresponds with a particular maximum co-ordination number. Although many exceptions may be cited, the results on the whole are in striking agreement with the facts.

N. H. H.

Solid State from the Electrical Point of View. Dispersion in the Hertzian Region. J. ERRERA (*Bull. Soc. chim. Belg.*, 1925, 34, 35—38).—The variation of the specific inductive capacity with frequency at temperatures both in the vicinity of, and far removed from, their melting points has been determined for ice and other solids. At all temperatures, the specific inductive capacity increases with the wave-length, especially at the melting point, although at lower temperatures the increase becomes very small, and practically no variation in the specific inductive capacity of ice is found between −47° and −200°. A sudden change in the value occurs on solidification, a diminution occurring with high frequencies, but an increase with low frequencies. The author suggests that two phenomena are concerned in electrical polarisation, (1) the movement, linear or angular, of the atoms, molecules, or ions, (2) the

movement of the electrons in the interior of each particle, and shows how the relative importance of these effects varies with the frequency and the temperature. At low temperatures, the former is negligible compared with the latter, and the specific inductive capacity is, therefore, almost independent of frequency, but the importance of the latter increases as the temperature rises. At high frequencies, the first effect is practically eliminated and the specific inductive capacity approaches a limit which is independent of temperature and thus from the electrical point of view the solid state begins at a different temperature according to the frequency, illustrating the continuity of state. J. W. B.

Valency Problems. E. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 143—157).—The author develops a scheme for the graphic representation of chemical compounds by an extension of the theory that atoms have a tendency to form an outer shell having the "inert gas number" of electrons, namely, eight. The number of electrons in the outer shell is denoted by strokes attached to the atomic symbol in a manner similar to the representation of ordinary valency. To simplify the formulæ, a thick stroke may be used to denote two electrons and a thin stroke one electron. Compounds may be either "heteropolar," in which electrons are given up by one component to "satisfy" the outer shell of the other, resulting in two oppositely charged ions, or may be "homopolar," in which the electrons are shared by the components. Application of the scheme serves to throw light on problems presented by the following: aliphatic and aromatic double bonds; the benzene ring and other single ring systems; naphthalene and other condensed ring systems; conjugated double bonds; bivalent carbon; quadrivalent oxygen; vinyl alcohol; nitro and *pseudo*-nitro compounds; chlorine dioxide; the oxides of nitrogen; ammonium salts; triphenylmethyl; the change from propyl to *iso*propyl alcohol; the formation of alcohol and carbon dioxide from sucrose; the hydration of ions; polymerisation. Reference is made to the views of Knorr (A., 1924, ii, 34). N. H. H.

Periodic Sphere and Position of the Rare-earth Metals. J. N. FRIEND (*Chem. News*, 1925, **130**, 196—197).—The elements are arranged in the form of a spiral coiled round the surface of a sphere. The rare-earth elements lie in the equatorial belt and show marked resemblances to adjacent elements. Many regularities not hitherto attainable are revealed. According to this scheme, the missing element 61 belongs to group V, and the metals of group VIII appear as a sub-group of group 0. F. G. T.

Physical Structure of the Elements. C. G. BEDREAG (*Compt. rend.*, 1925, **180**, 653—655; cf. *ibid.*, 1924, **179**, 768).—The probable distributions of electrons in the atom are described for elements of variable valency such as manganese, chromium, iron, sulphur, chlorine, and phosphorus. The reduction of valency corresponds with the transfer of various numbers up to eight of the mobile outer

electrons to a more permanent inner shell. The configurations proposed are supported by a consideration of the magnetic properties for the metals chromium, manganese, iron, and cobalt, and of discontinuity in absorption for sulphur, phosphorus, and chlorine, the frequency of such discontinuity being found to be largest for the element in the state of maximum valency, as is required by theory.

G. M. B.

New Determination of the Constant N of Avogadro. L. M. ALEXANDER (*Phil. Mag.*, 1925, [vi], **49**, 663—664).—Du Noüy's paper (this vol., ii, 109) contains errors. The probable error is $\pm 0{\cdot}009$ instead of $\pm 0{\cdot}08$. The value $N=(6{\cdot}003\pm 0{\cdot}009)\times 10^{23}$ is different from that of Millikan $N=6{\cdot}062\times 10^{23}$ by 1% and not 0·1% as claimed. Du Noüy's three experiments are dependent on one another; his "control" calculations are fallacious.

R. A. M.

Molecular Diameters. H. SIRK (*Phil. Mag.*, 1925, [vi], **49**, 708—711).—A re-statement (cf. this vol., ii, 184) showing that conclusions similar to Mokroushin's (A., 1924, ii, 820) had been reached independently. R. A. M.

Heats of Combustion of Three Oxides [α-Propylene Oxide, α-Trimethylethylene Oxide, and γδ-Hexylene Oxide]. P. W. ZUBOW and W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], **37**, 271—274).—The molecular heats of combustion at constant pressure of the above three (liquid) oxides, in the order named, are 450·5, 748·8, and 912·6 kg.-cal., respectively. Assuming Trouton's rule and taking the specific heat of each oxide as 0·55, the molecular heat of fusion over the range 18° to the boiling point, $t°$, is given by the expression: $0{\cdot}55M(t-18)+20{\cdot}7(273+t)$ The heats of combustion of the three oxides in the gaseous state are then calculated to be 467·4, 758·7, and 925·6 kg.-cal., respectively. S. K. T.

Thermochemistry of the α-Oxides. W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], **37**, 274—276).—From results previously recorded (see preceding abstract) the heats of formation of the carbon–carbon and carbon–oxygen linkings in the ethylene oxide ring are shown to differ from the values obtained in saturated hydrocarbons and carbon dioxide; the values also vary with the number of carbon atoms in the ring. They increase when the hydrogen atoms in ethylene oxide are replaced by methyl or ethyl groups.

S. K. T.

Molecular Heat of Combustion of Successive Terms of Homologous Series. P. E. VERKADE, H. HARTMAN, and J. COOPS, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 859—866).—The heats of combustion of the first twelve members of the oxalic acid series have been determined. At least two preparations of each acid were burned, the heats of combustion being based on that of benzoic acid, 6324 cal. per g. The results obtained agree well with those of Stohmann and his collaborators (A., 1889, 1097; 1893, ii, 59). Oxalic and malonic acids give

abnormally high values, whilst the other acids fall into two thermal homologous series, the odd and the even series, one series being shifted about 1·5 cals. with respect to the other. There are indications of a similar alternation of heat of combustion increments in the series of monoalkyl-substituted malonic acids, and that the alternation is of about the same order of magnitude. According to Garner and Randall (A., 1924, ii, 385), the heats of crystallisation of the normal fatty acids also show an alternation in the successive terms of the homologous series. The question is discussed as to whether the oscillation of the combustion heat increments in the crystalline normal saturated dibasic acids is due, partly or entirely, to a different crystal structure of the even and odd terms. To decide this, the molecular heats of combustion for the crystalline acids should be compared with those of the supercooled, liquid acids at the same temperature (19·5° in this case). A scheme of research to investigate a number of problems in connexion with this is outlined. L. L. B.

Dissipation of Heat of Reaction. M. Born and J. Franck (*Ann. Physik*, 1925, [iv], **76**, 225—230).—A theoretical paper in which the removal of the excess energy from a recently formed molecule by collision (Pólányi, *Z. Physik*, 1920, **1**, 337; Herzfeld, *ibid.*, 1922, **8**, 132), or by the emission of light rays (Lewis, A., 1920, ii, 100), is discussed. It is possible for a molecule to contain, without decomposition, a greater amount of energy than that required for dissociation. In the formation of non-polar molecules from neutral atoms or molecules no radiation is possible, but when polar molecules are obtained the removal of energy may take place by either method depending on the pressure. M. S. B.

Dissolution of Mixed Crystals of (Na,Ag)Cl and Tammann's *n*/8 Mol. Law. M. Le Blanc and A. Rössler (*Z. anorg. Chem.*, 1925, **143**, 1—59).—Rapid cooling of a fused mass of silver chloride and sodium chloride leads to a more coarsely dispersed solid than freezing brought about slowly and with constant stirring. By long tempering just below the m. p., further homogeneity is obtained. A study of the rate of solution of the mixed crystals by means of conductivity measurements showed that tempering essentially altered the attackability by saturated silver chloride solution. In the quenched untempered mixture, the relative quantity of sodium chloride going into solution rose continuously with increasing original sodium chloride content. The tempered solid, up to about ⅛ mol. silver chloride content, gave up its sodium chloride more rapidly and more completely than the corresponding untempered mixture. A strong retardation of the rate of solution was observed, however, with a silver chloride content of 0·68 mol. In the quenched solids, spontaneous decomposition of larger particles occurred at a sodium chloride content of 0·9 mol., whilst with tempered particles it was observed at 0·6 mol. With more resistant mixtures, the sodium chloride was given up slowly even after 800 hours' action of the solvent. For crystals of the same composition, the relative mass of sodium chloride given up increased with decreasing size of the

particles. Therefore only large particles of tempered mass with more than 0·68 mol. of silver chloride can be regarded as practically resistant. A comparative study was made for tempered and untempered particles of the colouring effect on the mixed crystal of hydrogen sulphide and of sunlight. An endeavour was made to explain the various results in terms of dispersoid chemistry, and it was concluded that the $n/8$ mol. law of Tammann is only approximately true, and that sharp resistance limits do not exist.

L. L. B.

X-Ray Investigation of some Mixed Crystals of the Systems (Na,Ag)Cl and K(Cl,Br). B. H. Broomé (*Z. anorg. Chem.*, 1925, **143**, 60—75).—The possibility of distinguishing disperse from homogeneous structures by means of *X*-ray analysis is discussed, and an attempt is made to confirm Tammann's hypothesis of regular atomic distribution. In the quenched masses of the system (Na,Ag)Cl, two kinds of lattice are found, of which the dimensions differ very little from those of the pure components. The "tempered" masses behave differently. For a mixed crystal of the composition $\frac{3}{8}$ mol. of sodium chloride and $\frac{5}{8}$ mol. of silver chloride, the sodium chloride lattice disappears after tempering. Such a crystal is relatively stable, whereas that containing $\frac{4}{5}$ mol. of sodium chloride and $\frac{1}{5}$ mol. of silver chloride decomposes at the ordinary temperature into two lattices which have the same dimensions as those of the quenched preparation. The observations confirm the conception of Le Blanc and Rössler (cf. preceding abstract) that a quenched mass is a dispersion of sodium chloride aggregates containing a little silver chloride in a molecular dispersed mass of (Na,Ag)Cl rich in silver chloride. The view that a finer structure is produced by tempering also receives confirmation. From a study of the *X*-ray spectra of the systems (Na,Ag)Cl and K(Cl,Br), it is concluded that the normal distribution postulated by Tammann does not exist.

L. L. B.

Extraction Limit of the NaCl–AgCl Mixed Crystal. G. Tammann (*Z. anorg. Chem.*, 1925, **143**, 76—79).—The work of Le Blanc and Rössler and of Broomé (cf. preceding abstracts) is criticised, and it is pointed out that, according to Schmidt (*Diss.*, Göttingen, 1917), the NaCl–AgCl mixed crystal cannot be obtained in a state of sufficient homogeneity to render it suitable for use in testing the $n/8$ law. It is probable that, if a completely homogeneous mixed crystal were obtained, an influence-boundary would be found at $\frac{6}{8}$ mol. of silver chloride.

L. L. B.

X-Ray Investigation of Saturated Aliphatic Ketones. W. B. Saville and G. Shearer (*J. Chem. Soc.*, 1925, **127**, 591—598).—A continuation of the work of Müller and Shearer (*ibid.*, 1923, **123**, 2043, 3152, 3156) on *X*-ray measurements of the higher members of the fatty acid series and their esters, in which it was shown that the spacings obtained represent within narrow limits the length of a single molecule or, in certain circumstances, of two molecules end to end. Sixteen ketones have been investigated, the

number of carbon atoms varying from 13 to 35. The substances fall into two sets, in each of which the spacing is a linear function of the number of carbon atoms, the increase per carbon atom being greater for the methyl ketones than for the others. Confirmation of the view that the presence of the active group, $-CO\cdot CH_3$, produces a tendency for the molecules to arrange themselves end to end in pairs is obtained from the fact that if the spacings of the methyl ketones be halved, the resulting values fall on the same straight line as for the remainder, in which the increase per CH_2 group is 1·30 Å. Although the position of the CO group has no effect on the length of the molecule, which appears to be a function of the total number of carbon atoms alone, it has a marked influence on the intensity distribution. This peculiar property may be used to locate within reasonably narrow limits the position of carbonyl groups in ketones from considerations of intensity distribution. The suggestion that these substances are not truly crystalline, but rather in an intermediate condition between the liquid and solid states, is considered to be untenable. J. S. C.

Further *X*-Ray Measurements on Long-chain Compounds (*n*-Hydrocarbons). A. Müller and W. B. Saville (*J. Chem. Soc.*, 1925, **127**, 599—603; cf. preceding abstract).—Ten normal hydrocarbons, the number of carbon atoms ranging from 17 to 35, have been investigated by the *X*-ray method. Two characteristic spacings are common to all the substances, one relatively large spacing which is a linear function of the number of carbon atoms and another set which is almost independent of this. The increase per carbon atom of the long spacing, 1·3 Å., is considerably larger than the value predicted from considerations of the theory of Müller and Shearer (T., 1923, **123**, 3158). Octadecane and eicosane have been shown to exist in two crystalline modifications. J. S. C.

X-Ray Researches on the Dehydration Products of Gypsum. H. Jung (*Z. anorg. Chem.*, 1925, **142**, 73—79).—Hydrated and anhydrous forms of calcium sulphate, both natural and artificial, have been examined by the *X*-ray method of Debye and Scherrer. All give results corresponding with $CaSO_4.2H_2O$, $CaSO_4.0{\cdot}5H_2O$, or $CaSO_4$. The gradual loss of water by the hemihydrate when heated up to 200°, does not alter the lattice structure; only at higher temperatures is the anhydrite structure formed. N. H. H.

Variation with Temperature of the Intensity of Reflexion of *X*-Rays from Quartz and its Bearing on the Crystal Structure. R. E. Gibbs (*Proc. Roy. Soc.*, 1925, **A**, **107**, 561—570).—Intensity of reflexion was measured at various temperatures up to 800°, also on cooling both rapidly and slowly. The results are in agreement with a transition point at about 575°. The oxygen atoms cannot lie in the same basal planes as the silicon, but in a plane between at a distance from them, d=0·63 Å. E. B. L.

Effect of a Surrounding Box on the Spectrum of Scattered *X*-Rays. A. H. Compton and J. A. Bearden (*Proc. Nat. Acad. Sci.*, 1925, **11**, 117—119).—In a recent paper by Allison, Clark, and

Duane (*ibid.*, 1924, **10**, 379), it appeared that the spectrum of the scattered *X*-rays altered considerably when the tube and the radiator were surrounded by a wooden box. It was suggested that the modified lines were due to tertiary radiation from the carbon of the wood. The present authors find no measurable " box effect." Woo, collaborating, examined the *K*-rays from a molybdenum target after scattering from magnesium, aluminium, silicon, and sulphur; the normal and modified lines appeared whether the wooden box was lead-lined or not.

A second experiment was made using sulphur as radiator, with no box, and a modified Seeman spectrograph. The photograph shows the $K\alpha$- and $K\beta$-lines distinctly, with a more diffuse modified α-line and indications of a modified β-line. Compton's formula requires a wave-length change for the α-line of $0{\cdot}036 \pm 0{\cdot}001$ Å.; measurement gives the value 0·037 Å. There is thus no evidence in this work for the Duane effect. R. A. M.

Compton Effect and Tertiary X-Radiation. Y. H. Woo (*Proc. Nat. Acad. Sci.*, 1925, **11**, 123—125; cf. preceding abstract).—Clark, Duane, and Stifler (A., 1924, ii, 368) have measured the wave-lengths of molybdenum $K\alpha$-rays scattered from ice, rock-salt, aluminium, and sulphur and find tertiary radiation (Duane effect) to be present. The author has now used rock-salt, magnesium, aluminium, silicon, and sulphur as secondary radiators. In all five cases the $K\alpha$-line appears unmodified together with a modified line the peak of which occurs at the position predicted by Compton's formula. The " tertiary " peak was not observed in any experiment, nor was any box effect recognised. R. A. M.

Compton and Duane Effects. G. E. M. Jauncey (*Nature*, 1925, **115**, 456—457).

Quantum Theory of the Unmodified Spectrum Line in the Compton Effect. G. E. M. Jauncey (*Physical Rev.*, 1925, [ii], 25, 314—321).—If certain assumptions are accepted, there must be certain positions of the electron in its orbit from which the electron cannot be ejected by the primary quantum. The mass of the whole atom is then added to that of the electron, and the change in wave-length given by Compton's equation, $\lambda_\phi - \lambda_0 = h(1-\cos\phi)/mc$, where ϕ is the angle of scattering, is negligible. Application of the theory to molybdenum K_α-rays scattered by the *K* electrons of carbon yields results in accord with known experimental data.

A. A. E.

Crystal Structures of Hæmatite and Corundum. L. Pauling and S. B. Hendricks (*J. Amer. Chem. Soc.*, 1925, **47**, 781—790).—A thorough *X*-ray study of crystals of hæmatite and corundum has been made, utilising the results of the theory of space groups in the interpretation of data from Laue and spectral photographs. The arrangement of atoms in the units of structure is such that each metal atom is surrounded by six atoms of oxygen which are not at the corners of a regular octahedron, three of these atoms being a few per cent. nearer the metal than the others. This indicates

that the location of electrons in the outer shells of an ion causes it to have different effective radii in different directions. The differences between the two oxygen–metal distances for hæmatite and corundum are in agreement with the conception that an iron ion with 23 electrons, with a volume only slightly larger than the 10-electron aluminium ion, would approximate much more closely to a sphere than would the aluminium ion. Each oxygen atom is surrounded by four metal atoms, two of which are nearer than the other two. The structures determined show that crystals of hæmatite and corundum consist of a compact arrangement of approximately spherical ions of oxygen and of iron or aluminium held together by inter-ionic forces of an electrostatic nature. The inter-ionic distances for hæmatite are: smallest oxygen–oxygen distance $2{\cdot}545\pm0{\cdot}060$, metal–oxygen distances $2{\cdot}060\pm0{\cdot}035$ and $1{\cdot}985\pm0{\cdot}025$ Å.; the corresponding numbers for corundum are $2{\cdot}495+0{\cdot}025$, $1{\cdot}990\pm0{\cdot}020$, and $1{\cdot}845\pm0{\cdot}015$ Å. J. S. C.

Crystal Structure of Tellurium and Selenium and of Strontium and Barium Selenides. M. K. Slattery (*Physical Rev.*, 1925, [ii], **25**, 333—337).—In addition to results already abstracted (A., 1924, ii, 849, 859), the following calculated densities are given: selenium, 4·84; tellurium, 6·25; strontium selenide, 4·53. A. A. E.

Electrolysis of Crystals. P. Lukirsky, S. Sčukarev, and O. Trapesnikov (*Z. Physik*, 1925, **31**, 524—533).—Crystals of rock-salt were clamped between metal electrodes at temperatures from 300° to 600° and submitted to potential differences from 300 to 3000 volts, whereby currents approaching 1 ma. become possible. The passage of current is permitted by motion of the crystal lattice, but essentially by the sodium, not the chlorine ion. Sodium is liberated at the cathode and chlorine at the anode and in conformity with Faraday's law. Fern-like structures are produced in the crystal at the electrodes, in some cases coloration, and the crystal structure breaks down in numerous centres inside the crystal. E. B. L.

Magnetic Properties of Iron Crystals. W. L. Webster (*Proc. Roy. Soc.*, 1925, **A**, **107**, 496—509).—Thin discs were cut from crystals of iron and the component of the magnetisation was measured parallel and perpendicular to the applied field. The results may be explained by the theory of Weiss, the deviation in the direction of magnetisation being ascribed to a "molecular field" due to the mutual action of the molecules of the crystal. The magnitude of this field was found to be 620 and 479 gauss, respectively, for two crystals; impurities affect the value considerably. The molecular field is considered not to be due to magnetic forces. E. B. L.

Relationship between Atomic Numbers and the Properties of Ions in the Crystal Lattice. A. F. Scott (*J. Physical Chem.*, 1925, **29**, 304—318).—The relation $d_0=a\log(Z_c-Z_a)+b$, where d_0 is the shortest distance between ions, Z_c-Z_a represents the absolute

value of the difference of the atomic numbers of the cation and anion, and a and b are constants, gives in a number of cases a linear relationship between lattice distance and a function of the atomic numbers. For elements, the equation becomes $d_0=a\log(Z+e)+b$, where d_0 is equal to one-half of the distance of nearest approach of ions, Z is the atomic number of the element, and e represents the number of valency electrons or the maximum valency of the element.

M. B. D.

Crystal Deformation and Hardening. M. Pólányi (*Z. Metallk.*, 1925, **17**, 94—95).—It is shown that the assumption that a thin layer of crystal dust is formed along the slip boundaries of metals as the result of cold work, whilst the remaining crystal grains are distorted but not broken, will account for the phenomena of hardening by cold work and recrystallisation on annealing, as well as for those exhibited by X-ray examination of the worked metal. [Cf. *B.*, 1925, 322.] A. R. P.

Hardening of Metals. G. Sachs (*Z. Metallk.*, 1925, **17**, 85—93).—From an extensive review of the results of previous investigators together with his own results the author concludes that the hardening of metals by cold work is due to distortion of the lattices, bending of the slip planes, or the development of internal stress varying in intensity from place to place; on annealing, the internal stress is relieved by the re-forming of the lattices. Hardening by alloying to form a solid solution is due to bending of the slip planes by the entrance of the solute atoms into the space lattices of the solvent and consequent distortion of the lattices; the hardening effect increases with an increase in the difference in size between the atoms of the solute and the solvent and with the number of the solute atoms. Hardening by heat treatment depends on the setting up of internal stress or internal deformation of the crystallites caused by volume changes due to the decomposition of solid solutions. The hardness of heterogeneous mixtures may be explained by considerations based on the size, shape, and distribution of the particles of the constituents, whilst that produced in eutectic mixtures by quenching from the liquid state is due to cold deformation of the crystallites or to a state of internal stress set up by the sudden cooling. The influence of decreasing grain size on the hardness of metals may be explained by the production of a very uneven state of internal stress due to deformation. [Cf. *B.*, 1925, 322.]

A. R. P.

Tensile Strength of Zinc and Cold Working. G. Masing and M. Pólányi (*Z. Physik*, 1924, **28**, 169—176).—The tensile strength of freshly-rolled zinc at 85° Abs. is 45 kg./mm.^{2}, and is much increased by cold rolling. The tensile strength is greater for samples composed of fine grains than for those of coarse grains, and is smaller for single crystals. S. B.

Strength and Elastic Limits of Rock-salt. A. Joffé and M. Lewitsky (*Z. Physik*, 1925, **31**, 576—583).—The breaking strain of rock-salt crystals of different area of cross-section was

found to be independent of the area; the presence of moisture may account for the different results of other workers. One piece of crystal which, when dry, broke under a load of 450 g./mm.^{2} remained unbroken under a stress of 4000 g./mm.^{2} when in water. The elastic limit for compression and extension is not affected by water and is about 920 g./mm.^{2} at the ordinary temperature. For bending, the transition temperature from brittle to plastic is about the ordinary temperature. E. B. L.

Strength and Elastic Limits of Natural Rock-salt. W. EWALD and M. PÓLÁNYI (*Z. Physik*, 1925, **31**, 746—749; cf. preceding abstract).—The authors claim that the increased strength of rock-salt crystals in water is due to the action of the water while the crystal is under stress and not merely to any change in the surface caused by solution; there is an internal change in the crystal, and the resistance to plastic change of shape is diminished. E. B. L.

Magnetochemistry of Polymerides. P. PASCAL (*Compt. rend.*, 1925, **180**, 664—666; cf. A., 1924, ii, 39, 171, 605, 856).—Values for the molecular susceptibility are recorded for ten distinct phosphates of various degrees of complexity, and from these figures, assuming a constant atomic susceptibility for the metal, the value contributed by the radical PO_3 is calculated for each compound, as follows: sodium monometaphosphate, 333; Maddrell's sodium salt, 325; sodium trimetaphosphate, 315; sodium tetrametaphosphate, 298; Graham's hexametaphosphate, 289; ethyl hexametaphosphate, 277; the three colloidal salts of Kurrol, 266, 268, and 268, and the non-colloidal salt, 254×10^{-7} C.G.S. units. From the known complexity of the mono-, tri-, tetra-, and hexa-metaphosphates and the regularity of the above figures, the conclusion is reached that Maddrell's salt is a dimetaphosphate, that Kurrol's colloidal salts are three forms of an octometaphosphate, and that the non-colloidal salt is probably a decametaphosphate. The change in diamagnetism with increased complexity is in the same direction and of the same order of magnitude as that caused by double bonds in organic compounds. G. M. B.

Magnetic Quality of Pure Nickel. A. M. MALCOLM (*Proc. Roy. Soc. Edin.*, 1924, **44**, 206—208).—Pure nickel has no retentivity and the susceptibility and permeability are constant. In a field of 9·18 gauss the susceptibility is 4·17 and the permeability 53·53 with a horizontal rod. In the same field and with the rod vertical, the values are 4·20 and 53·77, respectively. In these weak fields, the magnetic qualities are independent of stresses in the metal.

A. E. M.

Photomagnetic Properties of the Silver Halides. A. GARRISON (*J. Amer. Chem. Soc.*, 1925, **47**, 622—625).—The magnetic permeabilities of the silver halides are increased by the visible radiation, the chloride becoming less diamagnetic and the bromide and iodide more paramagnetic on illumination. Rise in temperature brings about a similar increase in permeability, the change being, however, comparatively slow. It is pointed out that an increase

in magnetic permeability will be accompanied by a parallel increase in electrical polarity. This view is supported by the fact that illumination increases the solubility and electrical conductivity of these halides. J. S. C.

Magnetic Properties of the 50% Iron–Nickel Alloy. T. D. YENSEN (*J. Franklin Inst.*, 1925, **199**, 333—342).—The magnetic and electrical properties of the 50% alloy determined by the author (*Trans. Amer. Inst. Elec. Eng.*, 1920, **39**, 791) are compared with those of the 78% Ni–Fe alloy (Arnold and Elmen, *J. Franklin Inst.*, 1923, **195**, 621), of pure iron, and of a 4% Si–Fe alloy. The 50% alloy has a much lower hysteresis loss and a higher permeability and resistance than pure iron, but, to preserve these properties, must be annealed in a reducing atmosphere. [Cf. *B.*, 1925, 320.] F. G. T.

Transformation of Nickel in the Neighbourhood of the Curie Point. W. DEL REGNO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 179—181).—The transformation of ferromagnetic α-nickel into the paramagnetic β-variety, with its accompanying changes in other physical properties, seems not to take place at any one definite temperature, but to occupy a range of temperature extending over about 100°, namely, 300—400°. Certain properties of the metal show a variation as soon as the smallest portion of the metal has undergone the change, whereas others require an appreciable proportion of the whole mass to undergo the transformation before they exhibit any peculiarity. T. H. P.

Effect of some Inorganic Salts on the Polarisation of Raw Sugar Solutions. R. J. BROWN (*Ind. Eng. Chem.*, 1925, **17**, 39—40).—The following values for K in the formula of Jackson and Gillis (cf. A., 1921, ii, 67) for the calculation of the effect of a salt on the polarisation of a solution of sucrose are given: sodium chloride, 0·00246; potassium sulphate, 0·00199; sodium sulphate, 0·00205, and disodium phosphate, 0·00305. For solutions of raw sugar, containing 10—15% of sucrose and about 5% of ash, the decrease in the polarisation caused by sodium chloride, for example, would be less than 0·01%, and is therefore negligible. J. P. O.

Significance of Cold Working in the Light of Electrical Measurements. II. W. GEISS and J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1925, **143**, 259—267).—The specific resistance of tungsten is increased to 160% and the temperature coefficient reduced to 60% of the original value by drawing to fine filaments at the ordinary temperature. The law of Matthiesen, that for mixed crystals the product of the specific resistance and the temperature coefficient remains constant, is found to apply to a pure metal after working in the cold. The change in conductivity is not due to lattice modification, nor to change in orientation of atomic axes; it is connected, as is also the change in mechanical properties, with the inter-crystalline relations. By cold working, as also by taking up a mixed-crystal component, the energy content of a metal is increased; calculation from the electrical measurements

indicates an increase of 775 cals. per g.-atom of tungsten after cold-working. S. I. L.

Measurement of the Ratio of the Specific Heats, using Small Volumes of Gas. Ratios of the Specific Heats of Air and of Hydrogen at Atmospheric Pressure and at Temperatures between 20° and −183°. J. H. BRINKWORTH (*Proc. Roy. Soc.*, 1925, **A**, **107**, 510—543).—The general method was the same as that of Clément and Désormes, except that the temperatures before and after expansion of the gas were measured by means of a compensated thermometer of platinum wire. For air, the values of γ at 17° and −118° were 1·4032 and 1·4154; for hydrogen at 17°, −118°, and −183°, the values were 1·4070, 1·4800, 1·6054. The variations of molecular heat with temperature were discussed; for hydrogen the experimental values are in better agreement with Callendar's formula than with the formulæ of Planck and Einstein. E. B. L.

Velocity of Sound and Ratio of Specific Heats of Organic Liquids. W. BUSSE (*Ann. Physik*, 1924, [iv], **75**, 657—664).—By modifying Doersing's method (A., 1908, ii, 153) of determining the velocity of sound in liquid in a Kundt's tube, measurements of the ratio of specific heats at constant pressure and constant volume have been made in a number of organic liquids, using aluminium or magnesium powder. The values obtained are in good agreement with those calculated thermodynamically. For compounds of the same homologous series, the ratio diminishes with increasing molecular weight if the phase remains the same, but increases in passing from a gaseous to a liquid member. Substitution of hydrogen in the alkyl or aryl group, especially by $-NO_2$, $-NH_2$, or $-OH$, appears to cause a decrease in the ratio. M. S. B.

Specific Heats of Carbon Monoxide and Hydrocyanic Acid Vapour. J. R. PARTINGTON and M. F. CARROLL (*Phil. Mag.*, 1925, [vi], **49**, 665—680).—Values of C_p/C_v ranging from 1·385 to 1·425 for carbon monoxide are recorded in the literature. Usherwood's results (T., 1922, **121**, 1604) for the specific heat of hydrogen cyanide are approximate only. The experimental methods used by the authors have been described earlier (A., 1923, ii, 214). Pure hydrogen cyanide was prepared by the action of hydrogen sulphide on mercuric cyanide, pure carbon monoxide by the action of cold concentrated sulphuric acid on sodium formate. The following results were obtained :—

Gas.	t.	P (mm. Hg).	$\gamma = C_p/C_v$.	C_p.	C_v.
Carbon monoxide	10·3°	760	1·404	6·94 cal.	4·94 cal.
Hydrogen cyanide	20·8	422	1·282	9·69 ,,	7·56 ,,
,, ,, ...	17·35	505	1·268	10·22 ,,	8·08 ,,

The values for carbon monoxide confirm those obtained by recalculating the more trustworthy earlier data. $C_p - C_v$ is given as 1·998 cals. The values of C_p and C_v and hence C_p/C_v for nitrogen and carbon monoxide agree closely. This might seem important, since the two gases have the same molecular weight and the same

number of electrons in the outer shell of the molecule according to the Lewis–Langmuir theory. Unpublished work on carbon dioxide and nitrous oxide shows that this agreement is fortuitous.

As the critical constants for hydrogen cyanide are not known, approximate values have been calculated by Walden's methods. The value of C_p/C_v given must therefore be regarded as provisional. Complicated factors make alternative interpretations possible, and it is concluded that since association almost certainly occurs in the gaseous state, specific heat data do not necessarily afford evidence of tautomerism in hydrocyanic acid. The applicability of Berthelot's equation of state to associated vapours is discussed, and thence it seems probable that association accounts for the results of Usherwood as well as for those of the authors. R. A. M.

Metastability of Elements and Compounds as a Result of Enantiotropy and Monotropy. E. Cohen and A. L. T. Moesveld (*Z. physikal. Chem.*, 1925, **115**, 151—159; cf. Cohen and others, A., 1924, ii, 382, 449, 603; this vol., ii, 23).—Examination of the methods by which the specific heats of the tin allotropes have been determined shows that the values obtained may be those of metastable mixtures of unknown composition. L. F. G.

Ratio Melting Point : Critical Temperature. J. J. van Laar and R. Lorenz (*Z. anorg. Chem.*, 1925, **142**, 189—192).—The equation $T_K/T_E=2/\gamma \cdot a_K/a_E+\gamma/(1+\gamma)$ is deduced. T_K and T_E are the critical and melting points, a_K and a_E the values for van der Waals' constant at the critical and melting points, whilst γ is the "reduced direction coefficient of the straight line joining d_K and $\frac{1}{2}d_0$," these symbols referring apparently to the density at the critical and zero points. N. H. H.

Melting Point and Vaporisation of Graphite. E. Rytschkewitsch (*Z. Elektrochem.*, 1925, **31**, 160).—A correction to a previous paper (see this vol., ii, 276). N. H. H.

Determination of the Melting and Transition Points of Potassium Dichromate. P. L. Robinson, G. E. Stephenson, and H. V. A. Briscoe (*J. Chem. Soc.*, 1925, **127**, 547—549).—A description of the phenomena accompanying the solidification and cooling of potassium dichromate is recorded. The salt separates from the fused state in a compact mass of dark brownish-red, tabular crystals with marked reduction in volume. On further cooling, the crystals change to a loose, orange-red powder. The m. p. of potassium dichromate was found to be $398{\cdot}4\pm0{\cdot}5°$ and the transition temperature of the two solid modifications, as determined by the thermometric method, $236{\cdot}8\pm0{\cdot}5°$. No evidence was obtained for the existence of two forms of the sodium salt.

J. S. C.

Properties of Simple Compounds and Types of the Solid State. E. Friederich (*Z. Physik*, 1925, **31**, 813—826).—The nitrides of zirconium, m. p. 3200° Abs., scandium, m. p. 2920° Abs., niobium, m. p. 2320° Abs., and erbium were prepared for the first

time by heating a mixture of the oxide with carbon in nitrogen at 1200°. The known nitrides of titanium, vanadium, boron, silicon, and lanthanum were similarly prepared. With the exception of tantalum, these nitrides have the same lattice form as sodium chloride. Carbides were prepared: titanium, m. p. 3400—3500° Abs.; zirconium, m. p. 3400—3500° Abs.; vanadium, m. p. 3100° Abs.; niobium, m. p. 4000—4100° Abs.; tantalum, m. p. 4000—4100° Abs.; molybdenum, Mo_2C, m. p. 2500—2600° Abs.; and MoC, m. p. 2840° Abs.; tungsten, m. p. 3150° Abs.; silicon, dissociates at 2220° Abs. The space lattices of the carbides of titanium, zirconium, vanadium, niobium, and tantalum were the same as that of sodium chloride. A list is given of compounds which exhibit metallic conductivity; the condition is that the metal should possess unsatisfied valencies. The classification of solids is based on the external fields of the valency electrons. The ionic lattice, as of sodium chloride, always shows electrolytic conductivity; the metallic conductivity of metals and their unsaturated compounds is due to the free valency electrons, and in some cases to the kernel electrons, and in these cases the metals show super-conductivity at low temperatures (cf. ii, 419). E. B. L.

Thermal Expansion of Alkali-metal Halides at Low Temperatures. A. Henglein (*Z. physikal. Chem.*, 1925, **115**, 91—120; cf. Baxter and Wallace, A., 1916, ii, 220).—The densities of the chlorides, bromides, and iodides of sodium and potassium have been determined at 0° and −79° by a pycnometric method. A gas-volumeter by which the densities of solid salts can be obtained at all temperatures is described. This was used at the ordinary temperature, 0°, −79°, and −184°, the results at 0° and −79° agreeing with those previously obtained. Fused salts have slightly higher densities than those crystallised from aqueous solution; this is ascribed to the enclosure of air, and perhaps mother-liquor, in the latter case. The coefficient of expansion decreases with decreasing temperature, and the ratio atomic heat/co-efficient of expansion is shown to be constant. The molecular volume at absolute zero can thus be calculated. The percentage change of molecular volume between −273° and 0° is approximately the same for each salt. For the same cation the coefficient of expansion increases with the atomic weight of the anion; for the same anion it decreases with increasing atomic weight of the cation. L. F. G.

Thermal Expansion of Aluminium and Various Important Aluminium Alloys. P. Hidnert (*U.S. Bur. Standards, Sci. Paper* 497).—The linear thermal expansion was determined for 4 samples of aluminium and 51 aluminium alloys. The formula $L_t=L_0[1+(22{\cdot}58t+0{\cdot}00989t^2)10^{-6}]$ represents the change in length between 20° and 600° for the purest cast aluminium (99·95%). Commercially pure rolled aluminium sheet (91·15%) showed a larger coefficient of expansion for nearly all temperature ranges. A series of cast aluminium–copper alloys containing 4—12% Cu showed a maximum between 6 and 8% Cu. The coefficients of expansion

of aluminium–silicon alloys decrease with increase in silicon up to 12%. The normal alloys showed irregularities at 250° which were not found when the alloys were modified with 0·1% of sodium. The expansion curves of zinc–aluminium alloys (Zn 77 and 95%) showed anomalous expansion at about 270°, due to the formation of β constituent. The coefficients of expansion were determined for duralumin in various conditions, and for the ternary alloys of aluminium with copper and silicon, and with copper and manganese. The permanent change in length of the specimens as a result of the heat treatment during test was recorded in each case. The expansion curves are discussed in connexion with the equilibrium diagrams for the alloys. [Cf., *B.*, 1925, 321.] C. S.

Van der Waals' Equation and the Liquid State of Aggregation. II. J. BERGER (*Z. physikal. Chem.*, 1925, **115**, 1—28). —A continuation of previous work (cf. A., 1924, ii, 654). Apart from the disturbance due to association, satisfactory results are obtained when Kopp's law is tested with the author's value for b. It is probable that the coefficient a is also additive. Deviations caused by association run parallel to deviations of thermal expansion and heat of vaporisation. The new values of a and b have been used in the calculation of compressibilities, critical volumes, saturation pressures, and boiling points. L. F. G.

Molecular Association and the Gas Equation of State. A. LEDUC (*Compt. rend.*, 1925, **180**, 502—505).—The gas equation obtained by Duclaux on theoretical grounds (*J. Phys. Radium*, 1924, [vi], **5**, 331) for a gas in which partial bimolecular association occurs is practically identical in conditions with that obtained previously by the author (*Compt. rend.*, 1923, **176**, 1132), viz., $p=RT[V/(V-A)^2-3\cdot160A(4\chi-1)/(V+A)^2]$, where A=molecular co-volume, V=g.-molar volume, R=gas constant, and χ=reciprocal of the reduced temperature. On the basis of these equations, the value of the heat of formation (Q), and the fraction of association (f) for carbon dioxide at various temperatures are calculated. It is found that in the saturated vapour f is about 0·4, and that the variation of Q is almost linear between 0° and 500°. The product fQ approaches zero as T is increased. J. W. B.

Viscosities of the Liquid Halogens. E. W. R. STEACIE and F. M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 754—762).—The viscosities of the liquid halogens have been investigated over the temperature ranges chlorine −76° to −34°, bromine −4° to +32°, iodine 116° to 179°, and the three viscosity–temperature equations obtained. The viscosity at the boiling point shows an increase with increasing atomic weight as expected from the periodic law. Evidence is put forward in support of the view that whilst chlorine and bromine have association factors in the liquid state of about 2, iodine possesses a higher degree of molecular complexity. J. S. C.

Thermal Diffusion Measurements. T. L. IBBS (*Proc. Roy. Soc.*, 1925, **A**, **107**, 470—486).—A glass cylinder was drawn out to a tube

at its lower end to which was attached a catharometer. When the cylinder was heated and the tube kept cold, the mixed gases tended to separate, the lighter gas going to the hot end, the catharometer measuring the change in composition in the cold end. Hydrogen and carbon dioxide, hydrogen and nitrogen, nitrogen and carbon dioxide, hydrogen and argon, and helium and argon were tried. The best separation was obtained in the last case; with 65% of helium in the mixture, the separation was 4·5%. E. B. L.

Vapour Pressure of Binary Mixtures. J. Brown (*J. Soc. Chem. Ind.*, 1925, **44**, 162T).—The divergence of the total vapour pressure of a binary mixture from the simple additive law is given by the expression $\Delta p_m=p_a(1-e^{-\Delta\lambda_a/RT})+p_b(1-e^{-\Delta\lambda_b/RT})$, where Δp_m= divergence of the total vapour pressure from that calculated from the simple mixture rule; p_a, p_b=vapour pressure of pure substances A and B; λ_a, λ_b the latent heats of vaporisation of the pure substances; λ'_a, λ'_b the latent heats of vaporisation of A and B in the mixture; $\Delta\lambda_a=\lambda_a-\lambda'_a$; $\Delta\lambda_b=\lambda_b-\lambda'_b$. The total vapour pressure of the mixture at temperature T may be expressed as a function of the concentration of one of the components, say B, thus: $p'_m=p_a+(p_b-p^n)\{(c_b-k)^n+k^n\}/\{(1-k)^n+k^n\}$, where n is a constant depending on the nature of the two substances A and B, c_b concentration of component B, k a constant. If the concentration of B is small when the divergence first becomes manifest $k=0$, and the equation becomes $p'_m=p_a+(p_b-p_a)c_b^n$. For mixtures of ether and 95% alcohol, $k\longrightarrow 0$, and $n=0{\cdot}69$. F. B.

Viscosity of Liquids containing Dissolved Gases. J. E. Lewis (*J. Amer. Chem. Soc.*, 1925, **47**, 626—640).—The viscosities and densities of the following solutions have been determined in concentrations ranging from zero to saturation at 25° and at atmospheric pressure: sulphur dioxide in carbon tetrachloride, acetone, benzene, toluene, xylene, ether, heptane, carbon disulphide, and acetone–water mixtures, chlorine in carbon tetrachloride, and hydrogen sulphide in chloroform. The complete series of mixtures of sulphur dioxide with ether, toluene, benzene, methyl alcohol, and carbon tetrachloride have also been examined. The viscosity and fluidity curves for these latter systems are discussed from the point of view of the mixture rule. J. S. C.

Copper and Silver Amalgams. G. Tammann and T. Stassfurth (*Z. anorg. Chem.*, 1925, **143**, 357—376).—The heating curves and microscopic structure of copper and silver amalgams have been studied. After prolonged heating at 100° amalgams with 5—76% of copper contain a crystalline compound X which on cooling forms CuHg by reaction with the surrounding liquid. The substance CuHg melts partly at 96·2°, and such amalgams when heated show halts at this temperature and at 149·9° corresponding with the crystals X. When the copper content is 40—76% mixed crystals containing 76% of copper are also present, and amalgams still richer in copper are homogeneous. Amalgams which have been allowed to harden at the ordinary temperature do not contain the crystals X,

and those with more than 25% of copper do not contain CuHg. Such amalgams show partial melting at 108—110°, but the heat of fusion of the crystals Y which are present is so small that no halt is seen on the heating curve; these crystals are intermediate in composition between X and CuHg, and are formed very slowly, thus accounting for the slow hardening of the amalgams.

Silver amalgams produced by heating turnings with mercury at 360° were found not to be homogeneous even after prolonged heating, and finely-divided silver prepared by the reduction of the chloride was therefore used. Amalgams containing 0·08—28·7% Ag consist of Ag_3Hg_4 and a saturated liquid amalgam containing 0·08% Ag. From 28·7% to 100% the composition is uncertain, but it is suggested that up to 83% it consists of Ag_3Hg_4 and mixed crystals containing 83% Ag, whilst richer amalgams are homogeneous. It is considered that the existence of other compounds is not proved. The slow hardening of the amalgams is due to the diffusion of liquid mercury into the solid mixed crystals, the mercury content of which increases with falling temperature.

A. G.

Definitions of Steel and Cast Iron. K. HONDA (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **13**, 187—191).—Neither the properties, which are variable, nor the method of production, which is not always known, are suitable criteria, but steel is completely defined as "an iron–carbon alloy with a content of carbon lying between 0·035 and 1·7%." The lower limit is given by the solubility of carbon in iron at the ordinary temperature, the upper limit being the maximum solubility of carbon in iron at high temperatures. On the same grounds, cast iron is defined as "an iron–carbon alloy with a content of carbon lying between 1·7 and 6·7%," the upper limit in this case representing pure cementite. C. S.

Reaction Limits of some Platinum Alloys. G. TAMMANN (*Z. anorg. Chem.*, 1925, **142**, 61—72).—The homogeneity of the mixed crystal alloys of platinum with nickel, copper, and silver has been investigated by means of determinations of the reaction limit with various reagents. The alloys were prepared by heating the intimately mixed powders of both components or of their compounds in an atmosphere of hydrogen. With the platinum–nickel alloys the normal reaction limit, viz., 25 mol.-% Pt, was found, but with platinum–copper it was 32%, and with platinum–silver greater than 35%. These abnormal results are explained by the assumption that after the removal of the atoms of the base metal from the surface of the alloy the protecting platinum atoms do not remain bound in the crystal lattice. N. H. H.

Electrical Conductivity of Metallic Solid Solutions. E. J. CUY (*Phil. Mag.*, 1925, [vi], **49**, 753—760; cf. Højendahl, A., 1924, ii, 647).—No satisfactory explanation of the catenary form of the electrical conductivity–composition curve of solid solutions has yet been given. Rayleigh regarded solid solutions as made up of submicroscopic particles of the pure components at the junctions of

which a Peltier counter-*E.M.F.* would decrease the conductivity. Another view was that the atoms of the second metal would lower the mean free path of the electrons and so increase the resistance. *X*-Ray analysis has rendered both views untenable. The curve for the system gold–silver, in which both kinds of atoms are equal in radius, is similar to the curves obtained for systems in which the atomic radii of the components are unequal. The view that the low conductivity is determined by differences in atomic size cannot therefore be valid.

It is assumed that the valency electrons, to which conduction is due, move in quantum orbits and that in a pure metal they are all in phase, *i.e.*, at the same instant they are all furthest from one atom, and nearest the adjacent one. Since rise of temperature increases the interatomic distance, the electron jump will be hindered and resistance increased. This source of resistance applies to both pure metals and solid solutions. Since, however, the vibration frequencies of the different atoms in the alloy are not the same, they cannot be in phase. The resistance of pure metals is entirely determined by the temperature, whereas only a part of that of solid solutions is affected; thus the temperature coefficient of the resistance of soil solutions should be, and in fact is, less than that of the pure metals. Similarly, the increased conductivity due to pressure can be ascribed to lessening "gap" resistance, and the pressure-coefficient of solid solutions should be less than that of their components. The supra-conducting state of pure metals is due to diminished "gap" resistance, but cannot occur in true solid solutions. In certain alloys where solution is incomplete, a few threads of atoms in phase may, however, render the alloy supra-conducting.

The assumptions account for the similarity of the conductivity–composition curves for various mixtures and for the absence of specific effects due to the properties of the second metal.

It also follows that the addition of a third or fourth metal will have little influence on the conductivity. R. A. M.

Fusibility and Viscosity of Glass. A. Lacrenier and P. Gilard (*Bull. Soc. chim. Belg.*, 1925, **34**, 55—65).—The variation of the viscosity and fusibility of glass with its composition is investigated. The fusibility is measured by determining the time necessary, at a given temperature, for the first drop of molten glass to fall when a known weight of the glass is fused in a platinum vessel fitted with a dropping tube. This period, expressed in seconds, gives the "fusibility number" for the glass, and the ratio of this to the corresponding value for a typical glass yields the "fusibility coefficient." The values of these coefficients for a number of glasses are given, and it is shown that the fusibility is diminished by a partial or total replacement of sodium by potassium, of lime by magnesia, and especially by a partial replacement of lime by alumina. A summary of the methods available for the determination of the viscosity of glass is given, and the authors apply their drop method used in the determination of the surface tension (*ibid.*, 1924, **33**, 119) to

determine the relative viscosities of glasses of different compositions. The period between the fall of two consecutive drops of molten glass from an orifice of circular section and known diameter is observed, and the time necessary for the fall of 1 g. of glass calculated. The results obtained for glasses of various compositions at temperatures of 1050° and 1150° are recorded, and it is shown that the viscosity is increased by the substitution of sodium by potassium and by the partial substitution of calcium by aluminium. The viscosity is decreased when the calcium is partly replaced by magnesium, especially in potash glasses, or by the addition of barium oxide. In soda–lime glasses the progressive diminution of calcium accompanied by a corresponding increase of sodium causes a regular variation in the viscosity. J. W. B.

Physico-chemical Composition of Glasses. P. Bary (*Rev. gén. Colloid.*, 1925, **3**, 1—8, 43—52).—The properties of glass can be explained by ascribing to it a colloidal structure, in which a crystalloidal alkali silicate (as Na_2SiO_3 or K_2SiO_3) is dissolved in a condensed and polymerised silicate of a bivalent metal, *i.e.*, $[CaO{=}(SiO_2)_4{=}CaO]_m$. Rigidity, which is due to the large size of the polymerised molecule, is gradually reduced on heating owing to depolymerisation and decondensation. [Cf. *B.*, 1925, 242.]

A. Cousen.

Solid Solutions. G. Bruni (*Chem. Reviews*, 1925, **1**, 345—375).

Solubility of some Inorganic Salts in Organic Solvents. R. Müller (*Z. anorg. Chem.*, 1925, **142**, 130—132).—The solubilities of silver nitrate in methyl, ethyl, *iso*amyl, and *iso*propyl alcohols, ethyl acetoacetate, acetone, pyridine, quinoline, aniline, acetonitrile, and benzonitrile, and of lead nitrate, aluminium bromide and iodide, manganous chloride, ferrous bromide, cuprous iodide, beryllium bromide, cadmium iodide, cerous chloride, lithium nitrate, sodium nitrite, ammonium nitrate, calcium nitrate, barium iodide, strontium nitrate, calcium chloride, magnesium bromide, zinc bromide and iodide in pyridine, lithium nitrate in acetonitrile and *iso*amyl alcohol, calcium nitrate in the latter and magnesium bromide in the former, are tabulated. All the salts of which the solubilities have been determined at more than one temperature show a positive temperature coefficient, with the exception of magnesium chloride in pyridine. Solvents belonging to the same class of organic substances show an increase of solvent power with increasing dielectric constant. The order of solubility of inorganic radicals of the same family is compared with the order in aqueous solutions.

N. H. H.

Aqueous and Acetone Solutions of Potassium Bromo- and Iodo-mercurates. M. Tourneux and [Mlle.] Pernot (*Compt. rend.*, 1925, **180**, 740—742).—The fact that the solubility of mercuric halides in water is increased on addition of small amounts of the corresponding sodium or potassium salts demonstrates the existence of soluble complexes of the type, mHg_2X, nKX. Solubility determinations in aqueous and acetone solutions show that

the value of the ratio $m : n$ is at least 2 for the bromides and 2·5 for the iodides (cf. A., 1919, ii, 344). J. S. C.

Co-precipitation of Radium and Barium Sulphates. H. A. DOERNER and W. M. HOSKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 662—675).—Investigations have been carried out to obtain a satisfactory explanation of the fact that in presence of a large excess of barium over radium, sulphate ions precipitate radium sulphate although the solubility product is not exceeded (Lind, Underwood, and Whittemore, A., 1918, ii, 144) and that barium sulphate will remove radium from radium–barium chloride solutions (Germann, A., 1922, ii, 16). The experimental method consists of a quantitative study of the reactions of a radium–barium chloride solution with (i) sulphuric acid and (ii) barium sulphate. The result of the addition of sulphuric acid is considered as a co-precipitation, and the action of barium sulphate a replacement, the essential difference between the two being that for the latter only the surface of the added barium sulphate comes into equilibrium with the radium–barium chloride solution, whilst in the former case each crystal layer as it forms is in partition equilibrium with the particular concentration of solution momentarily existing. Since the solution has a decreasing radium–barium ratio as the precipitation proceeds, the crystals are not of uniform composition throughout their mass. Equations representing in a fairly satisfactory manner the replacement and co-precipitation data are put forward. The conditions under which crystal growth occurs have a great influence on the equilibrium. The possibility of applying the equations deduced to the phenomena of adsorption and fractional crystallisation is discussed. J. S. C.

Influence of a Third Substance on the Critical Solution Temperature of Phenol and Water. J. DUCKETT and W. H. PATTERSON (*J. Physical Chem.*, 1925, **29**, 295—303).—On cooling a mixture of 36·1% phenol in water turbidity sets in at 66·0°. The opalescence, which occurs just above this temperature, polarises light, and there is a critical change in the angle just before turbidity sets in. For substances which are soluble only in water, the molecular rise of the critical solution temperature shows the following order: $Na > K > NH_4$ and SO_4 > hydrogen tartrate > Cl > Br > I = NO_3, which is the same as the Hofmeister series except that the iodide ion is equal to, instead of greater than, the NO_3 ion. Substances soluble in phenol only do not give the same change of critical solution temperature for equimolecular concentrations. An optically active tartrate and the racemate have an identical effect. Curves are given showing the changes in viscosity and electrical conductivity in the region of the critical solution temperature. M. B. D.

Adsorption of Vapours by Metallic Oxides: Its Bearing on the Catalysis of Ester Formation. J. N. PEARCE and A. M. ALVARADO (*J. Physical Chem.*, 1925, **29**, 256—270).—Observations on the adsorption of the vapours of water, ethyl alcohol, acetic acid, and ethyl acetate by aluminium and thorium oxides at

99·4° show that the only vapour which follows the adsorption isotherm is that of water. The adsorption of acetic acid vapour by aluminium oxide and of all four vapours by thorium oxide decreases with successive adsorptions and evacuations, and there seems to be a relation between the hydration of the oxide and its adsorbing power in these cases. The amount of adsorption is greatest for water and least for ethyl acetate. In the production of ethyl acetate by passing alcohol and acetic acid over a catalyst at 300° to 400°, the alcohol molecule is probably strongly adsorbed through the residual valencies of the hydroxyl group. The less highly attracted ethylidene group splits off and combines with the acid to form the ester. M. B. D.

Adsorption of Butane by Silica Gel. W. A. PATRICK and J. S. LONG (*J. Physical Chem.*, 1925, 29, 336—343).—The adsorption of butane by silica gel has been measured at 0°, 30°, 40°, and 100°. The water content of the gel was varied from 0·03 to 3·77%; maximum activity and capacity were shown by a gel with 1·96% of water. The adsorption data lend support to the capillary theory of adsorption (cf. A., 1920, ii, 417; 1922, ii, 262). M. B. D.

Influence of Temperature on the Evolution of Gases from an "Adsorber." R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1924, **139**, 324—332).—The composition of the gases evolved at different temperatures from active charcoal saturated at 0° in an atmosphere of carbon dioxide and hydrogen was determined. At lower temperatures, the less readily adsorbed hydrogen is evolved, being almost completely given off at a temperature below 125°, whereas the greater part of the carbon dioxide comes off between the latter temperature and 425°. The use of charcoal in separating or enriching such gaseous mixtures is discussed. H. T.

Adsorption Equilibria in Presence of Two Gases. R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1925, **143**, 268—276).—Mixtures of carbon dioxide with hydrogen and with carbon monoxide behave similarly towards adsorbent charcoal, the proportion of carbon dioxide in the solid being much greater than in the gaseous phase; thus at 0° charcoal containing carbon dioxide and hydrogen in the proportion of 3 : 1 is in equilibrium with a mixture of the gases containing only 5% of the former. With carbon dioxide and ethylene, the reverse is the case, the ratio of the former to the latter being lower in the adsorbent than in the gas mixture at equilibrium. Measurements of the adsorption of pure gases at varying pressures show that the adsorption of one gas is diminished in presence of another to an extent dependent on the degree to which the second is adsorbed. S. I. L.

Adsorption from Solution by Silica in Varying Degrees of Dispersivity. D. C. JONES (*J. Physical Chem.*, 1925, 29, 326—335).—The adsorption of acetic acid from its solution in gasoline [petrol] at 27° by silica has been studied, using powdered quartz, precipitated silica, and silica gel containing 6·2%, 3·4%, and 1% of water, respectively. Maximum adsorption was found to

occur with a silica gel containing 1% of water which had been heated at 680° in a stream of dry air for 18 hours. M. B. D.

Adsorption of Acids by Purified Silica. J. N. MUKHERJEE (*Nature*, 1925, **115**, 497).—Pure hydrated silica prepared from silicon tetrachloride, when partly dehydrated in air at the ordinary temperature, exhibits a marked increase in its capacity to adsorb acids (cf. this vol., i, 488), but the adsorptive power greatly diminishes if the silica is ignited. A. A. E.

Action of Silica on Electrolytes. A. F. JOSEPH (*Nature*, 1925, **115**, 460; cf. Mukherjee, this vol., i, 488).—Polemical and explanatory (cf. T., 1923, **123**, 2027). A. A. E.

Cryoscopic Method for Adsorption. H. L. RICHARDSON and P. W. ROBERTSON (*J. Chem. Soc.*, 1925, **127**, 553—556).—The adsorption by activated animal charcoal of a number of organic substances from aqueous solution has been determined by freezing-point measurements. For the compounds examined, the value of n in Freundlich's equation $C_2=KC_1^{1/n}$ lies between 1·45 and 4·8, thus varying round the mean value of 3 obtained by Freundlich. There is no apparent connexion between n and the relative adsorbability C_2/C_1. With solutions of methyl alcohol, stearic acid, methyl succinate, water, benzene, and more complex substances in phenol, no adsorption takes place. This is in agreement with the generally recognised fact that compounds such as phenol which are readily adsorbed prevent adsorption when employed as solvents.

A. E. M.

Adsorption of Electrolytes on Charcoal. I. M. KOLTHOFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 742—749).—The view is expressed that molecular adsorption of electrolytes takes place on charcoal. To test this, very pure charcoal, containing 0·08% of ash, was used, in order to exclude adsorption effects due to chemical reaction. Hydrochloric acid was almost entirely adsorbed as such, and there was no chemical adsorption. The molecularly adsorbed acid could not be completely removed by washing with water. Bases, *e.g.*, sodium and barium hydroxides, were also strongly adsorbed, but salts less readily. A marked "hydrolytic" adsorption was not observed. In the adsorption of the strongly hydrolysed sodium salt of veronal, the hydroxyl-ion concentration of the solution was much reduced after the adsorption, owing to the simultaneous adsorption of the salt itself and of the sodium hydroxide liberated by hydrolysis. Neutral salts were found to increase considerably the adsorbability of strong acids and sodium hydroxide, but to have no influence on non-electrolytes. Strong electrolytes are almost completely removed from charcoal by the capillary-active substances phenol and, to a smaller extent, amyl alcohol. In the case of impure charcoal, molecular and ionic adsorption occur simultaneously, and in order to study the adsorption of ions alone, the addition of some capillary-active substance is necessary to prevent molecular adsorption. L. L. B.

Absorption of Catalytically Poisonous Metals by Platinum. I. Absorption of Lead and Mercury. E. B. MAXTED (*J. Chem. Soc.*, 1925, **127**, 73—77).—Lead and mercury ions have been previously shown to exert a poisoning effect on the catalysis of hydrogen peroxide decomposition by platinum-black (T., 1921, **119**, 225; 1922, **121**, 1760). A suspension of platinum was added to a solution of a lead or mercury salt of known concentration, and the mixture agitated and left over-night at 20°. A portion of the clear solution was then analysed by determining its inhibiting effect on the activity of a standard catalyst for the decomposition of hydrogen peroxide. By this means small fractions of 1 mg. of lead or mercury can be determined with considerable accuracy. When either the initial or final concentration of metallic ion in solution is plotted against the amount adsorbed, a straight line is obtained, but when the saturation point is nearly reached there is a rather abrupt change and the graph then runs parallel to the axis of concentration of solution. Similar curves are obtained when the poisoning action is plotted against the concentration of the solution, but it has not yet been determined whether the change in direction in this case occurs at the point of incipient saturation or not. The behaviour observed seems to support the view that the poisoning is caused by the saturation of the free valency forces on the surface lattice of the platinum by lead or mercury, so that they are no longer available for the adsorption of, or association with, a potentially reactive system. M. S. B.

Mechanism of the Adsorption of Ions. R. AUDUBERT and [MLLE.] M. QUINTIN (*Compt. rend.*, 1925, **180**, 513—515).—The adsorption of ions by the walls of a vessel depends essentially on the osmotic pressure of the solution and on the electrostatic forces between the ions and the vessel, and not on any chemical interaction between the latter. The cations of the electrolyte diffuse into the electric field of the double layer surrounding the walls of the vessel and become adsorbed on the surface when their electrical pressure in the adsorbed portion is equal to their osmotic pressure in the solution and the electrostatic attraction. Assuming van der Waals' equation to apply to the solution, a quantitative expression for the density of the fixed ionic charge is deduced and broadly verified by measurements of the variation of charge in suspensions of mastic, gum arabic, and gelatin. J. W. B.

Comparative Adsorption of some Organic Acids and their Sodium Salts. C. FROMAGEOT and R. WURMSER (*Compt. rend.*, 1924, **179**, 972—974).—The adsorption of formic, acetic, propionic, oxalic, succinic, citric, and pyruvic acids by carbon when compared with the adsorption of the corresponding sodium salts shows that there is no simple relation between the adsorption and the ionisation constants of the acids. In the case of the acids, adsorption increases with the number of carboxyl groups and the salts are always less adsorbed than the corresponding acids. There are, however, great differences between the amounts of acid and salt which are adsorbed. H. J. E.

Electro-osmotic Experiments on Intensity of Adsorption of a Constituent Ion by an Insoluble Salt. I. J. N. MUKHERJEE and H. L. RAY (*J. Indian Chem. Soc.*, 1924, **1**, 173—188).—The adsorption of ions by carefully washed, precipitated lead chromate is studied by an electro-osmotic method with a view to a decision between the hypotheses, (1) that the adsorbed ions replace those of the same sign in the crystal lattice, thus leaving the crystal and its surface electrically neutral (Paneth, A., 1915, ii, 205), and (2) that they are adsorbed on the surface with or without exchange of ions, the surface thus becoming electrically charged (Mukherjee, A., 1922, ii, 198, 689). A well-digested precipitate of pure lead chromate is shown to be negatively charged in contact with water, this being due, probably, to the adsorption of chromate ions or, alternatively, to the adsorption of hydroxyl ions from the water. The velocity of electrical-osmosis is measured, under exactly similar experimental conditions, when the lead chromate is in contact with solutions of potassium chromate, iodate, nitrate, iodide, sulphate, and chloride, lead nitrate, barium chloride, and calcium chloride of concentrations varying between $N/15{,}000$ and $N/250$. The order of adsorbability of the cations is $Pb^{\cdot\cdot} > Ba^{\cdot\cdot} > Ca^{\cdot\cdot} > K^{\cdot}$, whilst with a constant cation, $K^{\cdot}$, the order of adsorption of the anions is that given above. The constituent ions of a precipitate are very strongly adsorbed by it, those of lead being so largely adsorbed as to reverse the charge at a concentration of $N/2000$. These observations cannot be explained on the type of adsorption assumed by Paneth (*loc. cit.*). The suggestion that there is a parallelism between the intensity of adsorption of the anion and the solubility of the salt of the adsorbed ion with opposite sign in the precipitate (Fajans and Beckerath, A., 1921, ii, 386) is not tenable, since the nitrate is more strongly adsorbed than the iodide or sulphate, whereas the order of increasing solubility of the lead salts is $CrO_4'' < IO_3' < I'$, $SO_4'' < Cl' < NO_3'$. J. W. B.

Occlusion of Magnesium [Oxalate] by Calcium Oxalate. M. LEMARCHAND (*Compt. rend.*, 1925, **180**, 745—748; cf. Richards, McCaffrey, and Bisbee, A., 1901, ii, 624; Korte, T., 1905, **87**, 1508; Murmann, *Monatsh.*, 1911, **32**, 105; Kallanauer and Preller, *Chem.-Ztg.*, 1914, **38**, 249; Canals, A., 1921, ii, 349).—The results of previous workers are shown to be affected by the tendency of magnesium oxalate to form supersaturated solutions, from which it is slowly deposited. Analysis of the precipitates obtained when calcium oxalate is precipitated from solutions, unsaturated, saturated, and supersaturated with regard to magnesium oxalate, shows that the apparent occlusion is the sum of two effects, the real occlusion, which is slight, and the slow deposition of magnesium oxalate from the supersaturated solution, which is mainly responsible for the presence of magnesium in the precipitate. J. S. C.

Adsorption. S. LIEPATOFF (*Kolloid-Z.*, 1925, **36**, 148—157).—A cellulose preparation with a low ash content was found to adsorb potassium, sodium, and barium hydroxides in the approximate ratio 1 : 1 : 2. The adsorption of potassium hydroxide was revers-

ible and could be represented equally well by the Freundlich equation or by a distribution formula. In the more concentrated solutions, irregularities were introduced by the swelling and structural changes of the cellulose. Addition of salts to the hydroxides reduced both the adsorption and the swelling, which are supposed to be closely connected. Adsorption is regarded as a chemical change involving hydrolysis. E. M. C.

Adsorption. IX. Influence of Various Substances and Importance of the Adsorption of Anions in the Coagulation of Arsenious and Antimonious Sulphide Sols. S. GOSH and N. R. DHAR (*Kolloid-Z.*, 1925, **36**, 129—137).—Dilution of arsenious and antimonious sulphide sols reduces the amounts of bi- and ter-valent cations required for flocculation, but increases the amounts of univalent cations. The presence of arsenious acid increases the flocculating power of univalent cations. Hydrogen sulphide reduces the flocculating powers of univalent cations, but increases those of cations of higher valency. The anomalous behaviour of the sols towards univalent cations on dilution is ascribed to hydrolysis, and to the peptising effect of the hydrogen sulphide being greater than the flocculating effect of the arsenious acid. Heating increases the stability of arsenious sulphide sol and decreases that of antimonious sulphide sol towards uni- and bi-valent cations. Both sols become less stable on ageing. The salt concentration for flocculation increases with the valency of the anion. E. M. C.

Distribution of Hydrogen Ions between Gelatin and Water. I. I. SHUKOFF and S. A. STSCHOUKAREFF (*J. Physical Chem.*, 1925, **29**, 285—294).—When hydrochloric acid is titrated with sodium hydroxide in the presence of commercial gelatin, a hydrogen electrode showed that the titration curves meet at a point corresponding with p_H 5·6. It is suggested that gelatin is a mixture of two substances with different isoelectric points. The decreased amount of sodium hydroxide required to produce a given p_H value between 3·5 and 5·6 is proportional to the amount of gelatin in solution. Similarly, the increased amount of sodium hydroxide required to produce a given p_H value between 5·6 and 10·5 is proportional to the amount of gelatin present. Hence, for a definite p_H value, the number of hydrogen or hydroxyl ions bound by 1 g. of gelatin is constant and independent of the concentration of the gelatin.

M. B. D.

Surface Tension, Surface Energy, and the Surface Layer. I. A. M. WILLIAMS (*Mem. Manchester Phil. Soc.*, 1924, **68**, 1—11).—The change in volume which occurs in the transference of a substance from the liquid phase to the surface layer makes it necessary to amplify the usual expression for the surface energy of a liquid. The alteration is, however, only of importance at temperatures near to the critical point. It is shown that the surface layer of a liquid, if normally unimolecular at the ordinary temperature, does not become 2 mols. thick until quite close to the critical point, where it increases rapidly. A. E. M.

Surface Tensions of Aqueous Solutions of Various Organic Compounds. P. R. EDWARDS (*J. Chem. Soc.*, 1925, **127**, 744—747).—The surface tensions of aqueous solutions of amyl alcohol, menthol, camphor, thymol, and *p*-toluidine have been measured by a capillary rise method at 15—18°. In all cases, the surface tension tends to approach a constant value with increasing concentration. The lowering of the surface tension is comparable with that produced by most active colloids, although the substances are crystalloids. Data for aqueous solutions of other organic substances are given; in all cases, the relative lowering produced is in accordance with the Harkins–Langmuir theory of "polar" molecules and surface tension. A. E. M.

Force of Adhesion between Metal Surfaces. IV. Synthetic Metal Structures. F. SAUERWALD and E. JAENICHEN (*Z. Elektrochem.*, 1925, **31**, 18—24; cf. A., 1922, ii, 746).—Investigations on the effect of pressure, temperature, and duration of heating on the strength and density of test pieces made of iron, copper, and nickel powders show that the force of adhesion increases with temperature, but that at high temperatures a decrease occurs owing to a crystallisation process. The tensile strength depends on the degree of compression and on the size of the original powder grains. Powders composed of two metals gave strengths of the same order of magnitude as those for pure metal powders. The force of adhesion of test pieces of Acheson graphite and carbides was very small. M. B. D.

Measurement of the Surface Tension of Molten Glass. A. LACRENIER and P. GILARD (*Bull. Soc. chim. Belg.*, 1925, **34**, 27—34).—The effects of various constituents on the surface tension of molten glass is determined by the authors' "drop" method (cf. *ibid.*, 1924, **33**, 119). The surface tension is increased in soda–silica glasses when the proportion of calcium is increased, when calcium is replaced by aluminium, or partly by barium or magnesium; it is decreased when the proportion of silica is reduced, when the proportion of sodium is increased, when the sodium is replaced either wholly or partly by potassium, and by the addition of sodium sulphate or boric acid. The increase of sodium relative to calcium causes a linear reduction in the surface tension. The results do not agree with those of Quincke, and the relative accuracy of the two methods is criticised. By means of comparative experiments, it is shown that the diameter of the tube used to produce the drops has practically no effect on the results. J. W. B.

Surface Tension of Dilute Electrolytes. C. WAGNER (*Physikal. Z.*, 1924, **25**, 474).—From a consideration of the potential at the interface of two dielectrics and the consequent change in concentration at the surface of an electrolyte a general expression is deduced for the change in the surface tension of an electrolyte in its dependence on the concentration. Good agreement is found between the values predicted by theory and those observed by Heydweiller (*Ann. Physik*, 1910, [iv], **33**, 145) for aqueous solutions

of sodium, potassium, and ammonium chlorides, sodium and potassium nitrates. R. W. L.

Surface Concentration of Gelatin at a Liquid–Gas Interface as Indicated by the Change in Surface Tension. J. M. JOHLIN (*J. Physical Chem.*, 1925, **29**, 271—284).—The surface tension of gelatin rendered ash-free by the method of Knaggs, Manning, and Schryver (A., 1923, i, 1144) has been determined by the capillary rise and the drop-weight method at 40°. The solutions show a gradual decrease in surface tension with time. For a given interval after the formation of the surface, the surface tension of a 1% solution shows a minimum at the isoelectric point p_H 4·7. M. B. D.

Hollow Channels Opening on to the Surface of Metals. G. TAMMANN and H. BREDEMEIER (*Z. anorg. Chem.*, 1925, **142**, 54—60).—A method is described for determining the volume of channels which open on to the surface of metals. The metal is immersed in a 20% solution of potassium eosin and is subjected to a pressure such that the air in the channels is completely dissolved, its place being taken by solution. The absorbed solution is subsequently expelled and its volume and hence the volume of the channels determined colorimetrically. A variation of the method consists of using water instead of dye solution, expelling it by heating, and absorbing in a weighed calcium chloride tube, but this involves complications in cases where the metal decomposes water on heating. The application of the method to zinc, copper, brass, iron, and bismuth, and the influence of annealing, cold working, polishing, and, in the case of brass and iron, composition are described. As was expected, by far the lowest result is given by bismuth, which expands on solidifying. N. H. H.

Behaviour of Crystals and Lenses of Fats on the Surface of Water. A. P. CARY and E. K. RIDEAL (*Nature*, 1925, **115**, 457—458).—Solid fatty acids and esters spread on water surfaces until the surface tension of the water falls to a definite equilibrium value, but the rate of spreading is slower than for liquids. A diagram is given for stearic acid in which the two-dimensional pressure of the equilibrium between crystals and liquid lenses and the condensed and expanded types of surface films is plotted as a function of the temperature. The latent heat of fusion of stearic acid is computed to be 12700 cals. A. A. E.

Deviations from van't Hoff's Law. W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], **37**, 263—271).—The osmotic pressure, P, of a solution may be approximately expressed by the equation: $P=xznRT$ (cf. A., 1923, ii, 546), where x represents the deviation from Raoult's law. The deviation from van't Hoff's law is positive when the molecular volume of the dissolved substance is greater than that of the solvent. When these volumes are practically equal, the solutions obey the law, provided $n/(n+N)<0{\cdot}02$. For most electrolytes, z is approximately unity, so that the deviations from van't Hoff's law are not large. S. K. T.

So-called "Metal Ammoniums." Vapour Pressure of Solutions of Lithium in Liquid Ammonia. C. A. KRAUS and W. C. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 725—731).—The vapour pressures of solutions of lithium in liquid ammonia at −39·4° have been investigated from the saturation point (3·61 mols. of ammonia per atom of lithium) to a concentration of 60 mols. of ammonia per atom of lithium. The pressure rises rapidly with increasing dilution and then more slowly until the region of two liquid phases is reached, when the pressure remains constant at 540 mm. (v. p. of pure ammonia 555 mm.). The curve is continuous and no indication is found of the abnormalities recorded by Benoit (A., 1923, ii, 635). There is no evidence of the formation of compounds of the alkali metals with ammonia of the ammonium type. J. S. C.

Spectrographic Study of the Formation of Complexes in Aqueous Solution. P. JOB (*Compt. rend.*, 1925, **180**, 928—930).—The existence of complexes in aqueous solution is indicated by the absorption spectra. The method may be used to determine the formula and stability of the complexes. J. S. C.

Method of Determining the Presence or Absence of Complex Salts or Ions in Dilute Aqueous Solution. H. W. PATTERSON and J. DUCKETT (*J. Chem. Soc.*, 1925, **127**, 624—628).—Determinations have been made of the elevations of the critical solution temperature for water and phenol, on the addition of single salts and pairs of salts. An additive elevation of critical solution temperature with increasing concentration of the salt pair is regarded as indicating no complex formation. Deviations from additivity are attributed to complex formation, the magnitude of the deviation affording a measure of the amount of complex formation. Potash alum and iron alum show indication of the existence of alum molecules only at concentrations greater than 7—8 molar. Definite complex formation is indicated in the case of mixtures of potassium iodide with mercuric iodide and cadmium iodide. A. E. M.

Viscosity of Rubidium Hydroxide Solutions. R. FRICKE (*Z. anorg. Chem.*, 1924, **139**, 419—420).—Measurements of the viscosity of solutions of rubidium hydroxide through the concentration range 0·09—1·0*N* show that this is smaller than that of potassium hydroxide solutions. This is attributed to the smaller degree of hydration of the rubidium ion. H. T.

Theory of Brownian Movement. F. ZEILINGER (*Ann. Physik*, 1924, [iv], **75**, 403—425).—The theory of the Brownian movement has been applied to the discussion of the reflexion, or condensation and subsequent evaporation, of particles at a boundary surface. S. B.

Nephelometry. H. KLEINMANN (*Kolloid-Z.*, 1925, **36**, 168—174; cf. A., 1920, ii, 634; 1921, ii, 56).—The failures of other workers to obtain a simple linear relationship between turbidity and concentration are ascribed to defects in the optical arrangements

employed. An accuracy of 0·3—0·5% can be obtained with the author's nephelometer, provided that the solutions are uniform and within suitable limits, that the turbidities compared are within the range 1 : 4, and that the solutions have equal degrees of dispersion. A systematic exploration of the turbidity–concentration relationships is a necessary preliminary to nephelometric analysis. A new micronephelometer and a standard of turbidity are described (cf. A., 1923, ii, 429). E. M. C.

Jelly State of Matter. I. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 175—176).—Disperse systems of salts of fatty acids in dry toluene change gradually from typical elastic transparent jellies into flocculent precipitates. The formation of a jelly is regarded as an extreme case of crystallisation. E. M. C.

Colloidal Sugar. II. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 176—177; cf. this vol., ii, 290).—A dispersoid solution of sugar prepared by pouring an acetone solution into an aromatic hydrocarbon was stable for a month with dextrose, a week with sucrose, and 10 minutes with lactose. The solutions exhibit polychromatic phenomena (cf. following abstract). E. M. C.

Disperse Systems, giving all the Spectrum Colours in Order on Temperature Changes. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 177—178).—The disperse system prepared by heating glycerol with a solution of caoutchouc in xylene exhibits a continuous colour change covering the whole of the spectrum when the temperature is raised or lowered. E. M. C.

General Colloid Chemistry. XIII. Analysis and Constitution of Silver Sols. III. E. FRIED and W. PAULI (*Kolloid-Z.*, 1925, **36**, 138—148; cf. A., 1923, ii, 636).—The silver sol prepared by the reduction of ammoniacal silver chloride by hydrazine hydrate is shown to contain the ammonium ion. On prolonged dialysis the electrical conductivity passes through a minimum value. The subsequent increase in conductivity is ascribed to the replacement of ammonium by hydrogen ion with the formation of an "acidoid." Direct measurements of the mobility agree with those calculated from the equivalent ionic mobility. The critical value for flocculation by aluminium sulphate corresponds with a concentration $6{\cdot}4\times10^{-5}N$ of ammonium ions in the sol. On the addition of increasing quantities of aluminium sulphate, the mobility decreases regularly, and only a single flocculation zone is given. Sols treated with sodium carbonate show with aluminium sulphate a reversal of the electrical charge and a series of flocculation zones. The sol is represented as of the type $(AgCl_2)'NH_4^{\cdot}$, with a little $Ag(NH_3)_2Cl_2'NH_4^{\cdot}$. E. M. C.

Preparation and Properties of Silicic Acid Gel. H. A. FALLS and J. B. FIRTH (*J. Physical Chem.*, 1925, **29**, 241—248).—The time of setting of silicic acid gel, prepared from sodium silicate and hydrochloric acid, has been determined. In acid solutions, the quickest set is obtained with concentrated acid, and the

time increases as the acid concentration is decreased until, in the vicinity of the neutralisation point, it becomes very indefinite. In alkaline solutions a slight alkalinity produces an immediate set and the time of setting increases with the hydroxyl-ion concentration. Under certain conditions, two gels are obtained, the first of which is cloudy, whilst the second is a very clear gel. The concentration of sodium chloride and the degree of hydration are much greater in the last-formed gel. The removal of sodium chloride from the gel after heating does not materially alter its sorptive capacity for water. M. B. D.

Preparation and Properties of some Protected Silver Sols. I. D. GARARD and G. E. DUCKERS (*J. Amer. Chem. Soc.*, 1925, **47**, 692—696).—Reversible silver sols have been prepared by reduction with dextrose or formaldehyde, agar-agar, dextrin, or gum arabic being used as protecting agent. The sols protected with gum arabic are stable within wide concentration limits and in the presence of relatively large concentrations of electrolytes. They react with the chlorides of antimony, bismuth, gold, mercury, and copper to give other sols, the rate of the reaction with copper chloride furnishing a measure of the extent of the protection. The bactericidal activity of a sol protected with agar-agar or gum arabic is of the same order as the commercial preparations protected with protein. J. S. C.

Isoelectric Points of Gliadin and Glutenin. E. L. TAGUE (*J. Amer. Chem. Soc.*, 1925, **47**, 418—422).—The isoelectric points of gliadin and glutenin, obtained from gluten by successive extraction with 70% alcohol and ether, respectively, were determined by finding a mixture of 0·01*M*-solutions of primary and secondary sodium phosphates, the p_H of which is not changed by the addition of the protein. The values are p_H=6·5 and p_H=7·0, respectively. [Cf. *B.*, 1925, 295.] F. G. W.

Lyophilic Colloids and Poiseuille's Law. H. R. KRUYT and C. ROBINSON (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 886—891).—The question as to whether lyophilic sols possess a real viscosity or whether they behave like elastic bodies is discussed. Freundlich and Schalek (this vol., ii, 112) have stated that sols investigated by them deviate from Poiseuille's law. To test this, the Hess viscosimeter, specially modified for the purpose, has been used to investigate gelatin sols at temperatures above and below that at which gelation begins, with the result that Poiseuille's law is found to hold exactly at 40° and 30°, whilst at 23° the expected deviations occur. The contention of Freundlich and others, that viscosity measurements on colloids should not be made with the Ostwald viscosimeter, but with the Couette or Hess apparatus, is criticised. From a review of previous work the authors conclude that sols consisting only of primary particles always follow Poiseuille's law, but that deviations occur when the primary particles have united to form aggregates either by temperature gelation or electrolytic coagulation. The theoretical bearing of this is briefly discussed. L. L. B.

Velocity Function of the Viscosity of Disperse Systems. II. W. OSTWALD (*Kolloid-Z.*, 1925, **36**, 157—167; cf. this vol., ii, 291).—The equation $\eta=kp^n.t$, where η is the viscosity, p the pressure, t the time, and k and n are constants, is applied to measurements of the viscosity of disperse systems by the Hess and Couette methods. Results with the Hess apparatus may be fitted with an accuracy of 1—2%, whilst those obtained with the Couette apparatus agree within the limits of the rather large errors involved. Attention is directed to certain sources of error in the Hess apparatus, especially for very small pressures. Ostwald's capillary viscosimeter, with lengthened arms or in conjunction with a manometer, is the most suitable for measuring the velocity function, or the structural viscosity, of colloidal systems. E. M. C.

Gel Replacement. A New Aspect of Metasomatism. W. LINDGREN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 5—11).—A paper of geological interest in which consideration is given to gel replacement as a factor in the transformation of minerals. These are decomposed and partly dissolved by aqueous sol solutions which move in subterranean interstices of capillary dimensions, coagulation resulting when the conditions are favourable. J. S. C.

Action of Bile Salts on Gelatin. G. V. STUCKERT (*Anal. Asoc. Quím. Argentina*, 1924, **11**, 352—364).—The effects produced by different bile salts on gelatin gels include liquefaction, periodic formations analogous to the Liesegang phenomenon, and the formation of gaseous spaces. G. W. R.

Effect of Neutral Salts on Gelatin. I. Swelling Action of Neutral Salts and the Value of the Hofmeister Series. E. STIASNY and S. R. D. GUPTA (*Collegium*, 1925, 13—23).—Commercial gelatin containing 2% of ash and having p_H 5·9 was rendered ash-free by washing in a buffer solution of p_H 4·7 until the p_H had been reduced to 4·7 and then in cold distilled water until free from the salts in the buffer. The product contained 0·015—0·027% of ash and had p_H 4·7—5·08. The specific rotation was 1·85 for a 1% solution. Small quantities of this ash-free gelatin were treated with solutions of sodium chloride, thiocyanate, chlorate, and nitrate of different strengths ($N/50$—$2N$) for 2 hours, 24 hours, and 6 days, and the swelling was measured by the increase in volume of the gelatin. The volume of the swollen gelatin, the p_H of the salt solution before and after use, and the p_H of the gelatin were determined in each case. The swelling was in accordance with the Hofmeister series, decreasing in the following order $CNS>NO_3>ClO_3>Cl>SO_4$, and was not proportional to the p_H value. The neutral salt effect outweighs the ordinary acid swelling effect, but the swelling is influenced by the p_H. The Hofmeister anion effect cannot be denied, but Loeb's view that swelling is due to potential differences only is erroneous, since the amount of swelling is not proportional to the differences in p_H in the jelly and its surrounding solution. D. W.

Effect of Neutral Salts on Gelatin. II. Their Dispersive Effect. E. STIASNY, S. R. D. GUPTA, and P. TRESSER (*Collegium*, 1925, 23—36).—Observations on ultra-filtration, specific rotation, viscosity, dialysis, turbidity, protective colloid action, and the delicacy of the tannin precipitation test are recorded which show that neutral salts increase the dispersivity of the gelatin. Thiocyanates have the greatest effect and for other salts a series is obtained which agrees with the Hofmeister series. Sodium sulphate appears to decrease the dispersion of the gelatin particles. It is uncertain whether the gelatin aggregates are actually dispersed or whether the gelatin is decomposed into simpler protein complexes.
D. W.

Protective Action of Soaps on Zsigmondy's Gold Sols. B. PAPACONSTANTINOU (*J. Physical Chem.*, 1925, **29**, 319—322).—At the ordinary temperature the greatest protective action is shown by sodium and potassium linoleates. In decreasing order follow the oleates, palmitates, stearates, myristates, and laurates. With the exception of the linoleates, all the soaps exert a greater protective action at higher temperatures. There is no appreciable difference between the protective action of the sodium and potassium salts.
M. B. D.

Protective Action of Soaps on Arsenious Sulphide Sols. B. PAPACONSTANTINOU (*J. Physical Chem.*, 1925, **29**, 323—325; cf. preceding abstract).—With arsenious sulphide sols, the protective effect of the different soaps varies within narrower limits than is the case with gold sols. The protective action is increased by a rise in temperature except in the case of linoleates, which have a greater protective action at the ordinary temperature on both arsenious sulphide and gold sols.
M. B. D.

Flocculation of Colloidal Solutions. A. BOUTARIC (*Bull. Acad. Roy. Belge*, 1924, [v], **10**, 560—570).—The change produced by the introduction of an electrolyte into a colloidal solution may be followed by measuring the coefficient of absorption of the solution for a definite ray by means of the Féry spectrophotometer. For an arsenic trisulphide sol containing potassium chloride, a guttapercha suspension containing sulphuric acid, a ferric hydroxide sol containing potassium hydroxide, etc., the absorption coefficient increases at first rapidly but with continually diminishing speed until a limiting value is approached. The liquid in its final state is comparable with an unstable jelly which, if kept still, persists for some time, but gives rise to a flocculent deposit when subjected to very slight disturbances. The speed of flocculation may also be followed by the spectrophotometric method, and observations show that, in all the cases studied, flocks appear before the solution attains its limiting opacity and before the granules assume their maximum size. The above results are in agreement with Spring's hypothesis that the evolution of a sol treated with an electrolyte leads to the formation of an unstable system consisting of a kind of jelly which is ruptured by agitation,

with separation of particles, these remaining suspended in the intermicellar liquid. T. H. P.

Coagulation of Hydrosols by Mixtures of Electrolytes and Ionic Antagonism. J. N. MUKHERJEE and B. N. GHOSH (*J. Indian Chem. Soc.*, 1925, **1**, 213—224; cf. Weiser, A., 1922, ii, 262).—The influence of various anions on the coagulation of hydrosols of arsenious sulphide by mixed electrolytes has been studied. The coagulation concentrations of the following electrolytes, both alone and in pairs, are recorded: sodium benzoate, barium chloride, calcium bromide, calcium benzoate, magnesium chloride, barium benzoate, potassium chloride, lithium chloride, sodium chloride, sodium acetate, barium acetate, potassium trichloroacetate, barium trichloroacetate, trichloroacetic acid, and potassium ferrocyanide. The effect of sodium benzoate and sodium acetate on the coagulation concentration of sodium chloride is to increase the concentration of cation required in the mixture, and since sodium acetate or benzoate has practically the same effect on sodium chloride as on barium chloride, this effect is equally pronounced both in cases where displacement of adsorption of one cation by another is or is not possible. It is suggested that the antagonistic effect observed (cf. Weiser, A., 1924, ii, 309) is due to the protecting effect of an initial rise in charge due either to a strong adsorption of an anion (*e.g.*, with sodium benzoate) or a weak adsorption of a cation (*e.g.*, lithium chloride), cations with low coagulating power exhibiting the greatest antagonistic effect on the coagulating concentrations of other ions. Thus the influence of sodium benzoate on the metals of the alkalis and alkaline-earths is in the order, Mg > Ca > Ba and Li > Na > K, *i.e.*, in the reverse order of their precipitating powers. The nature of these effects cannot be clearly understood until a simultaneous determination of the electric charge on the precipitate is made. J. W. B.

Influence of Radiations on the Flocculation of Colloidal Solutions. A. BOUTARIC and Y. MANIÈRE (*Bull. Acad. Roy. Belge*, 1924, [v], **10**, 571—577).—Neither red nor violet rays appear to exert any appreciable influence on the course or velocity of flocculation of colloidal solutions or suspensions by means of electrolytes. T. H. P.

Electrical Conductivity and Coagulating Power of Acids and Bases. G. ROSSI and M. ANDREANELLI (*Gazzetta*, 1925, **55**, 99—103).—The results of experiments on colloidal arsenic trisulphide, Congo-red, ferric oxide, and methyl-violet show the inaccuracy of the statement that solutions of acids (bases) of equal electrical conductivities exert the same coagulating action on a negative (positive) colloid (cf. Picton and Linder, T., 1895, **67**, 63; Hardy, A., 1900, ii, 396), the coagulating power depending on a number of different factors. Perrin's modification of the above rule, according to which the coagulating power is similar for solutions containing equal numbers of hydrogen (or hydroxyl) ions (*J. Chim. Physique*, 1905, **3**, 50) is valid only if the

coagulation is regarded solely as an electrical phenomenon (cf. Rossi, A., 1924, ii, 459). T. H. P.

Connexion between the Dispersion Process and the Production of Chemical Compounds. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 175).—The possible existence of dynamic forms of hydrogen chloride and silica is discussed. E. M. C.

Practical Results of the Theoretical Development of Chemistry. F. HABER (*J. Franklin Inst.*, 1925, **199**, 437—456).

Influence of J. Willard Gibbs on the Science of Physical Chemistry. F. G. DONNAN (*J. Franklin Inst.*, 1925, **199**, 457—483).

Atomic Dissociation of Chlorine and Hydrogen. I. Dissociation of Chlorine. K. WOHL (*Z. Elektrochem.*, 1924, **30**, 36—46). The mean molecular heat of chlorine determined by the explosion method between 291° and 1335° Abs. was found to be 6·83 cal. ± 1·3%. At any temperature up to 2000° Abs. the molecular heat is given approximately by the equation $C = 4{\cdot}963 + (E_T - E_{291})/(T-291)$, E being the Einstein function calculated for 2·2 degrees of freedom = 90·2. The heat of dissociation of 1 mol. of chlorine at the absolute zero amounts to 57000±2000 cal. and at constant pressure can be calculated for any temperature by the expression $Q = 57000 + 2{\cdot}978T - E$.

The influence of temperature on the dissociation of chlorine is given by $\log Kp = -57000/4{\cdot}571T + 1{\cdot}5 \log T - F/4{\cdot}571T + 1{\cdot}366$, p being expressed in atmospheres and F being the energy of atomic vibration. H. T.

Influence of Valency Direction on the Dissociation Constants of Dibasic Acids. C. H. SPIERS and J. F. THORPE (*J. Chem. Soc.*, 1925, **127**, 538—544).—The ionisation constants of various β-substituted glutaric acids indicate that the introduction of *gem*-groupings causes a large increase in the dissociation constant. For glutaric acid $K = 4{\cdot}69 \times 10^{-5}$, whilst for ββ-dipropylglutaric acid $K = 33{\cdot}9 \times 10^{-5}$. Introduction of alkyl groups into various fatty acids has little influence on the ionisation constants. Similar results are produced by substitution in malonic and succinic acids—the larger the substituting groups up to a certain limit the greater the effect on the value of the dissociation constant, whilst *gem*-groups have a very marked effect. A. E. M.

Water-gas Equilibrium. J. R. PARTINGTON and W. G. SHILLING (*J. Soc. Chem. Ind.*, 1925, **44**, 149—150T, 242T).—The equilibrium constant $K = [CO_2].[H_2]/[CO].[H_2O]$ has been calculated from the formula $\log K = -2125/T + 1{\cdot}077 \log T - 0{\cdot}0_3898T + 0{\cdot}0_6133T^2 + C$ derived by the application of Kirchhoff's equation to the following values for the molecular heat at constant volume, Cv in cal./g.-mol., carbon dioxide $6{\cdot}700 + 0{\cdot}0045t - 0{\cdot}0_5102t^2$, hydrogen $4{\cdot}850 + 0{\cdot}0_37t$, carbon monoxide $4{\cdot}970 + 0{\cdot}0_317t + 0{\cdot}0_631t^2$, water vapour $6{\cdot}750 - 0{\cdot}00119t + 0{\cdot}0_5234t^2$. The value used for C

is −0·5425, which is the mean of the values obtained by Hahn, Allner, and Haber and Richardt between 959° and 1645° Abs. The calculated values for K are 0·630 (1000° Abs.), 0·943 (1100°), 1·31 (1200°), 1·71 (1300°), 2·14 (1400°), 2·59 (1500°), 3·05 (1600°), 3·50 (1700°), 3·96 (1800° Abs.). F. B.

Equilibrium in Systems of the Type $Al_2(SO_4)_3$–M″SO_4–H_2O. I. Aluminium Sulphate–Copper Sulphate–Water and Aluminium Sulphate–Manganous Sulphate–Water at 30°. R. M. CAVEN and T. C. MITCHELL (*J. Chem. Soc.*, 1925, **127**, 527—531).—The former system shows no double salt formation. In the latter, the double salt $Al_2(SO_4)_3,MnSO_4,22H_2O$, identical with the mineral apjohnite, is formed. This bears no resemblance to the alums and should not be termed a "pseudo-alum." A. E. M.

Buffer Mixtures Prepared without Standard Acid as Base. I. M. KOLTHOFF (*J. Biol. Chem.*, 1925, **63**, 135—141).—The composition is recorded of mixtures of succinic acid and borax giving buffer solutions of p_H 3·0—5·8 and of succinic acid and potassium dihydrogen phosphate covering the range p_H 5·8—9·2. C. R. H.

Influence of Solvent on the Equilibrium of Isomerides. H. VIXSEBOXSE (*Annalen*, 1925, **442**, 306—308; cf. Smits, A., 1915, ii, 750; 1917, ii, 232; Vixseboxse, A., 1921, ii, 179).—A reply to Dimroth (this vol., ii, 36). H. W.

Aqueous Solutions of Carbamates and Carbonates. C. FAURHOLT (*J. Chim. physique*, 1925, **22**, 1—44).—Previous work (A., 1922, ii, 272) on the equilibrium ammonium carbamate $\rightleftharpoons$ ammonium carbonate is extended to the corresponding salts derived from methylamine, dimethylamine, and glycine. By methods similar to those used previously, the equilibrium constants and velocity coefficients of the reaction carbamate + water $\rightleftharpoons$ carbonate in buffer solutions of the free base and its chloride have been evaluated. The amounts of carbamate in the equilibrium mixtures at 18° are very much higher for glycine and methylamine than for ammonia and dimethylamine. In strongly alkaline solution, the decomposition of the carbamate is practically complete. Measurements of the velocity of this decomposition were made for the above substances for various concentrations of carbamate and alkali. It is shown on theoretical grounds that in the above equilibria the state of the system is fixed by the concentration of the amine and the amine salt. These concentrations, together with the equilibrium constants, also determine the velocity with which equilibrium is attained in a given mixture. Values for the velocity coefficients calculated for various concentrations of amine and salt are in most cases in agreement with experimental values. F. G. T.

Anomalous Behaviour of Strong Electrolytes. A. FRIVOLD (*Physikal. Z.*, 1924, **25**, 465).—On the basis of the theory of Debye and Hückel (A., 1923, ii, 459, 724; 1924, ii, 386) an expression is derived which connects the osmotic coefficient, *i.e.*, the variation of the diminution in vapour pressure from the classical value, with

the concentration of a solution whether strong or weak and with the dielectric constant of the solute. The form of this expression is such that as the concentration approaches zero a linear relation obtains between this coefficient and the square root of the molar concentration of the solute. Previous data for aqueous solutions of sodium and potassium chlorides are shown to be in accordance with the predictions of the theory. New observations on b. p. elevation for dilute solutions of lithium chloride in methyl, ethyl, and propyl alcohols lead to values for the osmotic coefficient which vary with the molar concentration of lithium chloride in the manner predicted by the theory. The divergence at higher concentrations is attributed to the solvation of the ions, of which the theory takes no account. A description is given of the technique employed in the work on lithium chloride. R. W. L.

Activities of Strong Electrolytes. I. The Activity of Hydrochloric Acid derived from the Electromotive Force of Hydrogen–Silver Chloride Cells. G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, **47**, 641—648).—The *E.M.F.* of the cell $Pt,H_2|HCl,AgCl|Ag$ at 25° has been measured over a range of hydrochloric acid concentration 0·01—1·5*M*. The activity coefficients of the ions have been calculated from these and from the earlier measurements of Linhart (A., 1919, ii, 444) and of Noyes and Ellis (A., 1918, ii, 27). They are in good agreement with those calculated from the freezing-point measurements of Randall and Vanselow (this vol., ii, 33), and at low concentrations are in accordance with the limiting equation of Debye and Hückel. J. S. C.

Activities of Strong Electrolytes. II. A Revision of the Activity Coefficients of Potassium, Sodium, and Lithium Chlorides, and Potassium Hydroxide. G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, **47**, 648—661).—The activity coefficients of the above electrolytes have been calculated from all the available measurements of electromotive force, freezing point, and vapour pressure, using the methods of Lewis and Randall ("Thermodynamics," 1923, Chaps. 26—28), modified in accordance with the theory of Debye and Hückel (A., 1923, ii, 459, 724). J. S. C.

Activity Coefficient of Sodium Hydroxide in Aqueous Solution. H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, **47**, 676—684).—The *E.M.F.* of cells of the type $H_2|NaOH(m_2)|Na_xHg|NaOH(m_1)|H_2$, where m_2 was varied from 0·005 to 3·0*M*, m_1 remaining constant at 0·01*M*, have been determined at 25°. From these, the activity coefficients of sodium hydroxide and the vapour pressures of the solutions have been calculated and compared with the corresponding values for potassium hydroxide, computed from the *E.M.F.* data of Knobel (A., 1923, ii, 116), employing the corresponding potassium hydroxide cells. The activity coefficient of potassium hydroxide is greater than that of sodium hydroxide at concentrations above 0·05*M*. Both coefficients pass through a pronounced minimum value with increasing concentration. J. S. C.

Activity Coefficient of Sodium Hydroxide in Sodium Chloride Solutions. H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, 47, 684—689).—The *E.M.F.* of cells of the type

$$H_2|NaOH(m_1),NaCl(m)|Na_xHg|NaOH(m_1)|H_2,$$

in which m_1 is 0·1 or 0·01*M*, and m varies over a considerable range, have been measured at 25°. The values are corrected for the activity of water in the solution and the activity coefficients of sodium hydroxide in the salt solutions calculated. The activity coefficients pass through minimum values with increasing concentration of the chloride. J. S. C.

Activity Coefficient of Potassium Hydroxide in Potassium Chloride Solutions. H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, 47, 689 692; cf. preceding abstract).—The activity coefficient of potassium hydroxide in 0·01 and 0·1*M* concentrations in potassium chloride solutions has been calculated from *E.M.F.* data for the corresponding potassium hydroxide–potassium chloride cells. As in the case of sodium hydroxide, the activity coefficient passes through a minimum value with increasing chloride concentration, the actual values being, however, greater. This behaviour is the reverse of that observed when the influence of the two chlorides on the activity coefficient of hydrochloric acid is investigated, the activity coefficient being greater in the sodium chloride solutions. J. S. C.

Activities of Strong Electrolytes. III. The Use of the Flowing Junction to Study the Liquid Junction Potential between Dilute Hydrochloric Acid and Saturated Potassium Chloride Solutions; and the Revision of some Single Electrode Potentials. G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, 47, 696—709).—Measurements have been made of the E.M.F.'s of the cells of the type Hg|HgCl,KCl(sat.)||HCl(*c*)AgCl|Ag at 25° (*c*, 0·01—1·5*M*) using a flowing junction. On stopping the flow, the liquid junction potential changes by about 3·5 millivolts. For acid solutions more dilute than 0·1*M*, the results obtained confirm the conclusion that the saturated potassium chloride bridge gives a liquid junction potential independent of the acid concentration, the absolute magnitude of which, using a flowing junction, is 4·7 millivolts. The results accord with the postulates of MacInnes (A., 1919, ii, 385) regarding individual ion activities. The following are the most probable values for some single electrode potentials at 25°, the potential difference between hydrogen at atmospheric pressure and hydrogen ion with an activity of one being considered as zero: Ag|AgCl(sat.)Cl⁻, −0·2222 volt; Hg|HgCl(sat.)Cl⁻, −0·2692 volt; saturated calomel electrode, flowing junction −0·2454 volt; decinormal calomel electrode, |KCl(sat.), flowing junction −0·3373 volt; without liquid junction −0·3353 volt. J. S. C.

Vapour-pressure Lowering of Aqueous Sulphuric Acid Solutions at 25°. A. GROLLMAN and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1925, 47, 712—717).—The vapour pressures of aqueous sulphuric acid solutions at 25° have been measured to a concentration 2·9*M*. The activity coefficients derived from these

are in agreement with the activity coefficients calculated by Lewis and Randall (" Thermodynamics," 1923, 354) from freezing points and *E.M.F.* measurements. The accuracy of Bronsted's vapour-pressure measurements (A., 1910, ii, 112) is questioned. J. S. C.

Activity Coefficients and Transference Numbers of the Alkaline-earth Chlorides. W. W. Lucasse (*J. Amer. Chem. Soc.*, 1925, **47**, 743—754).—The activity coefficients and transference numbers of the alkaline-earth chlorides have been derived from measurements of the *E.M.F.* of cells with and without liquid junctions. The cells investigated were $Ag|AgCl|MCl_2(c)|MHgx|MCl_2(0{\cdot}01)|AgCl|Ag$, and $Ag|AgCl|MCl_2(c)|MCl_2(0{\cdot}01)|AgCl|Ag$, where M represents barium, strontium, and calcium. All measurements were made at 25°. The concentrations of strontium and calcium chlorides were varied from 0·01 to 3*M*, and that of the barium salt from 0·01 to 1·65. The values obtained for the cation transference numbers agree with previously recorded data. J. S. C.

Dissociation of Polyatomic Salts. N. Sasaki (*Z. anorg. Chem.*, 1924, **139**, 387—393).—A mathematical discussion in the case of ferric chloride of the dependence of the concentration of the molecule and all its possible dissociation products on the total and on the anion and cation concentrations. H. T.

The Method of Willard Gibbs in Chemical Thermodynamics. W. L. Miller (*Chem. Reviews*, 1925, **1**, 293—344).

Equilibria in Systems in which the Phases are separated by a Semipermeable Membrane. I and II. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 701—720).—The author considers systems in which the liquids (i) remain homogeneous and (ii) separate into conjugate pairs. The equilibria of isotonic liquids in binary and ternary systems are also discussed. L. L. B.

Moving Boundaries and the Phase Rule. E. R. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 795—797).—Beattie's (A., 1924, ii, 838) derivation of the phase rule in its application to the equilibrium state of a system containing N components, P phases, and S surfaces at which electric potentials exist, $F=N-P+S+2$, F being the number of degrees of freedom, applies equally well to the equilibrium conditions attained in the determination of ionic mobilities by the moving boundary method. As an illustration, the determination of the mobility of the potassium ion in potassium chloride, by means of a moving boundary between solutions of lithium chloride and of potassium chloride, is considered. The restriction imposed on such a system is expressed by the relation $C_{Li}/C_K=T_{Li}/T_K$, where C denotes concentrations and T transference numbers. The number of independent variables is thus reduced from four to three. The mobility is constant with respect to variations in potential gradient only when the above relation is satisfied (Smith and MacInnes, A., 1923, ii, 828; 1924, ii, 727). J. S. C.

Dehydrating Power of Salts. N. SCHOORL (*Pharm. Weekblad*, 1925, 62, 276—280; cf. Scheringa, this vol., ii, 296).—Since salts may form solid hydrates, as well as saturated solutions, account should be taken of the "wet" and "dry" hygroscopicity. Scheringa's conclusion that salts are more deliquescent at higher temperature is not aways true—sodium nitrate may be left exposed in summer, but must be protected in winter, the relative vapour pressure being 0·78 at 0° and 0·70 at 38°. The humidity of the air must be considered in each case. S. I. L.

Dissociation of Lead Carbonate. M. CENTNERSZWER, G. FALK, and A. AWERBUCH (*Z. physikal. Chem.*, 1925, 115, 29—53; cf. Colson, A., 1905, ii, 304; 1909, ii, 400; Brill, A., 1907, ii, 233).—The dissociation pressures of normal lead carbonate and of its decomposition products have been measured by dynamic and static methods previously described (Centnerszwer and Andrusov, A., 1924, ii, 655). Under a pressure of 760 mm. the following compounds are formed at the temperatures stated: $3PbO,5PbCO_3$, 274°; $PbO,PbCO_3$, 286°; $2PbO,PbCO_3$, 360°. The several stages of the dissociation are reversible. L. F. G.

Partial Formaldehyde Vapour Pressures of Aqueous Solutions of Formaldehyde. I. E. W. BLAIR and W. LEDBURY (*J. Chem. Soc.*, 1925, 127, 26—40).—The partial vapour pressures of aqueous formaldehyde solutions have been determined by the dynamic method at 20° and 0°, after the solutions had previously remained for some time at 15°. As increasing volumes of air were passed through, the vapour pressure gradually rose at 20° until it reached a constant maximum value; at 0°, on the contrary, it fell to a constant minimum value. The addition of methyl alcohol decreased the divergence between the initial and final values, and, at 20°, increased the constant maximum value attained, but did not greatly affect the final value at 0°. The formaldehyde vapour pressure at 20° is more than doubled by 15% alcohol. In the presence of methyl alcohol, also, the relationship between the formaldehyde partial vapour pressure and concentration in solution becomes more nearly linear. The results may be interpreted by assuming an equilibrium between complex or hydrated formaldehyde molecules and simple molecules. On raising the temperature from 15° to 20°, the new equilibrium conditions, involving an increase in the number of simple molecules, and therefore in the value of the vapour pressure governed by these, are only attained gradually. Delay is also caused by the removal of formaldehyde vapour on the passage of an air current. Ultimately, however, a maximum constant vapour pressure will be reached at which the rate of formation of simple molecules is equal to the rate of removal. Similarly, when the temperature is lowered a constant minimum value should be reached. This theory has been tested by keeping solutions at 20° and also at 0° for several days before determining the vapour pressures. They were then found to remain practically constant. The effect of the presence of methyl alcohol explains the relatively high values

generally found for the formaldehyde vapour pressure of commercial formalin solutions, which contain methyl alcohol as an impurity.
M. S. B.

Partial Vapour Pressures of Aqueous Hydrogen Chloride Solutions. F. C. ZEISBERG (*Chem. and Met. Eng.*, 1925, **32**, 326—327).—Hurter's formula (*J. Soc. Chem. Ind.*, 1889, **8**, 861) is shown to be untrustworthy and the following substitute is proposed: $\log p = 10{\cdot}9528 - 0{\cdot}009725w - 0{\cdot}000868w^2 - (4{\cdot}557 - 65{\cdot}3w)/T$, where p is the pressure in mm. of the hydrogen chloride over a solution containing a weight percentage w, and T is the absolute temperature. Over the range 0—100° and w=18—32, the error with this formula is less than 5%. S. K. T.

Total Vapour Pressure of Cuprous or Lithium Chloride Solutions in Hydrochloric Acid. N. C. YANNAKIS (*Bull. Soc. chim.*, 1925, [iv], **37**, 253—262).—The vapour pressure of solutions of cuprous chloride in hydrochloric acid solutions is a linear function of the salt concentration; the gradient decreases with decreasing acid concentration and becomes zero when this concentration corresponds with the acid of minimum vapour pressure. In the case of lithium chloride, the pressure increases at first slowly and then very rapidly as the salt concentration increases; these curves, obtained with a salt which can only react with the water, differ entirely from those obtained with cuprous chloride, which only reacts with the acid. With solutions containing less than 22% of acid, the lithium chloride curves show a slight minimum; the lithium salt behaves as though it increases the acid concentration. S. K. T.

Affinity of the Metals for Sulphur. K. JELLINEK and J. ZAKOWSKI (*Z. anorg. Chem.*, 1925, **142**, 1—53).—The equilibrium $MS + H_2 \rightleftharpoons M + H_2S$ has been determined at several temperatures over a range of 500° to 1100° for the compounds Ag_2S, Cu_2S, SnS, PbS, Sb_2S_3, Bi_2S_3, MnS, FeS, and sulphides of the approximate composition NiS and CoS. From this the values of the sulphur tension of the sulphides have been calculated by a simultaneous consideration of the dissociation constant of hydrogen sulphide and the heats of dissociation of the sulphides. At a sufficiently low temperature (about 0°) the values increase in general with decreasing normal potential; thus the affinity of the metals for sulphur decreases with decreasing "nobility." Application of the Nernst and van't Hoff reaction isochores is made and the results are compared with the heats of formation calculated by indirect thermodynamical processes. In this section the figures for the reduction of mercuric sulphide and As_2S_3 obtained by Pélabon (*Z. anorg. Chem.*, 1908, **59**, 278; 1909, **62**, 89) are included. The discrepancies are in most cases considerable, a fact which is attributed to lack of accurate knowledge of the effect of temperature on the molecular heats of the reactants.
N. H. H.

Iron–Carbon Diagram and the Most Important Constituents of Plain Carbon Steels. K. DARVES (*Stahl u. Eisen*, 1925, **45**, 427—434).—The liquidus in the system iron–iron carbide

(cementite) consists of two slightly curved lines starting from the m. p. of iron at 1528° and the m. p. of cementite at 1550° and meeting at the eutectic point at 1146° and 64·2% Fe_3C (4·29% C). The solidus in alloys containing more than 2·9% Fe_3C is a straight line terminating in a curve and meeting the eutectic line at 1146° at 26·2%Fe_3C (1·75% C). There is a peritectic line at 1486° in alloys containing 1·1 to 4·9% Fe_3C (0·07 to 0·36% C) corresponding with the reaction between δ mixed crystals and liquid to form γ mixed crystals (austenite). The area of the δ phase is bounded by lines joining 1401° and 1528° on the iron axis with the end of the peritectic, whilst the γ mixed-crystal region is bounded by the lower of these two lines, by the solidus to the eutectic line, and by two lines, one joining the end of the eutectic and the other the Ac3 point of pure iron (906°) with the eutectoid point at 720° and 13·3% Fe_3C (0·89% C). The eutectoid line, above which pearlite cannot exist, extends right across the diagram at 720°, whilst the Ac2 line, caused by a magnetic transformation, extends from pure iron to the boundary of the γ phase at 769°. In the iron–graphite system the eutectoid line occurs at 1152° and is extended slightly further towards the iron end, thus reducing the area of the γ phase. [Cf. *B.*, 1925, 356.] A. R. P.

In-, Uni-, and Multi-variant Equilibria. XXVIII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 800—808; cf. A., 1924, ii, 389, 601).—A continuation of previous work. L. L. B.

Electrical, Adiabatic Calorimeter, and its Use in the Determination of Heats of Solution. E. COHEN, A. L. T. MOESVELD, and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 657—664).—The adiabatic, electrical calorimeter, described in an earlier paper (A., 1920, ii, 584), has been adapted for the determination of heats of solution. The modified apparatus, the method of its use, and an experiment are described. L. L. B.

"Electrolytes" and "Ionogens." W. BLUM (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 99—102).—The dual use of the word "electrolyte" for solutions which conduct electricity and for the dissolved substances which give rise to this conduction sometimes leads to confusion. It is suggested that the word "ionogen," originally proposed by A. Smith, should be adopted for a chemical compound which undergoes ionisation when placed in a suitable environment. The word "electrolyte" would then be retained for any medium or system which may be decomposed by the passage of an electric current, and would include both solutions and fused salts. C. S.

Volta Effect between Metals and Electrolytes. J. GUYOT (*Ann. Physique*, 1924, [x], 2, 506—521).—The potential difference between a metal and a dilute electrolyte has been measured by a potentiometer and quadrant electrometer using a null method. The standard ionisation method is adopted in which a metal

electrode is placed parallel to the surface of the electrolyte, the intervening layer of air being maintained slightly ionised.

It has been shown that (1) the Volta effect is independent of the nature of the electrolyte for equimolecular solutions containing the same reversible electrodes; (2) the effect increases or decreases with the concentration according to whether the electrode provides the solution with positive or negative ions, the increment being proportional to the logarithm of the concentration; (3) the apparent potential difference between two solutions L and L', in which are immersed electrodes M and M', respectively, differs but little from that of the pile $M|L|X|L'|M'$, formed of the same elements, in which X is a saturated solution of potassium chloride or of ammonium nitrate; (4) the potential difference between a metal and a solution of one of its salts is given by the expression $-a \log C+K+\phi(L)$, where K is a characteristic constant of the electrode and $\phi(L)$ a function of the properties of the solution.

Thin films of organic substances on the surface of an electrolyte diminish the Volta effect between a metal and an electrolyte. This diminution increases with the number of molecules on the surface but approaches a limiting value independent of the nature and concentration of the electrolyte. From this limiting value, the quotient m/α is calculated for trilaurin, trimyristin, myristic and palmitic acids, where m is the electric moment of the molecule and α is its degree of polymerisation. The values obtained range from 10^{-19} to 10^{-18} E.S.U., and do not vary appreciably between 18° and 33°. The effect is attributed to a regular orientation of the molecules of the organic substance on the surface of the electrolyte. R. W. L.

Influence of Acid Concentration on the Oxidation–Reduction Potential of Cuprous and Cupric Chlorides. S. R. Carter and F. M. Lea (*J. Chem. Soc.*, 1925, **127**, 499—510).—For solutions which contain equivalent quantities of cuprous and cupric chloride (0·1N or 0·025N) and varying amounts of hydrochloric acid the cuprous–cupric potential increases with the concentration of the acid and reaches a maximum of 0·88 volt at 7N-hydrochloric acid. Above this concentration the potential falls slightly. The initial increase of potential is attributed to a reduction of cuprous-ion concentration by formation of the complex compound H_2CuCl_3. The maximum at 7N corresponds with the concentration at which the ion concentration has a maximum value. The decrease in potential after the maximum is attributed to complex formation between cupric chloride and hydrogen chloride, yielding possibly $CuCl_2,HCl,3H_2O$. On varying the cuprous–cupric ratio the potential changes approximately in accordance with the usual logarithmic law. These results, combined with those of Carter and James (this vol., ii, 134) for the sulphur dioxide oxidation potential, afford an explanation of the oxidation of cuprous chloride by sulphur dioxide. A. E. M.

Electrode Potentials. R. H. Gerke (*Chem. Reviews*, 1925, **1**, 377—395).

Electrode, Contact, and Electro-kinetic Potentials of Galvanic Cells. J. HEYROVSKY (*J. Physical Chem.*, 1925, 29, 344—352).—A thermodynamic formula has been derived for the electrode potential of metals and metalloids (cf. A., 1923, ii, 114). M. B. D.

Method of Measuring Reduction Potentials of Quinhydrones. E. BILMANN, A. L. JENSEN, and K. O. PEDERSEN (*J. Chem. Soc.*, 1925, 127, 199—208).—The reduction potential of a quinhydrone can be determined by measuring the potential of an electrode immersed in a solution which contains the quinol of the quinhydrone under consideration together with the quinone of some other quinhydrone of known reduction potential. It has been shown that the reduction potential of the quinhydrone (A, AH_2) is given by $\pi_0'=2\pi-\pi_0=2\phi+\pi_0$, where π is the potential of a mixture of the quinol AH_2 with an equimolecular quantity of the quinone B (or conversely), against a hydrogen electrode, ϕ the potential of this mixture against the quinhydrone electrode (B, BH_2), and π_0 the reduction potential of the quinhydrone electrode (B, BH_2). ϕ has been determined experimentally for a number of mixtures against a benzoquinhydrone electrode of potential π_0, and the value of π_0' thus found compared with that determined by other methods. Satisfactory agreement has been obtained. From the value of ϕ, the amounts of the quinhydrone formed in the mixture may also be calculated. M. S. B.

Current-Potential Curves for Nickel and Aluminium. E. LIEBREICH and W. WIEDERHOLT (*Z. Elektrochem.*, 1925, 31, 6—15).—The complete current-potential curves for nickel and aluminium in 0·02*N*-sulphuric acid, 0·1*N*-hydrochloric acid, and in 0·1*N*-sodium hydroxide solution have been determined and their characteristics compared with those of similar curves previously obtained by the authors for other metals (this vol., ii, 44). On the anodic side, passivity phenomena are observed and are ascribed to the intervention of insoluble films of metallic hydroxide or oxide. It is concluded that anodic passivity, in general, is due to chemical conditions in the immediate neighbourhood of the electrode rather than to some abnormal condition of the metal itself. On the cathodic side, with increasing current density, the formation of metallic salts or hydroxides precedes the evolution of hydrogen, as previously observed with other metal cathodes, but with nickel and aluminium the hydroxides are very insoluble and difficult to reduce and persist even when vigorous hydrogen evolution has set in.

With nickel in 0·02*N*-sulphuric acid, very high anodic current densities cause reversion to an active condition which persists on reducing the current density again, so that, after strong anodic polarisation, the potential in the currentless condition is notably baser than after weak anodic polarisation. Cathodic polarisation of nickel in 2*N*-nickel sulphate solution does not cause deposition of nickel on the electrode until evolution of hydrogen has also set in. On anodic treatment of aluminium in 0·1*N*-hydrochloric acid,

evolution of hydrogen continues up to considerable current densities and eventually may even accompany evolution of oxygen to some extent. The film produced on aluminium by anodic polarisation in 0·1*N*-sodium hydroxide can be observed directly in that it peels off when the current is suddenly reversed so as to cause evolution of hydrogen. M. B. D.

Mixed Electrodes of the Second Type. P. Gross and O. Halpern (*Z. physikal. Chem.*, 1925, **115**, 54—60).—A theoretical discussion of the differences of potential at the surface of contact of solid–liquid phases of the glass–water type. The conclusions are applied to the results obtained with glass electrodes by Haber and Klemensiewicz (A., 1909, ii, 785), by Horovitz (*Z. Physik*, 1923, **15**, 369), and by Schiller (A., 1924, ii, 459). L. F. G.

Overvoltage and Transfer Resistance. E. Newbery (*Proc. Roy. Soc.*, 1925, **A**, **107**, 486—495).—The overvoltage for ten metals was measured, using a rotating commutator and a cathode-ray oscillograph, the deflexions of which were produced by the difference of potential between the metal under examination and the solution in which it was immersed. This potential was magnified by means of a thermionic valve. Photographs are reproduced showing the effect of breaking the main current. There is an instantaneous drop of potential indicating an irreversible resistance effect between the metal and the electrolyte (transfer resistance). The total opposition to the passage of a current is, therefore, made up of two distinct parts, true overvoltage and transfer resistance. All the phenomena observed are explicable on the hydride theory of overvoltage. E. B. L.

Influence of Acidity on the Polarisation of Nickel. S. Triandafil (*Compt. rend.*, 1925, **180**, 737—739).—The polarisation of nickel has been investigated in its relation to the acidity of the aqueous medium, the nickel-ion concentration remaining constant (*N*-nickel chloride solution), whilst the p_H value was varied from 0 to 7. For a given p_H value, the polarisation diminishes with increasing temperature. At constant temperature, the polarisation decreases with increasing acidity. The curves representing the polarisation as a function of p_H at 0°, 25°, and 50° exhibit points of inflexion corresponding approximately with a constant value of $[H^+]/[Ni^{++}]=0·29$. At higher temperatures, 75° and 100°, the influence of acidity is very slight. J. S. C.

Passivity of Metals. E. Becker and H. Hilberg (*Z. Elektrochem.*, 1925, **31**, 31—41).—The "contact distance," *i.e.*, the distance which a metal point can be withdrawn from a metal surface and still give a measurable current, gives no indication as to whether the metals are active or passive. With one and the same metal, the contact distance is greater in the passive than in the active state. The photo-electric effect and passivity undergo similar changes, but there is no precise relation between the two effects. The most certain method for differentiating between the active and the passive states consists in determining whether the metal dis-

solves according to Faraday's law or not. Contrary to the results of Muthmann and Frauenberger (*Sitzungsber. Bayr. Akad. Wiss.*, 1904, **34**, 201), molybdenum could not be obtained in the passive condition. Chromium cathodically deposited on iron by the electrolysis of chromic acid remained active for many hours, whereas on copper it became quickly passive. M. B. D.

Passivity of Iron and Other Metals. A. S. Russell (*Nature*, 1925, **115**, 455—456).—It is considered that chromium, manganese, iron, cobalt, and nickel, when in the active state, each have two electrons in the fourth quantum orbit, and that they become passive when one of these electrons is removed to a third quantum orbit. The order of the potentials of certain metals in mercury, proceeding from electropositive to noble metals, is: zinc, cadmium, thallium, tin, lead, copper, manganese and iron, bismuth, cobalt, mercury, nickel, platinum. Only the metals known to show passivity fall out of the normal order for the free metals. The view that the passive state is a definite condition which is produced and maintained when the metal is amalgamated is consistent with Lambert's observation that pure iron is a noble metal when its surface is electrically neutral. The ions of the passive metals do not behave as if they were the ions of noble metals, and it is argued that passive iron, for instance, may have one of the electronic configurations, 2, 8, 15, 1, or 2, 8, 13, 3, probably the former, and nickel, possibly, 2, 8, 17, 1.

Metals, when dissolved in mercury, are much more efficient reducing agents in the presence of sulphuric acid than when in the free state. A. A. E.

Theories of Passivity. H. Gerding and A. Karssen (*Z. Elektrochem.*, 1925, **31**, 135—143).—A critical survey of the theories of the passivity of metals. The theories are classified under the headings: purely physical, purely chemical, and physico-chemical. The theory of Smits is favoured since it explains in addition the phenomena of polarisation and overvoltage. N. H. H.

Deficit of the Condensed Substances obtained by the Action of the Electric Discharge. M. Z. Yovitchitch (*Bull. Acad. Roy. Belge*, 1924, [v], **10**, 465—477).—The sum of the percentages of carbon and hydrogen in the condensed or polymerised compounds obtained by subjecting hydrocarbons to the influence of the silent electric discharge is often considerably below 100 (cf. A., 1908, i, 118; Löb, A., 1908, i, 117). The author's experiments show that this deficit persists even when precautions are taken to render contact of the condensed compounds with the air as short as possible. The conclusion is reached that the deficit is due partly to absorption of oxygen, water, or other substance, and partly to some action of the electric discharge. T. H. P.

Calculation of Reaction Velocity Coefficients. C. Wagner (*Z. physikal. Chem.*, 1925, **115**, 130—136).—Theoretical, with special reference to the effect of errors (cf. Moesveld, A., 1923, ii, 141). L. F. G.

Influence of Temperature on Reaction Velocity in Solution. C. WAGNER (*Z. physikal. Chem.*, 1925, **115**, 121—129).—No simple relation is found between the values of the integration constant B in the equation $\log k=-q/2{\cdot}3RT+B$, where k is the velocity coefficient, and those quantities which for reacting substances in solution correspond with the chemical constants of gases. L. F. G.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. X. J. HOLLUTA (*Z. physikal. Chem.*, 1925, **115**, 137—142; cf. Schiloff, A., 1903, ii, 720; Holluta, A., 1922, ii, 448; Holluta and Weiser, A., 1922, ii, 628).—The reduction of potassium permanganate by dilute formic acid is accelerated by the addition of the fluorine ion as sodium fluoride. The general conclusion is reached that all complex-building anions accelerate the reduction. L. F. G.

Landolt's Reaction. III. J. EGGERT and L. PFEFFERMANN (*Z. anorg. Chem.*, 1924, **139**, 310—316).—The course of the Landolt reaction from the commencement to the separation of iodine is more satisfactorily explained as a bimolecular than as a unimolecular reaction (cf. Skrabal, A., 1924, ii, 543). H. T.

Pernitric Acid. F. POLLAK (*Z. anorg. Chem.*, 1925, **143**, 143—163).—The highly-oxidised compound observed by Raschig on mixing nitrous acid and hydrogen peroxide has been more closely investigated with regard to the conditions for its formation and decomposition. For its determination, the bromine liberated from potassium bromide is titrated with phenol solution in presence of carbon disulphide. The fact that simple stoicheiometric relations are not found between the reactants indicates that its structure can best be investigated kinetically. The formation of pernitric acid from nitrous acid and hydrogen peroxide, as well as its decomposition into the latter and nitric acid, are difficult to investigate on account of the extreme rapidity of the reaction, and because in the latter case the reverse reaction has a disturbing effect. The formation of pernitric acid from nitric acid and hydrogen peroxide in presence of potassium bromide has been definitely established. At 15°, the initial velocity of bromine separation is proportional to the first power of the nitric acid concentration and the potassium bromide concentration. The exponent for the hydrogen peroxide, however, is approximately 0·80. Different reactions are found to predominate if the same relative quantities of reactants are present, but the total concentration is different. The influence of light is also a disturbing factor. L. L. B.

Nitric Oxide Reaction. A. KLEMENC (*Ber.*, 1925, **58**, [*B*], 492—494; cf. Stechow, A., 1924, i, 1157).—It does not appear possible to consider the oxidation of arsenious acid, sulphite, sodium sulphide, and ferrous hydroxide by nitric oxide in alkaline solution from a general, kinetic point of view. The oxidation of arsenious oxide (cf. Gutmann, A., 1922, ii, 845) is probably a termolecular change, $H_3AsO_3+2NO=H_3AsO_4+N_2O$, the rate of which increases

with increasing concentration of alkali hydroxide. Oxidation of sulphite and sulphide, on the contrary, is retarded by increasing alkalinity of the solution. H. W.

Velocity of Addition of Hydrogen Chloride to Quinone in Methyl Alcohol. L. EBERT (*Z. Elektrochem.*, 1925, **31**, 113—123).—The velocity of the reaction between hydrogen chloride and quinone in methyl alcohol solution has been determined by measurements of the conductivity (giving the hydrogen chloride concentration), the optical extinction (giving the sum of the concentrations of the coloured substances present) and the *E.M.F.* of the quinhydrone electrode (giving the ratio of the concentrations of quinone and quinol). The results correspond with a slow initial reaction $C_6H_4O_2+H^{\cdot}+Cl'=C_6H_3(OH)_2Cl$ followed by the extremely rapid reaction $C_6H_4O_2+C_6H_3(OH)_2Cl=C_6H_3O_2Cl+C_6H_4(OH)_2$. The velocity of chlorination is proportional to the product of the activities of the hydrogen and chlorine ions. In dilute solutions of hydrogen chloride, the velocity coefficient for the first reaction is given by $\log k=14{\cdot}45+\log [H^{\cdot}]+\log [Cl']-1{\cdot}61\ ([H^{\cdot}]+[Cl'])^{1/3}$ when the concentrations of quinone and quinol are small compared with that of the hydrogen chloride. With concentrations of the latter greater than 0·2*N*, deviations occur which are probably due to undissociated acid. The addition of water slows down the reaction, which is in agreement with the assumption that the ion $CH_3OH_2^{\cdot}$ reacts more rapidly than the ion $OH_3^{\cdot}$. The equilibrium lies strongly on the side of chlorination. For the constant for the first reaction the preliminary value $\log k=5$ is given. N. H. H.

Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. II. Mixtures of more than One Gas and Air. A. G. WHITE (*J. Chem. Soc.*, 1925, **127**, 48—61).—Le Chatelier's formula connecting the limiting composition for the propagation of flame in a mixture containing two inflammable gases and air, with the limits for these gases mixed separately with air, has been tested for the following pairs of gases mixed with air: H_2+CH_4, H_2+NH_3, $C_2H_4+H_2$, $C_2H_2+H_2$, $C_2H_4+CH_4$, CH_4+H_2S, H_2S+H_2, $H_2S+C_2H_2$, $C_2H_2+CH_4$, and $CH_4+C_5H_{12}$. The experimental values approximate more closely to those calculated for downward than for upward propagation, and for lower than for upper limits. Deviations are not always, however, in the same direction, so that mass action is evidently not the most important factor responsible for the divergences (cf. Payman, T., 1923, **123**, 412). In some cases it was possible to get two ranges of inflammability, so that the mixtures showed four limits instead of two. In mixtures containing hydrogen it was frequently found that propagation in a given mixture occurred or did not occur according as the type of flame started was the hydrogen type or the ordinary lower limit type. M. S. B.

Ignition of Gases. V. Ignition by Induction Sparks. Mixtures of the Paraffins with Air. R. V. WHEELER (*J. Chem. Soc.*, 1925, **127**, 14—26).—The variable conditions in the

production of inductance sparks may be electrical, namely, the self-inductance of the circuit, the impressed voltage, and the current flowing in the circuit before rupture; or mechanical, that is, the nature of the metal at the spark gap, the rate of break of the circuit, and the area of contact at the moment of break. The influence of each of these factors on the ignition of mixtures of the paraffins with air has been determined. The relationship between the inductance of the circuit and the igniting current is not constant. The amount of current in the circuit is of more importance than the impressed voltage, especially when the voltage is low. When the latter is high, however, the igniting current diminishes as the voltage increases. Contrary to the observations of Thornton (A., 1914, ii, 524), the alternating current necessary for ignition has about the same value as the direct current, but ignition is more "difficult" with the former because the production of a spark at the crest value of the current is a matter of chance. With a more volatile metal a lower igniting current is required, because the break flash has a longer duration. The igniting current diminishes as the speed at which the metallic contacts are separated is increased, and also as the area of the contacts is diminished. Optimum conditions are: low battery voltage and high induction, metal contacts which are not readily oxidised, rapid break of circuit, and small area of contact at moment of break. Experiments made with different hydrocarbons indicate that inductance sparks behave similarly to capacity sparks (or secondary discharges) as a means of ignition (A., 1924, ii, 747), but the longer duration and larger volume of the inductance sparks appear to mask small differences of ignitibility in the mixtures most readily ignited. Three different types of apparatus have been described. M. S. B.

Rôle of Water in Reactions in the Solid State. IV. D. Balarew (*Z. anorg. Chem.*, 1925, **143**, 89—96; cf. A., 1924, ii, 483, 611, 858).—The heating and gas evolution curves for the system barium dioxide–silica are given, and it is maintained that an insight into the mechanism of the system can best be obtained by a study of the two curves. For the system barium monoxide–calcium carbonate, the temperature at which reaction begins depends on the velocity of heating. The reaction between the solid components from 335° to 350° either proceeds to completion or remains unfinished, according to the duration of heating and the velocity with which the temperature rises. The reaction only takes place between the barium hydroxide, which is present in the barium monoxide, and the calcium carbonate, and the velocity of the reaction is determined by the velocity of diffusion of water from the place at which the reaction is already complete, to the free barium monoxide. A comparison of the heating curves of the system barium monoxide–calcium carbonate with those of the system barium monoxide–molybdenum trioxide shows that in the latter case the points at which the reaction takes place are at a much higher temperature than in the first case—possibly above 1500°. The rôle of water in the catalytic decomposition of potass-

ium chlorate by manganese dioxide is further investigated, by a study of the heating curves and gas evolution curves. The mechanism of the reaction is similar to that of the systems barium or strontium oxide and other solid substances, except that, in this case, the potassium chlorate or the system potassium chlorate–potassium chloride melts or softens, and is as such catalysed by the solid manganese dioxide. There is no definite temperature at which the catalytic influence of manganese dioxide on the decomposition of potassium chlorate begins. L. L. B.

Reaction Kinetics in a System consisting of Two Liquid Phases. K. Jabłczyński, W. Wieckowski, and (Frl.) A. Klein (*Z. anorg. Chem.*, 1925, **143**, 343—356).—The velocities of the reactions between iodine in chloroform and aqueous sodium thiosulphate and between benzoic acid in carbon tetrachloride and aqueous sodium hydroxide have been measured. As for other heterogeneous reactions, the velocity is controlled by the rate of diffusion through surface layers at the boundary of the phases, and the general equation is deduced: $K=v/0{\cdot}4343t\times\log c_0/c$, in which v is the volume of chloroform or carbon tetrachloride, c_0 the initial concentration of iodine or benzoic acid, and c the concentration after time t. This equation was verified by experiment and it was found, in accordance with expectation, that the velocity constant depended on the rate of stirring of the aqueous layer (the lower layer not being stirred) and that the temperature coefficient was much lower than for chemical processes. A. G.

Decomposition of Sulphur Chloride by Water. B. Neumann and E. Fuchs (*Z. angew. Chem.*, 1925, **38**, 277—280).—The extent of the decomposition was measured by the hydrogen chloride formed; it proceeds to the extent of 84·4% in 15 minutes, 85·6% in 8 hours when the chloride is shaken with six times its weight of water, 63·3% in 15 minutes with an equal weight and 37·3% in 30 minutes with half its weight of water. Even with 625 parts of water, the decomposition only proceeds to the extent of 93·68%. The decomposition is restrained by the presence of the hydrochloric acid formed; the separated sulphur encloses undecomposed chloride, and also dissolves in it, both these factors influencing the extent of the action. Hydrogen sulphide is always evolved, and the mechanism suggested by Curtius, $S_2Cl_2+2H_2O=H_2S+2HCl+SO_2$, with subsequent reaction between hydrogen sulphide and sulphur dioxide, and between the latter and the sulphur formed, is considered to represent the real course of the decomposition. After complete decomposition by boiling for several hours, the sulphur was found to be present as follows:—as separated sulphur, 29·80; colloidal, 35·14; as trithionic acid, 4·84; as tetrathionic acid, 9·09; as pentathionic acid, 18·26; as sulphuric acid, 1·00; as sulphurous acid, 0·31; as hydrogen sulphide, 0·57; total 99·01% of the sulphur present. S. I. L.

Effect of the Addition of some Alkaloids on the Rate of Dissolution of Iron in Dilute Hydrochloric Acid. M. B. Rane and M. Prasad (*J. Physical Chem.*, 1925, **29**, 249—255).—The rate

of dissolution of iron wire in hydrochloric acid rises to a maximum after a given period, which is not due to a change in concentration of the acid, but to the increase of porosity of the wire. The evolution of hydrogen is inhibited by alkaloids, the influence of which decreases in the order: brucine, strychnine, cinchonine, nicotine, codeine, cocaine, and coniine. This action is similar to that found by Conroy (A., 1901, ii, 388) for the effect of arsenious oxide on the rate of dissolution of iron by acid. M. B. D.

Conditions of Maximum Stability for some Organic Substances. I. Bolin (*Z. anorg. Chem.*, 1925, **143**, 201—230).—The stability of organic substances has been determined by measurement of the initial velocity of hydrolysis in solutions of known hydrogen-ion concentration. For ethyl formate, chloroacetate, and aminoacetate at 20°, the values of p_H for maximum stability are 4·65, 4·8, and 3·8 respectively. Benzamide was hydrolysed in 0·02*N* solution in silica vessels at 80°, the reaction velocity at 20° being too small for accurate measurement, using sodium hydroxide and sulphuric acid; by extrapolation the value of p_H for maximum stability was found to be 5·80, with a temperature coefficient of 3 for 10° ($k_{80}/k_{50}=30$). With α-methylglucoside hydrolysis was also effected at 80° in silica vessels, the rate being determined in solutions of p_H value from 0·8 to 1·5 both polarimetrically and by titration with Fehling's solution; hydrolysis occurs only in acid solution, the velocity sinking with increase in p_H, the curve becoming asymptotic to the p_H axis. The temperature coefficient is very high. For acetanilide at 40°, the value for maximum stability was determined by extrapolation as p_H 6·2.

Those substances which are hydrolysed both by acids and bases may be divided into two classes, the first having maximum stability in solutions of p_H 5 and above, the second in more nearly neutral solutions. The acidity of solutions in which the stability of esters of the fatty acid series is a maximum is lower for esters of weaker acids, increasing with the strength of the acid. S. I. L.

Kinetics of Hydrogenation. II. Stationary Films. E. J. Lush (*J. Soc. Chem. Ind.*, 1925, **44**, 129—134T).—Hydrogenation of stationary thin films of cotton-seed oil and trilinolin on nickel was found to be a unimolecular reaction and constant values for *K* were obtained when the catalyst was maintained at a constant temperature. Hydrogenation consists of three successive reactions: when unsaturated oil is in excess and hydrogen can reach the catalyst in limited amount only, the rate of hydrogenation is linear and is proportional to the hydrogen pressure; when unsaturated oil is in excess and the amount of hydrogen reacting is increased the rate is linear and proportional to the square root of the hydrogen pressure; when the oil approaches saturation the reaction is unimolecular and the rate is proportional to the hydrogen pressure. F. B.

Rôle of Oxygen in Catalytic Hydrogenation by means of Platinum. E. Waldschmidt-Leitz and F. Seitz (*Ber.*, 1925, **58**, [*B*], 563—566).—A reply to Bodenstein (this vol., ii, 216), in

which justification is deduced from the literature for the conception, denied by Bodenstein, of the co-existence of oxygen and hydrogen in the presence of platinum. H. W.

Catalytic Hydrogenation of Inorganic Substances. H. GALL and W. MANCHOT (*Ber.*, 1925, 58, [*B*], 482—485).—Catalytic reduction of nitric acid in aqueous solution in the presence of spongy platinum yields ammonia and nitrous acid. Hydrogenation of complex metallic salts occurs with initial reduction of the complex metallic atom; thus potassium ferricyanide yields potassium hydrogen ferrocyanide and sodium nitroprusside gives a compound of bivalent iron, whereas the expected conversion of the NO into the NH_3 group could not be established definitely. Simpler relationships are observed with the normal salts of metals which exhibit varying valency. Thus, ferric and cupric chlorides are smoothly converted into ferrous and cuprous chlorides; copper sulphate, however, could not be reduced. Quadrivalent titanium is converted into an equilibrium mixture of the quadrivalent and tervalent forms. Quinque- or quadri-valent vanadium is transformed quantitatively into the tervalent condition and sexavalent uranium is reduced to the quadrivalent stage. It is not possible, however, to limit the action to a definite, reproducible phase in all cases. Thus, chromic acid and chromates give variable and indefinite results. Potassium chlorate and iodate yield the corresponding chloride and iodide smoothly in neutral solution; potassium perchlorate could not be reduced, whereas potassium periodate gives potassium iodide in quantitative yield. Chlorine is converted into hydrogen chloride and bromine in dilute aqueous solution into hydrogen bromide. The quantitative conversion of iodine into hydrogen iodide appears to be in contradiction to Willstätter's view that the presence of oxygen in platinum is essential to its catalytic activity. H. W.

Reducing Action of Hydrogen Adsorbed in Silica Gel. M. LATSHAW and L. H. REYERSON (*J. Amer. Chem. Soc.*, 1925, 47, 610—612).—Negatively charged silica gel does not reduce silver nitrate to metallic silver. Hydrogen adsorbed in silica gel reduces the ions of copper, silver, gold, platinum, and palladium, but not of nickel. Microscopical examination shows the entire gel surface to be covered with the reduced metal and that the deposit is distributed throughout the gel granules. The bonds between the atoms of hydrogen molecules are weakened by adsorption and the atoms may act independently, *e.g.*, $H+Ag^+=Ag+H^+$. The metallised silica gels are active catalysts. J. S. C.

Decomposition of Hydrogen Peroxide in Presence of Nickel Hydroxide. (MLLE.) S. VEIL (*Compt. rend.*, 1925, 180, 932—934).—When nickel hydroxide is suspended in aqueous solutions of hydrogen peroxide, it becomes less and less magnetic. The corresponding values for the oxide obtained by calcination of the hydroxide are found to pass through a maximum value. The magnetic properties of nickel hydroxide are unchanged after con-

tinued suspension in pure water. These facts are believed to have an important bearing on the catalytic decomposition of hydrogen peroxide in presence of nickel hydroxide. J. S. C.

Explosive Limits of Mixtures of Gas or Vapour with Air. E. BERL and H. FISCHER (*Z. Elektrochem.*, 1920, **30**, 29—35).—The limits of explosion for mixtures of air and other gases and vapours are dependent on the size and material of the container as well as on the temperature, pressure, and method of sparking. The phenomenon of pre-ignition noted previously with mixtures of carbon monoxide and air was also observed with mixtures of acetylene, ethylene, alcohol, and carbon disulphide with air. In the upper limits, products of incomplete combustion were observed, *e.g.*, formaldehyde, acetaldehyde, and acetic acid from air and ether, acetaldehyde and acetic acid from ethyl alcohol, and acraldehyde from mixtures of air with acetone and ethylene. H. T.

So-called Poisoning of Oxidising Catalysts. C. MOUREU and C. DUFRAISSE (*J. Chem. Soc.*, 1925, **127**, 1—4).—The fact that certain combustible gases prevent the combination of hydrogen and oxygen by the electric spark or by contact with platinum-black is closely related to recent observations of the action of gases such as acetylene, hydrogen sulphide, and hydrogen phosphide in hindering the catalytic oxidation of gaseous ammonia in the presence of platinum (Decarrière, A., 1921, ii, 503, 546; 1922, ii, 284). This action evidently cannot be due in all cases to the poisoning of the catalyst, and it has been ascribed to the "antioxygenic" action of the inhibiting compound (cf. A., 1922, i, 250). The antioxygens decompose catalytically the peroxide A[O_2] produced by the union of the autoxidisable substance A with a molecule of free oxygen. This peroxide oxidises the antioxygen B, giving two peroxides A[O] and B[O], which are antagonistic and destroy each other, giving A, B, and O_2. An antioxygen must necessarily be an oxidisable substance, and every oxidisable substance should show some antioxygenic properties under suitable conditions. Further, a given catalyst, B, should be able to function either as a positive or negative catalyst, according as the peroxide B[O] attacks more readily the substance A or the peroxide A[O_2]. The theory accounts for the facts already known and has enabled the authors to foretell catalytic properties in substances in which they were hitherto unsuspected, for example, iodine, sulphur, etc. (A., 1923, ii, 308; 1924, i, 635; ii, 602). The "poisoning" of a platinum-black catalyst may be due to the simultaneous oxidation of A and B, by the catalyst, to form antagonistic peroxides which destroy each other, or, assuming that the catalytic effect of platinum is the result of the intermediate formation of an unstable Pt[O_2], the latter may be unable to exist in the presence of the anti-oxygen B. M. S. B.

Material Basis of the "Nitroxan" Process for the Catalytic Oxidation of Ammonia to Nitric Acid. G. KASSNER (*Arch. Pharm.*, 1925, **263**, 112—120; cf. A. 1924. ii, 604).—A digest of

an earlier paper. Barium orthoplumbate, required in the preparation of nitroxan, may be prepared in a very reactive condition by heating a mixture, in the required proportions, of lead monoxide and barium hydroxide (or peroxide), in a stream of air free from carbon dioxide at 500—600°. B. F.

Dissociation of Sodium Hydrogen Carbonate. A. RANC (*Bull. Soc. chim.*, 1925, [iv], **37**, 276—277).—The rate of thermal dissociation of sodium hydrogen carbonate is greatly retarded by the presence of small quantities (3%) of "saccharin." S. K. T.

Catalytic Decomposition of Formaldehyde. III. E. MÜLLER and F. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 41—45; cf. A., 1922, i, 110; 1924, i, 833).—A 13% aqueous solution of formaldehyde is decomposed at its b. p. by highly-dispersed metals of the platinum group or their compounds. In neutral or slightly acid solutions, the chief decomposition products with ruthenium, palladium, and osmium are carbon dioxide, hydrogen, carbon monoxide, and a small quantity of methane. With osmium, only a small amount of carbon monoxide is evolved. Iridium and platinum and their compounds have very little action, but rhodium produces slight decomposition. The compounds are reduced during the reaction to colloidal metal. Excepting the reaction obtained with osmium, the decomposition is similar to that observed with formic acid (cf. A., 1924, ii, 844). M. B. D.

Catalytic Decomposition of Pyruvic Acid. E. MÜLLER and F. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 45—46; cf. preceding abstract).—A 20% aqueous solution of pyruvic acid is catalytically decomposed by highly-dispersed osmium, palladium, and ruthenium at 100° into acetaldehyde and carbon dioxide. No carbon dioxide is evolved on boiling the solution for 4 hrs. when a catalyst is not added. M. B. D.

Course of Organic Reactions. E. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 46—50; cf. preceding abstracts).—The author explains the decomposition of formic, malonic, and pyruvic acids on Knorr's theory (cf. A., 1924, ii, 34) by assuming a rearrangement of the electron orbits in the interacting molecules. M. B. D.

Formation of Perborates by Electrolysis using Unsymmetrical Alternating Current. S. BODFORSS and A. ARSTAL (*Z. Elektrochem.*, 1925, **31**, 1—5).—The optimum conditions for the anodic production of perborates by electrolysis are: a temperature of 0° or lower, an electrolyte containing sodium hydroxide and boric acid in the molecular ratio of 5 : 1, a ratio of direct to alternating current of 1 : 2·8, and a total current density of 0·06 amp./cm^2. The zinc anode is enclosed in a porous pot, and it is essential to have good temperature control. The alternating current used had a period of 48 cycles and was very nearly a pure sine wave. The quantity of perborate formed is a maximum after 15 mins. and then sinks to a steady value. There appears to be no connexion

between the amount of zinc dissolved and the perborate formed. The probable explanation is that, whilst the electrode is acting as a cathode under the influence of the alternating current, the oxygen is reduced to hydrogen peroxide by the hydrogen evolved (cf. Fischer and Priess, A., 1913, ii, 285). M. B. D.

Production of Antimony Hydride at an Antimony Cathode in Alkaline Solution. II. E. J. WEEKS (*Rec. trav. chim.*, 1925, **44**, 201—205; cf. Sand and Weeks, A., 1924, ii, 152).—The percentage yield x of stibine at an antimony cathode in alkaline solution varies with the temperature according to $x=c/T-20$, and with varying hydrogen concentration [H] in the electrode according to $x=c_1-c_2 \log [H]$, where c, c_1, and c_2 are constants. G. M. B.

Sensitiveness of Actinometers with Mercury Electrodes. G. ATHANASIU (*Compt. rend.*, 1925, **180**, 587—589).—Actinometers having electrodes of mercurous chloride, bromide, and iodide or of mercuric sulphide in contact with 10% sulphuric acid (cf. *ibid.*, 1922, **175**, 214), have now been examined as regards sensitiveness to light of various wave-lengths. The wave-length corresponding with maximum sensitiveness increases with the atomic weight of the halogen involved, and has the values 2536 Å., 2967 Å., and 4046 Å. for the chloride, bromide, and iodide, respectively. The chloride and bromide are only sensitive to ultra-violet light; under its influence they show fluorescence, emitting a strong visible orange-rose light. The actinometer with mercuric sulphide electrode gives a much smaller E.M.F. of opposite sign and has a maximum sensitiveness at 4046 Å. G. M. B.

Variation of Temperature Coefficients of Photochemical Reactions with the Frequency. M. PADOA (*Gazzetta*, 1925, **55**, 87—92; cf. A., 1915, ii, 678, 719; 1916, ii, 508, 592; 1918, ii, 345; also Trautz, A., 1918, ii, 151; Pratolongo, A., 1918, ii, 70).—The results previously obtained are discussed in the light of modern views on chemical kinetics. In all the photochemical reactions as yet studied the temperature coefficient increases as the frequency of the light diminishes. This is regarded as the result of a variation of the affinity between atoms and electrons, separation of these requiring increasing expenditure of energy as the light absorbed by the atoms or molecules diminishes in frequency.

[With N. VITA.]—The temperature coefficient of the photochemical oxidation of hydriodic acid shows, however, a diminution as the light frequency falls. This may be due either to the affinity between atoms and electrons or the energy of activation being greater with the greater frequencies in this instance or, more probably, to transformation of the frequency by the absorbent substance. T. H. P.

Oxalic Acid–Uranyl Sulphate Ultra-violet Radiometer. W. T. ANDERSON, jun., and F. W. ROBINSON (*J. Amer. Chem. Soc.*, 1925, **47**, 718—725).—The photochemical decomposition of

oxalic acid in oxalic acid–uranyl sulphate solutions is found to be a reaction of zero order, not greatly influenced by temperature, and possessing the characteristics desired in an efficient chemical radiometer for use in the ultra-violet region. The results obtained using this method are in excellent agreement with those obtained by the employment of the usual copper–constantan thermopile and filters. J. S. C.

Action of Light on the Ferrous Ferric Iodine Iodide Equilibrium. E. K. RIDEAL and E. G. WILLIAMS (*J. Chem. Soc.*, 1925, **127**, 258—269).—The reaction $2Fe^{\cdot\cdot}+I_2 \rightleftharpoons 2Fe^{\cdot\cdot\cdot}+2I'$ is photosensitive to both ultra-violet and visible light, the latter within the range 5500—6500 Å., with an apparent maximum at 5800 Å. The triiodide ion is the photosensitive constituent and the energy of excitation is equivalent to 2·14 volts, almost identical with the resonance potential of the iodine molecule. One quantum of absorbed radiant energy causes 1 mol. of iodine to react. The dark equilibrium constant, $(Fe^{\cdot\cdot})(I_2)^{1/2}/(Fe^{\cdot\cdot\cdot})(I')$ is 23·6 at 25°. The ratio of the velocity constant of the liberation of iodine at 35° to that at 25° is 2·713, whilst for the photochemical reaction this ratio is 1·17. The addition of potassium chloride increases the thermodynamic concentrations of all the reactants, increasing the velocity of reaction thereby, but not affecting the final equilibrium.

L. J. H.

Action of Bromine on Sodium and Silver Azides. D. A. SPENCER (*J. Chem. Soc.*, 1925, **127**, 216—224).—Dry bromine vapour reacts with sodium or silver azide, giving bromoazoimide, N_3Br. This substance is extremely unstable, decomposing explosively on shock in all states of aggregation, and even at −200°; it has m. p. about −45°. It is instantly hydrolysed by water, consequently bromine water reacts with sodium azide to form sodium bromide, azoimide, and hypobromous acid, and these further react, yielding nitrogen. Hypobromous acid reacts even more rapidly with sodium azide so that two equivalents of bromine are able to decompose two equivalents of sodium azide.

No polymeride of nitrogen was formed in the experiments with bromine vapour, but some compound rich in bromine, perhaps nitrogen tribromide, appeared to be present. L. J. H.

Behaviour of Gold and Platinum towards Silicate and Salt Fusions. W. JANDER (*Z. anorg. Chem.*, 1925, **143**, 377—382).—It is probable for geological reasons that gold and platinum are dissolved by molten silicates as metals and not as ions. This conclusion is confirmed by the investigation of the partition of gold between metals (lead, tin, silver, and iron) and fused chlorides and glass, the proportion of gold found in the metallic layer being very much less than that calculated from the differences of potential of gold and the other metal used in their aqueous solutions. Natural platinum always contains iron and it is shown that at its m. p. platinum takes up iron from fused silicates in the presence of reducing gases. A. G.

Action of Acids and Water on Magnesium Boride. R. C. RAY (*J. Indian Chem. Soc.*, 1925, **1**, 125—132).—When magnesium boride is treated with water the quantity of hydrogen liberated, containing only traces of boron hydrides, is only one-half that obtained by the action of dilute hydrochloric acid, the main action being $Mg_3B_2+6H_2O=Mg_3B_2(OH)_6+3H_2$. The product of the reaction is completely insoluble in and inactive towards hot and cold water, and is regarded as a magnesium salt of the borohydrate, $[B_2(H_2O)_6]_n$. The mechanism of the reaction may be similar to that suggested for the action of water on magnesium silicide (Schwarz and Konrad, A., 1922, ii, 846), viz., $Mg_3B_2+3H_2O=H_3B_2(MgOH)_3$; $n[H_3B_2(MgOH)_3]+3nH_2O=n[Mg_3B_2(OH)_6]+3nH_2$, the latter equation representing the decomposition of 90% of the initial product. The secondary reactions, by means of which borohydrates and boron hydrides are produced, may be represented, $H_3B_2(MgOH)_3+5H_2O=3Mg(OH)_2+H_6B_2O_2+2H_2$ and $H_3B_2(MgOH)_3+6HCl=3MgCl_2+3H_2O+B_2H_6$. No boric acid or magnesium borate is formed by the action of water on magnesium boride as is the case when dilute hydrochloric acid is employed: $Mg_3B_2(OH)_6+6HCl=3MgCl_2+2B(OH)_3+3H_2$. J. W. B.

Behaviour of Calcium Fluoride in Strong Acids. T. SABALITSCHKA and W. MOSES (*Pharm. Zentr.*, 1925, **66**, 177—178).—Calcium fluoride is readily soluble in boiling 25% hydrochloric acid, and does not separate from the solution on cooling. S. I. L.

Thermal Analysis of the Binary Systems: Aluminium Bromide and various Halides. W. ISBEKOV (*Z. anorg. Chem.*, 1925, **143**, 80—88).—Electrolytes in aluminium bromide solution exist in the associated condition, and form molecular compounds with the solvent. Only solvated molecules undergo electrolytic dissociation. Non-electrolytes, on the other hand, form no molecular compounds. M. p. curves are given for the systems aluminium bromide with aluminium chloride, arsenic tribromide, carbon tetrabromide, mercuric bromide, antimony tribromide, and bismuth tribromide, respectively. The first three of these and zinc bromide do not form compounds with aluminium bromide. For the fourth, the curve shows a maximum at 33% $HgBr_2$, corresponding with a compound $2Al_2Br_6,Hg_2Br_4$. Antimony and bismuth tribromides form the compounds Sb_2Br_6,Al_2Br_6 and Bi_2Br_6,Al_2Br_6, respectively. The thermal analysis, in conjunction with cryoscopic measurements (A., 1914, ii, 26), proves that polymeric complexes occur in the systems investigated. L. L. B.

Gallium. R. FRICKE and W. BLENCKE (*Z. anorg. Chem.*, 1925, **143**, 183—200).—Gallium sulphate, $Ga_2(SO_4)_3,18H_2O$, obtained from gallium ammonium alum, is stable in air. Gallium oxide is slightly volatile in sulphuric acid vapour. The acidic nature of the hydroxide is more strongly marked than that of aluminium hydroxide, the alkaline properties less so. By measuring respectively the conductivity, the velocity of hydrolysis of

ethyl acetate, and the depression of f. p. for dilute sodium gallate solution, it was found that at the ordinary temperature the second hydrogen atom is largely replaced by sodium. The solubility curve of gallium hydroxide in sodium hydroxide showed a maximum at about 10·3*N*-sodium hydroxide. This represents the boundary of the region of existence of trisodium gallate (solid phase soluble in water), and of di- or mono-sodium gallate (solid phase insoluble in water). The hydroxide shows ageing phenomena, closely connected with which is the fact that the solubility of the hydroxide in sodium hydroxide solution of low and medium concentration increases with the quantity of solid phase in excess. The hydroxide is readily soluble in aqueous ammonia. L. L. B.

Mechanism of Silane Formation. II. R. Schwarz and T. Hoefer (*Z. anorg. Chem.*, 1925, **143**, 321—335).—The residue of the approximate composition $Si_2H_2O_3$ previously obtained (A., 1922, ii, 846) by the interaction of hydrochloric acid and magnesium silicide has been investigated. The composition depends on the conditions of its formation, and the action of aqueous hydrochloric acid at 0° is preferred. The reaction takes place in three stages, during the first and last of which hydrogen is evolved, whilst the silane is obtained in the middle stage. The solid residue reacts with sodium hydroxide with evolution of hydrogen, and the ratio of the hydrogen thus obtained to that found by combustion slowly decreases to 2 : 1 if the material is kept in air; the silicon content simultaneously decreases and the change is thus due to absorption of oxygen. If the temperature is raised, all the hydrogen is evolved as water and elementary silicon is liberated; this does not occur at the ordinary temperature. Apparently the oxidisable substance is a hydride, and when the temperature is raised its combustion causes thermal decomposition of the oxyhydride with deposition of silicon. The only known oxyhydrides which would yield twice as much hydrogen when treated with sodium hydroxide as is found by combustion have the compositions $Si_2H_2O_3$ and SiH_2O. When the substance is treated with ammonium hydroxide, which decomposes the oxyhydride with evolution of hydrogen and formation of ammonium silicate whilst the other constituents of the mixture are only slowly attacked, the ratio obtained of hydrogen to silica dissolved agrees best with the formula SiH_2O and the solid residue thus contains a hydride, "prosiloxan" (SiH_2O) and silica. The mechanism of the reaction is therefore formulated as follows: $Mg_2Si+2H_2O=(MgOH)_2SiH_2$; $(MgOH)_2SiH_2+4HCl=2MgCl_2+2H_2O+SiH_2+H_2$. The radical SiH_2 polymerises to polysilenes, $(SiH_2)_x$, which remain in the solid residue, but before this is complete the hydrides formed as intermediate products are partly decomposed, yielding "prosiloxan" and silanes, *e.g.*, $Si_2H_4+H_2O=SiH_2O+SiH_4$; $Si_3H_6+H_2O=SiH_2O+Si_2H_6$. This explains how various silanes can be produced from a single silicide. Finally, silica may be formed either from "prosiloxan" or from slightly polymerised silene: $SiH_2O+H_2O=SiO_2+2H_2$; $SiH_2+2H_2O=SiO_2+3H_2$. A. G.

Chemical Equilibria between Lead Sulphide and its Roasting Products. II. R. SCHENCK and W. BORKENSTEIN (*Z. anorg. Chem.*, 1925, **142**, 143—179).—In answer to the criticisms by Reinders of the previous work of Schenck and Albers on the chemical equilibria between lead sulphide and its roasting products (A., 1919, ii, 222), the system has been reinvestigated without any appreciable divergences from the earlier results being obtained. The fundamental reactions are shown to be $10(PbSO_4,PbO)+PbS \rightleftharpoons 7(PbSO_4,2PbO)+4SO_2$; $13(PbSO_4,2PbO)+PbS \rightleftharpoons 10(PbSO_4,3PbO)+4SO_2$; $3(PbSO_4,3PbO)+PbS \rightleftharpoons 13PbO+4SO_2$; $2PbO+PbS \rightleftharpoons 3Pb+SO_2$. Vapour-pressure curves for these reactions have been obtained and a chemical and microscopical examination of the solid phases has been made. The isothermal decomposition of the compound $PbSO_4,PbO$ in the presence of lead sulphide gives results in accordance with the equations. The investigation includes a thermodynamical treatment and the representation of the equilibria by means of a solid figure. N. H. H.

Lead Nitrite. A. THIEL and L. STOLL (*Z. anorg. Chem.*, 1924, **139**, 317—323).—By the action of lead on lead nitrate solutions at 25° about 40 mol.-% of the nitrate undergoes reduction to nitrite, part of which separates together with nitrate as basic salts. This reduction is more complete at 100° or in the presence of acetic acid. Conversely, lead nitrite solutions, alone or in the presence of lead, are partly converted, with the simultaneous formation of basic salts, into nitrate. Thus, only by treating solid lead bromide with solid silver nitrite in the presence of a little water can pure lead nitrite be obtained. Some measurements were made on the conductivity and on the electrode potential of lead in nitrite solutions (cf. Chilesotti, A., 1908, ii, 845, 948; 1909, ii, 43). H. T.

Reduction of Metallic Oxides by Alkali Cyanides. L. HACKSPILL and R. GRANDADAM (*Compt. rend.*, 1925, **180**, 930—931).—Although under ordinary atmospheric conditions metallic oxides are reduced by fusion with alkali cyanides to form the metal and the alkali carbimide, lead, tin, copper, iron, nickel, barium, and strontium oxides, when heated at 570—750° with sodium cyanide in a vacuum yield heavy metal and sodium in approximately equivalent proportions, nitrogen, carbon monoxide and dioxide, and finely-divided carbon. Alumina, chalk, and manganese dioxide undergo only partial reduction under these conditions. Sodium carbimide is probably first formed, since under the same temperature conditions this salt rapidly decomposes under considerably reduced pressure to form sodium, nitrogen, carbon oxides, and carbon. J. S. C.

Preparation and Properties of Nitrides. E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **143**, 293—320).—Nitrides of the compositions TiN, VN, Si_3N_4, BN, and LaN have been prepared in the pure state by heating the corresponding oxides with the calculated weight of carbon at 1250° in nitrogen. By the same method, the previously unknown nitrides ZrN, ScN,

NbN, and ErN have been obtained, but only traces of nitrides of yttrium, ytterbium, cerium, didymium, thorium, and uranium were formed. The previously unknown or doubtful sesquioxides, Ce_2O_3 and Nb_2O_3, have been prepared by reducing the higher oxides with hydrogen. The m. p. of the nitrides were determined by passing a current of electricity through a rod of the material and comparing the energy consumption at the m. p. with that at the known m. p. of molybdenum and tungsten. (Cf. ii, 374.)

Titanium nitride, TiN, is a light brown powder, m. p. 2930°, specific resistance ($10^4\sigma$) 1·3 ohms at the ordinary temperature, *d* 5·29. *Zirconium nitride*, ZrN, is a yellowish-brown powder or golden-yellow crystals, m. p. 2930°, *d* 6·93, specific resistance 1·6 ohm at the ordinary temperature. Vanadium nitride, VN, is a greyish-brown powder, m. p. 2050° (decomp.), *d* 5·91. The statement of Roscoe that vanadium nitride is formed when the oxide is heated in a current of ammonia (or N_2+3H_2) is confirmed, but the nitride so obtained is not pure. Niobium sesquioxide, Nb_2O_3, a grey powder, was prepared by the reduction of the higher oxide with hydrogen. The *nitride*, NbN, a light grey powder, has m. p. 2050°, *d* 8·4, specific resistance 2 ohms at the ordinary temperature. Tantalum nitride, TaN, was obtained by heating metallic tantalum in hydrogen, powdering, and then heating in nitrogen; it has m. p. 2800° (decomp.). Only traces of *scandium nitride*, ScN, were obtained by the usual procedure, but the nearly pure nitride was formed if a mixture of sodium carbonate and carbon was added to the mixed sesquioxide and carbon, or if the temperature was raised to 1700—1800°. It is dark blue, m. p. 2650°, *d* 4·2, specific resistance 3·08 ohms at the ordinary temperature. Boron nitride, BN, has m. p. above 2530°. Silicon nitride, Si_3N_4, is formed quantitatively at 1250° if 10% of ferric oxide is added to the mixture of silica and carbon; otherwise a temperature of 1500° is required. It is a nearly white powder insoluble in acids but decomposed by molten alkalis; it volatilises at 1900°. *Erbium nitride*, ErN, was prepared by the normal procedure with the addition of sodium carbonate and carbon to the mixture of oxide with carbon. It decomposes in air. Cerium sesquioxide, Ce_2O_3, was prepared by reducing the dioxide with hydrogen at 1250°. It is a yellow powder slowly oxidised by the air. The formation of the dark blue, unstable oxides previously described is due to the use of impure hydrogen.

Nitrides of cerium, didymium, thorium, and uranium were not obtained pure. Titanium, zirconium, vanadium, niobium, and scandium nitrides are decomposed by aqueous alkali hydroxides.

A. G.

Definition and Preparation of Hexametaphosphates. P. PASCAL (*Compt. rend.*, 1924, 179, 966—968; cf. A., 1924, ii, 856 and previous abstracts).—"Graham's soluble salt" behaves as $Na_2[Na_4(PO_3)_6]$, a complex hexametaphosphate with a portion of the sodium masked by reason of its position in the complex. It is unstable when in solution and in presence of excess of a lead salt

is precipitated as a hexametaphosphate from which the corresponding alkaline salts, $M_6(PO_3)_6$, may be obtained. H. J. E.

Action of Arsenious Anhydride on Alkali Carbonates. B. L. VANZETTI (*Gazzetta*, 1925, **55**, 110—118).—Quantitative measurement of the interaction of sodium or potassium carbonate and arsenious anhydride in aqueous solution at the temperature of boiling water shows that the reaction proceeds only slowly, but may be brought virtually to completion if the carbon dioxide gradually liberated is eliminated by means of a current of hydrogen. T. H. P.

Existence of Alkali Ortho-arsenites. B. L. VANZETTI (*Gazzetta*, 1925, **55**, 106—110).—In order to ascertain if alkali arsenites are obtainable in absence of water in accordance with the reaction, $As_2O_3+6NaOR=2Na_3AsO_3+3R_2O$, arsenious anhydride was dissolved in a methyl-alcoholic solution of the theoretical amount of sodium methoxide and the excess of the alcohol evaporated to give a syrup, which was left to crystallise in a vacuum exsiccator over calcium chloride. The crystals formed were all highly hygroscopic and varied in composition, the arsenic content, determined either iodometrically or as sulphide, diminishing from about 80% to about 20% of that required by the formula Na_3AsO_3. Very little ether is apparently liberated during the reaction. T. H. P.

So-called Molybdenum Dibromide and some of its Derivatives. K. LINDNER and H. HELWIG (*Z. anorg. Chem.*, 1925, **142**, 180—188).—Pure molybdenum "dibromide," Mo_3Br_6, was prepared by passing nitrogen and bromine vapour over pure molybdenum powder heated at 600—700°. With pyridine, the bromide forms the *compound* Mo_3Br_6,C_5H_5N and with ammonia in alcoholic solution the *ammine*, $Mo_3Br_6(NH_3)_2,2EtOH$. The action of alcoholic halogen acids gives acids which were isolated in the form of their pyridine salts. Thus the *compounds* C_5H_5N,HMo_3Br_7, $(C_5H_5N)_5,H_5Mo_6Br_{17},2EtOH$, and $C_5H_5N,HMo_3Br_4Cl_3$; $C_5H_5N,HMo_3Br_4Cl_3,EtOH$; $(C_5H_5N)_3,H_3Mo_6Br_8Cl_7,3EtOH$; and $C_5H_5N,HMo_3Br_4Cl_3$ were prepared. The compounds are of the same type as those obtained previously with bivalent molybdenum, tungsten, and tantalum. N. H. H.

Binary Systems Sodium and Lithium Tungstates, Potassium and Lithium Tungstates, Lithium Tungstate–Tungsten Trioxide, Sodium Tungstate–Tungsten Trioxide and Potassium Tungstate–Tungsten Trioxide. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1925, **143**, 285—292).—Lithium tungstate melts at 742°, and has no transition points. With sodium tungstate (m. p. 705°), it forms a simple eutectic at 45% of the latter (crystallisation begins at 501°, eutectic crystallises at 491°). Potassium tungstate (m. p. 933°; transition point 352°) forms with lithium tungstate a compound, K_2WO_4,Li_2WO_4, crystallising at 632°, which gives eutectics with both simple salts (70% Li_2WO_4, 579°; 40% Li_2WO_4, 607°). With tungsten trioxide, sodium tungstate forms a compound, $Na_2W_2O_7$ (m. p. 738°), which gives a eutectic

with the normal tungstate (m. p. 628°); addition of the trioxide also lowers the second transition point (577°) of the latter. Lithium tungstate behaves similarly ($Li_2W_2O_7$ has m. p. 745°, transition point 687°); the eutectic has m. p. 696°. The system potassium tungstate–tungsten trioxide has a eutectic at 50% WO_3 (crystallisation begins at 637°, eutectic crystallises at 584°), no stable compound being formed. S. I. L.

Decomposition of Permanganate. J. Holluta (*Z. physikal. Chem.*, 1925, **115**, 143—150; cf. this vol., ii, 49).—Carefully prepared 0·004*N*-solutions of potassium permanganate are not decomposed on long boiling, even on addition of small quantities of manganese sulphate. More dilute solutions (0·002*N*) are slowly decomposed by boiling. It is probable that the compound $KMnO_3$ (cf. Moles and Crespi, A., 1922, ii, 565; 1923, ii, 374) is the primary decomposition product and that this decomposes further with the formation of K_2MnO_4 and MnO_2. L. F. G.

Reaction between Ferric Chloride and Potassium Thiocyanate. K. C. Bailey (*Proc. Roy. Irish Acad.*, 1924, **37**, [*B*], 6—15).—The apparently anomalous behaviour on extraction with ether of solutions of potassium thiocyanate and ferric chloride containing predominating proportions of each constituent is discussed, and evidence is put forward that in the case where the thiocyanate predominates, and where the colour is paler, the ether extracts practically pure thiocyanate, whilst when the ferric chloride is in excess and the solution is sufficiently concentrated to impart some colour to the ether, hydrochloric acid formed by hydrolysis of ferric chloride liberates thiocyanic acid, and the extract contains both ferric chloride and thiocyanic acid. The reason for the variation in the colours of the two types of solution is investigated, and it is shown that Lachs and Friedenthal's method (A., 1911, ii, 542) for determining small quantities of iron must be used with caution since extraction of iron by the ether becomes progressively more difficult with diminution in the proportion of iron present. The behaviour of thiocyanic acid in organic solvents is also discussed. [Cf. *B.*, 1925, 313.] D. G. H.

Freezing Points of Solutions containing Ferric Chloride and Potassium Thiocyanate. K. C. Bailey and J. D. Kidd (*Proc. Roy. Irish Acad.*, 1924, **37**, [*B*], 16—18).—The freezing-point curve for solutions containing a constant proportion of ferric chloride (0·54%) and varying proportions of potassium thiocyanate (0·1 to 9·7%) showed no breaks indicative of the formation of molecular compounds, although the depression of the freezing-point was slightly smaller than would be expected. D. G. H.

Complex Cobaltic Selenates. J. Meyer, G. Dieska, and F. Clemens (*Z. anorg. Chem.*, 1924, **139**, 333—386).—The substitution of sulphate ion by the selenate ion in mono- and poly-nuclear cobaltic sulphates has little influence on the properties of the salt. The differences are less as the complexity of the cobalt-

ammine increases, and are most marked in the case of the solubility and the degree of hydration, both the latter being greater with the selenates than with the sulphates. The following new compounds are described.

Hexamminecobaltic selenate persulphate, $[(NH_3)_6Co]_2(SeO_4)_2(S_2O_8)$; *acid diaquodipyridinediamminecobaltic selenate*, $[(H_2O)_2(C_5H_5N)_2(NH_3)_2Co](SeO_4)(SeO_4H)$; *nitratopentamminecobaltic selenate*, $[(NO_3)Co(NH_3)_5]SeO_4$; *thiocarbimidopentamminecobaltic selenate*, $[(NCS)(NH_3)_5Co]SeO_4,2H_2O$; *carbonatopentamminecobaltic selenate*, $[(CO_3)(NH_3)_5]_2SeO_4$; *normal* and *acid oxalatopentamminecobaltic selenate*, $[(NH_3)_5CoC_2O_4]_2(SeO_4),3H_2O$ and $[(NH_3)_5CoC_2O_4]SeO_4H,H_2O$; *hydroxyaquotetramminecobaltic selenate*, $[(OH)(H_2O)Co(NH_3)_4]SeO_4$; *chloro-* and *bromo-aquotetramminecobaltic selenate*, $[X(H_2O)Co(NH_3)_4]SeO_4$; *chlorodiaquotriamminecobaltic selenate*, $[Cl(H_2O)_2Co(NH_3)_3]SeO_4$; *dibromotetramminecobaltic selenate*; ' *acid dichlorodiaquodiamminecobaltic selenate*, $[Cl_2(H_2O)_2Co(NH_3)_2]SeO_4H$; *oxalatotetramminecobaltic selenate*, $[(NH_3)_4CoC_2O_4]_2SeO_4,2H_2O$; *oxalatodiethylenediaminecobaltic selenate*, $[en_2CoC_2O_4]_2SeO_4,3H_2O$; *dithiocarbimidodiethylenediaminecobaltic selenate*, $[en_2Co(CNS)_2],SeO_4H$; *diamminebisdimethylglyoximinocobaltic selenate*, $[(NH_3)_2Co(C_4H_7O_2N_2)_2]_2SeO_4$.

Hexamminetetranitro-μ-selenatodicobalt, $[(NH_3)_3(NO_2)_2Co{\cdot}O{\cdot}SeO_2{\cdot}O{\cdot}Co(NO_2)_2(NH_3)_3],2H_2O$; the *decammineperoxodicobalt selenates*, $(SeO_4)[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5](SeO_4),3H_2O$, $(HO_4Se)_2[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5](SeO_4H)_2$; and $(SeO_4)_2[(NH_3)_5CoO_2Co(NH_3)_5](SeO_4)_3,8H_2O$; *decammine-μ-aminodicobaltic selenate*, $(SeO_4)_2[(NH_3)_5Co{\cdot}NH_2{\cdot}Co(NH_3)_5]_2(SeO_4)_3$; *chloroaquo-octammine-μ-aminodicobaltic selenate*, $(SeO_4)[Cl(NH_3)_4Co{\cdot}NH_2{\cdot}Co(NH_3)_4(H_2O)](SeO_4)$; *acid octammine-μ-aminoselenatodicobaltic selenate*,

$$(SeO_4H)[(NH_3)_4Co\langle{}^{SeO_4}_{NH_2}\rangle Co(NH_3)_4](SeO_4);$$

octammine-μ-aminoselenatodicobaltic nitrate,

$$(NO_3)[(NH_3)_4Co\langle{}^{SeO_4}_{NH_2}\rangle Co(NH_3)_4](NO_3)_2;$$

acid octammine-μ-aminoselenatodicobaltic sulphate,

$$(HO_4S)[(NH_3)_4Co\langle{}^{SeO_4}_{NH_2}\rangle Co(NH_3)_4]SO_4;$$

acid octammine-μ-aminosulphatodicobaltic selenate,

$$(HO_4Se)[(NH_3)_4Co\langle{}^{SO_4}_{NH_2}\rangle Co(NH_3)_4]SeO_4;$$

octammine-μ-aminoperoxodicobaltic selenate),

$$(SeO_4)[(NH_3)_4Co\langle{}^{NH_2}_{O_2}\rangle Co(NH_3)_4]_2(SeO_4)_2;$$

octammine-μ-aminohydroxydicobaltic selenate,

$$(SeO_4)[(NH_3)_4Co\langle{}^{OH}_{NH_2}\rangle Co(NH_3)_4](SeO_4);$$

octammine-μ-aminonitrodicobaltic selenate,

$$(SeO_4)[(NH_3)_4Co\langle^{NO_2}_{NH_2}\rangle Co(NH_3)_4](SeO_4),2H_2O;$$

octamminedihydroxydicobaltic selenate,

$$(SeO_4)[(NH_3)_4Co\langle^{HO}_{HO}\rangle Co(NH_3)_4](SeO_4),2H_2O;$$

hexamminetrihydroxydicobaltic selenate,

$$(SeO_4)[(NH_3)_3Co\langle^{HO}_{HO}{}^{HO}\rangle Co(NH_3)_3](SeO_4)_2,6H_2O;$$

hexammine-μ-nitrodihydroxydicobaltic selenate,

$$(SeO_4)[(NH_3)_3Co\langle^{OH}_{OH}{}^{OH}\rangle Co(NH_3)_3](SeO_4)_2,2H_2O;$$

dodecammine-hexahydroxytetracobaltic selenate,

$$\left[Co\left(\begin{matrix}HO\\HO\end{matrix}Co(NH_3)_4\right)_3\right](SeO_4)_3.$$

H. T.

Non-existence of Nickel Suboxide. G. R. Levi and G. Tacchini (*Gazzetta*, 1925, **55**, 28—32).—*X*-Ray examination (cf. Levi, A., 1924, ii, 681) shows that the products obtained by Glaser (A., 1903, ii, 646) from partial oxidation of nickel and partial reduction of nickeloso-nickelic oxide, Ni_3O_4, are mixtures of nickelous oxide and nickel containing no nickel suboxide, Ni_2O. W. E. E.

Chlorides of Ruthenium. L. Wöhler and P. Balz (*Z. anorg. Chem.*, 1924, **139**, 411—418).—By treating finely-divided ruthenium with chlorine between 300° and 840°, only the trichloride is formed, which decomposes into its elements at 845°. No evidence was obtained for the formation of mono- or di-chloride by the direct action or by the decomposition of the trichloride. The product formed by the action of a mixture of carbon monoxide and chlorine at 400° has the same vapour pressure as the trichloride, and the formation of a blue colour by treatment of this product with dilute alcohol is probably due to reduction of the formed trichloride to dichloride by the alcohol. The anhydrous tetrachloride could not be obtained from chlororuthenic acid nor by chlorinating the trichloride. The vapour-pressure curve of the trichloride from 450° upwards was determined. Owing to the volatility of the trichloride, the values above 700° are unsatisfactory. H. I.

Iridium Tetroxide. F. Krauss and H. Gerlach (*Z. anorg. Chem.*, 1925, **143**, 125—128).—The oxide is prepared by heating the pure hydroxide for a short time in nitrogen at 350°. The hydroxide is prepared free from chlorine and alkali by employing the method used by Krauss and Kükenthal for the preparation of pure ruthenium trihydroxide (A., 1924, ii, 770). The compound was analysed by heating in carbon dioxide, absorbing the water by calcium chloride and weighing, and reducing the residual oxide in hydrogen to metal, which is finally weighed. L. L. B.

Boron and Boron Suboxide. H. H. KAHLENBERG (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 59—91).—Boron was prepared by all the important methods, but in most cases was impure. Reduction with sodium or potassium gave a product which could not be freed from the alkali metal and oxides. Moissan's method of reduction with magnesium gave a substance of composition B_7O contaminated with magnesium. Reduction with aluminium and sulphur gave a product containing the former, as also did interaction of aluminium and potassium fluoborate. Boron trichloride formed by passing chlorine over Moissan's "boron" (B_7O) was passed mixed with hydrogen over an electric arc between copper electrodes, and gave a deposit of pure amorphous boron, but in low yield. A small quantity of pure amorphous boron was obtained by electrolysing a fused mixture of potassium carbonate, potassium chloride, and boron trioxide, using a copper cathode and a carbon anode. Fused boron was obtained by reduction of Moissan's "boron" with aluminium powder in an arc. The single potential of boron is −0·028 volt with neutral potassium borate as electrolyte. The single potential is lower in acid, and higher in alkaline, electrolytes. Boron replaces gold, platinum, palladium, silver, mercury, copper, and lead from their solutions, the last-named very slowly. In the electrochemical series, boron comes just above lead. Moissan's "boron," which is shown to be a mixture of boron with a new *oxide*, B_3O, will not entirely replace gold from its solutions, the residue consisting of displaced gold and the oxide B_3O, which has a lower potential than boron. Boron has a high electrical resistance when cold, but becomes a good conductor at high temperatures. C. S.

Separation of Hafnium from Zirconium. G. VON HEVESY and E. MADSEN (*Z. angew. Chem.*, 1925, 38, 228; cf. A., 1924, ii, 53, 571).—A partial separation of hafnium and zirconium can be effected by means of fractional precipitation of the phosphates (cf. A., 1923, ii, 570), and also by recrystallisation through the double oxalates, double sulphates, and the oxychlorides. The preparation of pure hafnium salts is best effected by fractional crystallisation of the double fluorides. The following solubilities are given: K_2HfF_2, 0·1008 mol./litre in *N*/8-hydrofluoric acid at 20°; K_2ZrF_6, 0·0655 mol./litre; $(NH_4)_2HfF_6$, 1·425 mol./litre; $(NH_4)_2ZrF_6$, 1·050 mol./litre.

The mineral (silicate) is decomposed by fusion with ammonium hydrogen fluoride, by alkaline fusion, or by treatment with hydrofluoric acid. The product is converted into the sulphate and then into the oxychloride. This is either recrystallised or treated with sulphur dioxide, which precipitates hafnium and zirconium from the boiling solution, leaving most of the iron in solution.

The double fluorides are obtained by warming the dioxide with ammonium fluoride and hydrofluoric acid; the compound $(NH_4)_3ZrF_7$ resulting from the fusion is unsuitable. The hafnium content (2—5%) is raised to 38% by means of the ammonium compounds; subsequent fractionation of the potassium compounds

yields a hafnium salt of more than 99·9% purity. Incidentally a product probably analogous to Marignac's $KZrF_5,H_2O$ was obtained.

The separation was controlled by *X*-ray spectroscopy and by density determinations; the hafnium content x is given by the expression $x=(d-5{\cdot}73)/0{\cdot}0394$, where d is the observed density of the mixture of oxides. R. A. M.

Separation of Thorium from Zirconium and from the Tervalent Rare-earth Metals. L. FERNANDES (*Gazzetta*, 1925, 55, 3—6; cf. A., 1924, ii, 861).—A concentrated solution of thorium sulphate cooled with a large excess of thallous sulphate deposits thorium thallous sulphate (I), $2Th(SO_4)_2,7Tl_2SO_4$, stable over a wide range of temperature. Evaporation at a low temperature of thorium sulphate solution containing a little thallous sulphate yields $Th(SO_4)_2,Tl_2SO_4,4H_2O$, much less stable than I. A hydrate, $2Th(SO_4)_2,7Tl_2SO_4,3H_2O$, is stable from 70° to 100°. A solution of zirconium and thallous sulphates in concentrated sulphuric acid, when evaporated at a high temperature and then cooled gives two zirconium thallous sulphates: $Zr(SO_4)_2,2Tl_2SO_4,4H_2O$ (II), and $2Zr(SO_4)_2,Tl_2SO_4,8H_2O$. On the other hand, evaporation at the ordinary temperature at reduced pressure, over concentrated sulphuric acid, of a solution of the mixed salts in dilute sulphuric acid produces the double salt, $2Zr(SO_4)_2,7Tl_2SO_4$, and finally the compound II. A study of the solubility curves of $2Th(SO_4)_2,7Tl_2SO_4$, and $Ce_2(SO_4)_3,3Tl_2SO_4,H_2O$ in water and of that of zirconium sulphate in the presence of excess of thallous sulphate in 20% sulphuric acid, suggested the following method of separating cerium, thorium, and zirconium. The mixed hydroxides, precipitated by ammonium hydroxide, are washed with boiling water and dissolved in dilute sulphuric acid and treated cold with excess of thallous sulphate; this precipitates nearly all the cerium. After evaporating the filtrate to less than two-thirds of its volume, it is again filtered. On cooling, the first fraction of thorium is deposited in a pure state. Succeeding fractions of thorium are obtained by evaporating the filtrate until the sulphuric acid is nearly concentrated and the last traces are deposited on boiling. The liquid is then filtered through asbestos and the zirconium precipitated by cooling. W. E. E.

Preparation of Selenium Monochloride and Monobromide. V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, 47, 772—774).—Selenium monochloride, b. p. 130°, is prepared in 90% yield by the addition of selenium, followed (dropwise) by sulphuric acid, to a solution of selenium dioxide in concentrated hydrochloric acid; the reddish-brown, oily layer is separated, and washed with sulphuric acid or precipitated by hydrogen chloride from its solution in fuming sulphuric acid. Selenium monobromide is prepared similarly, using the mixture of sulphuric and hydrobromic acids produced by interaction of bromine, sulphur dioxide, and water at 0°.

J. S. C.

Laboratory Circulating Pump for Corrosive Vapours. H. C. KREMERS (*Ind. Eng. Chem.*, 1925, **17**, 298—299).—The circulation of hydrogen chloride (*e.g.*, for the dehydration of rare-earth chlorides) is effected by a reciprocating pump constructed of glass, the plungers in which are of an elongated bell-shape and work in a liquid seal composed of high b. p. paraffin oil or other suitable liquid. The valves are of glass. W. A. S.

Micropyrometer of the Spectrometer Type. F. HENNING and W. HAUSE (*Z. Physik*, 1924, **29**, 157—174).—A complete description is given of the instrument together with a detailed account of the method of calibration. The principle adopted is that of comparison of the intensity of radiation of a given wave-length from the source of which the temperature is to be determined with that of the same wave-length emitted by a glowing filament the temperature of which is under very sensitive control. Typical data are given of the behaviour of the instrument in the region 1500—2000°, and it is stated that temperatures up to 3000° can be determined in this way. R. W. L.

Destruction of Berthelot's Calorimetric Bomb. Its Replacement by a New Type of Bomb. C. MOUREU (*Compt. rend.*, 1925, **180**, 557—560).—In replacing the original calorimetric bomb of Berthelot, which exploded in 1918, the design has been modified in order to reduce the amount of platinum used in its construction. The lining consists of 0·4 mm. thickness of copper, covered with 0·4 mm. of gold and finally 0·2 mm. of platinum. G. M. B.

Process and Apparatus for Carrying out Chemical Reactions. E. BUHTZ (*Chem.-Ztg.*, 1925, **49**, 267).—An apparatus for carrying out reactions between two or more solid substances so that no part of the mixture is overheated and an efficient mixing of the reagents is effected, thereby avoiding as far as possible any side reactions, consists of a closed reaction vessel containing a large rotating plate slightly conical in shape, above which is a smaller rotating baffle plate which serves to distribute the reacting substances over the larger plate. The apparatus is charged through two concentric tubes, the outer of which leads directly to the baffle plate and the inner to the reaction plate. Provision is made for heating or cooling the latter by passing a stream of hot or cold liquid through pipes in the plate. A. R. P.

Effect of Chemicals on various kinds of Glass. C. E. KLAMER (*Chem. Weekblad*, 1925, **22**, 140—141).—Tables are given showing the losses of weight of vessels of Pyrex, Jena, Sphinx, and Murano glass after heating acids and alkalis in them. The conductivities of distilled water after being boiled in selected vessels were also determined. S. I. L.

Dynamic Study of Dehydration by means of a Hydrostatically-compensated Balance. M. GUICHARD (*Bull. Soc. chim.*, 1925, [iv], **37**, 251—253).—The apparatus and method used

in previous experiments are described in detail. The furnace is arranged so that its temperature increases regularly. The substance being dehydrated is balanced against a long cylindrical body partly immersed in oil, the level of which can be raised by addition from a burette. The volume thus added to preserve equilibrium after an experiment is proportional to the loss in weight of the substance. S. K. T.

Simple Apparatus for the Distillation of Mercury in a Vacuum. J. ŠVÉDA (*Chem. Listy*, 1925, 19, 51—53).—The apparatus consists of a large glass bulb connected, by a long glass tube provided with a stopcock, with a reservoir of mercury, and having at its upper end an upwardly inclined tube bent vertically downwards at its upper end and sealed to a long glass tube terminating in a receiver with side tube for connexion to the vacuum pump. The apparatus will distil 600—700 g. of mercury per hour. A. R. P.

Drying Tube for Phosphorus Pentoxide. L. M. DENNIS (*J. Amer. Chem. Soc.*, 1925, 47, 797).—A modified form of drying tube is described, in which the gas is passed in and out through side tubes, the phosphorus pentoxide in the tube being stirred and a fresh surface exposed by turning two stoppers fitted at the ends of the tube and carrying heavy bent glass rods. J. S. C.

Simple Tangentimeter. M. LATSHAW (*J. Amer. Chem. Soc.*, 1925, 47, 793—794).—A simple apparatus whereby the slope of a plotted curve at any point may be determined, consists of a plane mirror mounted on one leg of a steel "square" so that the mirror face extends to the plane at the bottom of the square and is normal to the other leg. When the mirror is standing normally across a given curve, there will appear no break between the curve and its image at the foot of the mirror. The second leg of the square is then parallel to the tangent to the curve at that point. J. S. C.

Simple Automatic Mercury Pump. H. M. MCLAUGHLIN and F. E. BROWN (*J. Amer. Chem. Soc.*, 1925, 47, 613—615).—A modified form of Toepler pump is described, which, with the aid of a small water pump, will operate continuously and automatically, returning the mercury to the reservoir after each stroke. The design of the apparatus permits collection of the exhaust gas and guards against its contamination. J. S. C.

Fractionating Column with Moving Parts. J. E. MYERS and W. J. JONES (*J. Chem. Soc.*, 1925, 127, 4—8).—The column is divided into sections by downwardly-directed conical trays equally spaced at 3·5 cm., each having at the centre a circular hole 1·25 cm. in diameter. Through these holes passes a vertical shaft which bears horizontal discs, 2·5 cm. in diameter, one just below each tray. The shaft works on a bearing fixed to the bottom of the column and emerges at the top through a stuffing-box. At about 2400 revolutions per minute the column compares very favourably with other patterns. L. J. H.

Mineralogical Chemistry.

New Type of Eruptive, Mesocratic Alkaline Rock. A. LACROIX (*Compt. rend.*, 1925, **180**, 481—484).—A new type of mesocratic, alkaline rock, intermediate between lujavrite, which is poor in silica, and fasibitikite, rich in silica, has been found amongst the quaternary gravels in the deserts of Santas-ho, China. The name "ordosite" is proposed for this rock. It consists of needles of green ægyrine with porphyritic crystals of felspar showing crossed albite twinning and enclosing laminæ of mica. It belongs to the syenite class, but for this class contains an unusually large amount (60%) of pyroxene soda, which is embedded in the felspar and is acicular in form. The analyses of nine ægyrine mesocratic rocks are given, that of ordosite being :

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.
56·90	7·00	17·41	1·25	1·22	1·62	6·86
K_2O.	TiO_2.	P_2O_5.	H_2O (+).	H_2O (−).	MnO.	
5·36	1·60	0·10	0·20	0·11	0·27	

The richness in pyroxene soda is shown to be independent of the nature of the felspar of which the rock is composed. J. W. B.

Native Arsenic in Cornwall. A. RUSSELL [with H. F. HARWOOD] (*Min. Mag.*, 1925, 20, 299—304).—Massive material with a curved lamellar structure and columnar jointing was found in some quantity (several cwt.) along a joint in dolerite in a road-metal quarry near Saltash in Cornwall. Analysis gave :

As.	Sb.	Fe.	S.	Insol.	Total.	Sp. gr.
94·80	5·15	0·15	0·11	0·10	100·31	5·636

Native arsenic has also recently been found in small amount in the Tolgus mine at Redruth. These are the first authentic records of the occurrence of this mineral in the British Isles. The occurrence of bismuthinite in granite at Shap in Westmorland, and of smaltite and niccolite in the old copper mine at Coniston in Lancashire, are also recorded. L. J. S.

Pyrites of Majdan-Pek (Serbia). J. BARTHOUX (*Compt. rend.*, 1924, 179, 982—984).—The beds of pyrite and chalcopyrite result from magmatic differentiation. These minerals tend to occur in vertical bands, most freely in contact with the face of an eruptive formation. The method of investigating the deposits consists, therefore, in finding the edge of the eruptive rock and exploring the lateral surface of contact. H. J. E.

Afwillite, a New Hydrous Calcium Silicate. J. PARRY and F. E. WRIGHT (*Min. Mag.*, 1925, 20, 277—286).—A columnar aggregate of clear, colourless crystals was found by A. F. Williams in the Dutoitspan diamond mine at Kimberley, South Africa. The crystals are monoclinic ($a : b : c = 2·097 : 1 : 2·381$, $\beta = 81° 34'$) with

prismatic habit in the direction of the axis of symmetry, and perfect (001) cleavage. d 2·630, hardness 4. The optical characters are given in detail and compared with those of the several known hydrous calcium silicates. Analysis I by J. PARRY was made by decomposing the mineral with hydrochloric acid, and II by H. S. WASHINGTON by fusion with sodium carbonate.

	SiO_2.	Al_2O_3+ Fe_2O_3.	MgO.	CaO.	BaO.	H_2O (+110°).	H_2O (−110°).	Total.
I.	33·96	0·60	—	49·28	—	15·89	0·12	99·85
II.	35·10	0·05	0·02	49·00	Nil	15·81	0·01	99·99

The formula is $3CaO,2SiO_2,3H_2O$, which may be written $2H_2CaSiO_4,Ca(OH)_2$, since two-thirds of the water is lost at about 300° and only one-third of the lime is taken up by water from the ignited material. The rate at which water is lost at different temperatures depends on the pressure of aqueous vapour in the atmosphere. The mineral gives an alkaline reaction; it is slowly decomposed by water and more readily by hydrochloric acid.

L. J. S.

Hafnium Content of Zirconium Ores. II. G. HEVESY and V. T. JANTZEN (*Chem. News*, 1925, **130**, 179—180; cf. A., 1924, ii, 492, 571, 620).—A comparison of the proportion of hafnium in 20 zircons of known radioactivity, helium content, and density, showed a rough connexion between the proportion of hafnium present and the radioactivity, but not with the density. The ratio HfO_2/ZrO_2 was found to be appreciably lower in zirconium minerals than in minerals of a less silicious magma. [Cf. *B.*, 1925, 314.]

D. G. H.

Tyuyamunite from the Tyuya-Muyun Radium Mine in Fergana. P. N. CHIRVINSKY (*Min. Mag.*, 1925, **20**, 287—295).—Tyuyamunite ($CaO,2UO_3,V_2O_5,mH_2O$) corresponds in composition with carnotite ($K_2O,2UO_3,V_2O_5,nH_2O$) and is consequently also known as calciocarnotite. An account is given of its occurrence and mining in Russian Turkestan. It is found with copper ores in limestone. Analyses of the ore show CuO 3·10—10·88%, U_3O_8 0·80—4·61%, V_2O_5 1·83—6·39%, together with barytes and calcite. The copper is present as malachite and the vanadate turanite ($5CuO,V_2O_5,2H_2O$). Of wide distribution in the same region is a nickel vanadate, named kolovratite by Vernadsky in 1922. The optical characters of the minute orthorhombic crystals of tyuyamunite are described.

L. J. S.

X-Ray Examination of Calcium Formate. K. YARDLEY (*Min. Mag.*, 1925, **20**, 296—298).—It is shown that crystals of calcium formate are orthorhombic bipyramidal, and not bisphenoidal as suggested by Plathan (*Z. anorg. Chem.*, 1898, **18**, 86). The dimensions of the unit cell containing eight molecules are a=10·19, b=13·41, c=6·27 Å. The half spacing for certain of the planes shows that the lattice is Γ_s and the space-group Q_h^5.

L. J. S.

Analytical Chemistry.

Laboratory Vacuum Gauge. M. L. HAMLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 709—712).—Details are given for the construction and calibration of a vacuum gauge having a useful range of 10—0·05 mm., which may be so modified as to cover a second range of pressures one-fifth or one-tenth of this. J. S. C.

Gas Absorption Pipette. A. O. JONES (*J. Soc. Chem. Ind.*, 1925, **44**, 115—116T).—A two-bulbed absorption pipette is described in which the bulbs are joined by rubber tubing in place of the usual rigid glass tube, and a funnel and tap are attached to the top of the absorption bulb. By this means, the gas in the pipette may be washed with more than one reagent without transferring it to the burette, one pipette can be used for all the reagents, and fouling of the mercury in the burette by the reagents is lessened. L. F. H.

Modification of Geissler's Bulbs. G. ODDO (*Annali Chim. Appl.*, 1925, **15**, 3—4).—When the tightness of the joints of a combustion apparatus is being tested, the potassium hydroxide solution tends to spurt into the calcium chloride tube. This is prevented if the narrow tube passing down into the first small bulb of the Geissler absorption apparatus is continued, at its upper end, into the large bulb and bent over in the form of a crook. T. H. P.

Apparatus for Quantitative Microanalysis. J. POLLAK (*Mikrochem.*, 1924, **2**, 189—192).—When mixing solutions in test-tubes immersed in a water-bath for quantitative microanalysis, stirring by means of a slow current of air is the only satisfactory way. The air should be purified from dust and possible halogen compounds by passing it from an aspirator through a wad of cotton wool, then through asbestos soaked in silver nitrate solution, and bubbled into the test solution through a capillary tube. For suspending a number of test-tubes in a water-bath (beaker), a stand consisting of two perforated brass plates some distance apart and fixed to arms bent at right angles at the top to rest on the edge of the bath is useful. A. R. P.

Use of Glass Filters in Qualitative Analysis. G. F. HÜTTIG and M. NETTE (*Z. anal. Chem.*, 1925, **65**, 385—399).—Büchner or Nutsche funnels with porous filter-beds of sintered glass have many advantages over filter-papers for qualitative group analysis. The one funnel may be used throughout the analysis; the precipitate is sucked dry on each occasion, thereby keeping the volume of the filtrate low, and the different constituents of a group precipitate may be extracted by passing the appropriate solvents through the filter in succession. None of the ordinary group reagents except alkali hydroxides has any solvent action on the filter, which may, if necessary, be cleaned by the use of the strongest acids at high temperatures. Suitable forms of apparatus for the purpose are

described and a detailed account is given of the procedure for conducting an ordinary group analysis. A. R. P.

Shimer Filter Tube. E. C. BINGHAM (*Ind. Eng. Chem.*, 1925, 17, 293—294).—The improved form is described (cf. A., 1905, ii, 349). The " filter-mat " is now made of surgical lint. W. A. S.

Determination of Combustible Gases by Combustion with Cupric Oxide. II. J. ŠVÉDA (*Chem. Listy*, 1925, 19, 41—48, 73—79).—A fuller account of work previously published (this vol., ii, 154). The combustion of the gases is carried out in a special gas pipette which may be exhausted of air before introducing the gas mixture, thus eliminating errors due to absorption of air and carbon dioxide by the contact mass of ceric and cupric oxides. The combustion of both hydrogen and carbon monoxide is complete at 280—290°, contrary to the statement of Scherb that the completeness of the oxidation of carbon monoxide depends on the partial pressure of the hydrogen. A. R. P.

Adsorption of Cresol-red by Serum in Spectrophotometric Determination of p_H. E. F. HIRSCH.—(See i, 606.)

Bromate Determination of Hydrogen Peroxide, Peroxides, and Per-salts. E. RUPP and G. SIEBLER (*Pharm. Zentr.*, 1925, 66, 193—196).—0·1*N*-Solutions of potassium bromate and arsenious acid do not alter on keeping. Titration of the latter with the former is carried out in hot, strongly acid solution in presence of methyl-orange; excess of bromate liberates bromine, which decolorises the indicator. Hydrogen peroxide is run into excess of arsenious oxide in alkaline solution, the whole acidified, and the excess titrated with bromate. Other peroxides are treated, in presence of excess of the arsenic solution, with acid, to liberate hydrogen peroxide, and the determination is completed as for the latter. Persulphates are reduced by excess of the arsenic solution in 5 min., at the b. p., perborates even more quickly. S. I. L.

Preparation of *o*-Tolidine Solution for the Determination of Chlorine [in Chlorinated Water]. C. E. ROAKE (*Ind. Eng. Chem.*, 1925, 17, 257).—The *o*-tolidine is first treated with concentrated hydrochloric acid; dissolution is then easier. [Cf. *B.*, 1925, 333.] W. A. S.

Detection and Determination of Chloride, Bromide, and Thiocyanate in the Presence of Cyanide. E. SCHULEK (*Z. anal. Chem.*, 1925, 65, 433—435).—In the presence of free alkali or of sodium hydrogen carbonate, cyanides are converted by formaldehyde into alkali glycollate and hexamethylenetetramine. If the solution is then acidified with nitric acid, the chloride, bromide, or thiocyanate ions may be determined by Volhard's method in the usual way. An alternative procedure for the elimination of the cyanide consists in distilling the liquid with boric acid; the residual solution in the distilling flask is then acidified with nitric acid and the analysis finished as described above. A. R. P.

Electrometric Titration of Hypochlorous Acid. A. SCHLEICHER and L. TOUSSAINT (*Z. anal. Chem.*, 1925, 65, 399—405).—In Treadwell's process for the electrometric titration of hypochlorous acid (A., 1921, ii, 410), the comparison electrode may consist of solutions of many neutral salts or weak oxidising agents instead of a previously titrated hypochlorite solution. Such salts are sodium chloride, nitrate, and sulphate, ammonium chloride and acetate, and chromates of the alkali metals. The potential at the end-point may be displaced as much as 0·2 volt without affecting the results if the titration is carried out in the simplified compensation apparatus of A. Fischer ("Elektroanalytische Schnellmethoden," Stuttgart, 1908). A. R. P.

Electrometric Titration of Chlorous Acid and its Determination in Presence of Hypochlorous Acid. A. SCHLEICHER and W. WESLY (*Z. anal. Chem.*, 1925, 65, 406—411).—Chlorous acid reacts with potassium iodide and sulphuric acid, liberating 2 mols. of iodine, which may be measured by titration of the solution with sodium thiosulphate and electrometric determination of the end-point. This acid does not react with sodium arsenite in the presence of sodium hydrogen carbonate, whilst hypochlorous acid may be determined electrometrically by titration with this reagent. The titrated solution is treated with potassium iodide and sulphuric acid and the chlorous acid determined as above, allowance being made for the excess of arsenite used in the first titration. Chlorites are not decomposed by heating the solution for 15 hrs. on the water-bath, but hydrogen peroxide decomposes them readily without attacking any chlorate present. A. R. P.

Volumetric Determination of Iodides. N. SASAKI (*Z. anorg. Chem.*, 1924, 139, 394—396).—Iodides in the presence of an equal amount of bromide and forty times as much chloride can be accurately determined by treating a solution with an excess of 0·1*N*-potassium dichromate solution, followed after 10—60 secs. by an excess of ferrous ammonium sulphate solution, and titrating the liberated iodine immediately with thiosulphate solution, the reactions between iodide and ferric salts and free iodine and ferrous salts taking place very slowly. Direct sunlight should be avoided and the iodide solution should contain 1 mg.-equivalent of iodide in 300 c.c. and be acidified with sulphuric acid until the solution has about *N*-acidity. If more bromide or chloride is present, approximate results can be obtained by shortening the time of action of the dichromate solution. H. T.

Determination of Hydrofluoric Acid. O. WAELZEL (*Z. Unters. Nahr. Genussm.*, 1925, 49, 31—37).—The method of Greef (A., 1913, ii, 975) by which soluble fluorides are titrated with ferric chloride in the presence of ammonium thiocyanate, is adapted for the analysis of disinfectants etc. A. G. P.

Determination of Sulphur in Polysulphides. A. KURTENACKER and K. BITTNER (*Z. anorg. Chem.*, 1925, 142, 115—118).—Sodium polysulphide solution is converted into thiosulphate and

sulphide by the action of sodium sulphite solution as in the methods of Chapin and of Wöber. The sulphide is then precipitated with zinc acetate and the excess of sulphite removed with formaldehyde. After addition of acetic acid, the thiosulphate is titrated with iodine. The results show excellent agreement with those obtained indirectly by oxidation of the sulphur with bromate and bromide (Treadwell and Mayr). N. H. H.

Determination of Polythionic Acids in Presence of One Another. A. KURTENACKER and K. BITTNER (*Z. anorg. Chem.*, 1925, **142**, 119—129).—A volumetric method is described for the determination together of the radicals S_3O_6'', S_4O_6'', and S_5O_6''. By treatment with excess of mercuric chloride, all the radicals react to give four equivalents of acid for each mol. of polythionate, $2S_{3+x}O_6''+3HgCl_2+4H_2O \rightarrow Hg_3S_2Cl_2+4Cl'+8H^{\cdot}+2xS$. Thus titration with sodium hydroxide solution gives the total polythionate. On treatment of another portion with excess of sodium sulphite solution, the reactions $S_4O_6''+SO_3''=S_3O_6''+S_2O_3''$ and $S_5O_6''+2SO_3''=S_3O_6''+2S_2O_3''$ occur, and after removal of the excess of sulphite with formaldehyde the thiosulphate may be titrated with iodine. A third portion is treated with potassium cyanide solution, giving $S_4O_6''+3CN'+H_2O=SO_4''+CNS'+2HCN+S_2O_3''$ and $S_5O_6''+4CN'+H_2O=SO_4''+2CNS'+2HCN+S_2O_3''$. If the original solution contains x, y, and z mols. of tri-, tetra-, and penta-thionate, respectively, and the three titrations are a mols. of sodium hydroxide and b and c mols. of iodine, then $x=a/4-c$, $y=2c-b$, and $z=b-c$. The results are in satisfactory agreement with the theoretical when arbitrary mixtures of the pure substances are used and with results obtained by certain other methods. N. H. H.

[Quantitative] Separation of Selenium and Tellurium by Sulphur Dioxide in Hydrochloric Acid Solution. V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, **47**, 769—772).—Selenium is precipitated by sulphur dioxide from cold solutions of the two oxides in concentrated hydrochloric acid, washed with concentrated hydrochloric acid, water, and finally with alcohol and ether, care being taken to remove the last traces of water. The precipitate is dried for 3 or 4 hrs. at 30—40° and finally for 2 hrs. at 120—130°. Tellurium is precipitated from the concentrated filtrate by the sulphur dioxide–hydrazine hydrochloride method previously described (A., 1908, ii, 426), washed with hot water and alcohol, and finally dried at 105°. J. S. C.

Determination of Nitrogen by Kjeldahl's Method; an Attempt at Generalisation and One Source of Error. P. FLEURY and H. LEVALTIER (*Bull. Soc. chim.*, 1925, [iv], **37**, 330—335).—In the determination of nitrogen by the Kjeldahl–Gunning method, using potassium sulphate, some nitrogen is always lost as such (70% in the case of phenylhydrazine) and some is lost in another, unknown form (about 28% with piperidine). Carbon monoxide is always produced, so that the mechanism of the reaction

must involve mainly a process of reduction (cf. A., 1924, ii, 273; this vol., ii, 66). S. K. T.

Preparation of Nessler's Solution. R. C. FREDERICK (*Analyst*, 1925, **50**, 183).—Increasing age does not increase the sensitiveness of Nessler's solution, and the maximum effect following from sensitising the reagent by means of saturated mercuric chloride solution lasts only for 2 hrs. D. G. H.

Determination of Phosphoric Acid in Metabolic Investigations. C. SCHMITT-KRAHMER.—(See i, 613.)

Qualitative Microanalysis. II. F. FEIGL (*Mikrochem.*, 1924, **2**, 186—188).—Addition of ammonium molybdate followed by a strongly acid solution of stannous chloride to a hydrochloric acid solution containing phosphoric acid, but free from arsenic acid, produces a brown to yellow colour, and on shaking the mixture with amyl alcohol the latter is coloured blue if only 1 part of phosphoric acid is present in 1,250,000 parts of solution.

Magnesium salts, when boiled with alcoholic potassium hydroxide and diphenylcarbazide, yield a red precipitate insoluble in hot water; to detect traces of magnesium, the solution must be filtered and the paper washed with hot water to remove the soluble potassium salt.

Bismuth nitrate solutions yield characteristic orange-yellow, crystalline precipitates with pyrogallol and tribromopyrogallol; lead does not interfere in the test.

Barium and strontium salts give red precipitates with sodium rhodizonate in neutral solution; the strontium compound is readily soluble in 1% hydrochloric acid, whilst the barium compound is turned scarlet by the acid. By converting the barium into chromate before testing with the reagent, strontium may be detected in presence of barium. [Cf. *B.*, 1925, 340.] A. R. P.

Double-reacting Turmeric Paper. W. BRINSMAID (*Ind. Eng. Chem.*, 1925, **17**, 264).—When the paper is prepared as described, the effect of boric acid is, as usual, to change the colour to pink or cherry-red, but a confirmatory reaction is now possible, in that this colour is turned to a clear blue by the action of 0·1*N*-sodium hydroxide. [Cf. *B.*, 1925, 342.] W. A. S.

Volumetric Determination of Small Quantities of Carbon in Tungsten. W. J. KING (*J. Amer. Chem. Soc.*, 1925, **47**, 615—621).—The method depends on the combustion of tungsten in pure oxygen, passage of the products of combustion into a special absorption apparatus containing hot 0·01*N*-barium hydroxide solution, and titration of the cold, filtered solution with 0·01*N*-hydrochloric acid, using thymolphthalein as indicator. The special absorption apparatus provides for the complete absorption of carbon dioxide, the precipitation and filtration of barium carbonate in the hot solution, and finally a method of titrating the excess of barium hydroxide without transferring to a second vessel. The addition of 15% of ethyl alcohol and 1%

of barium chloride to the standard 0·01*N*-solutions is recommended. The combustion furnace is maintained at 700—1000°, and 65° is selected as the most suitable temperature for the barium hydroxide solution from considerations of minimum corrosion of the glass, complete absorption of carbon dioxide, and coagulation of the precipitated barium carbonate. J. S. C.

Determination of Carbon in Organic Substances. A. Desgrez and R. Vivario (*Compt. rend.*, 1925, **180**, 886—890).—By the action of a large excess of potassium dichromate and sulphuric acid, the carbon of organic matter is oxidised to carbon dioxide, which is absorbed by weighed potassium hydroxide; before absorption, the vapours are passed over potassium ferrocyanide and borax to remove the volatile chlorine and nitrogen derivatives, and then over heated cupric oxide to complete the oxidation. The method is recommended for the determination of carbon in blood. [Cf. *B.*, 1925, 342.] F. M. H.

Conditions for Applying the Argentosulphochromic Method in Determining Carbon. L. J. Simon (*Compt. rend.*, 1924, **179**, 975—977; cf. A., 1924, ii, 567, and previous abstracts).—The determining factors in the sulphochromic oxidation of organic compounds are the relative quantity of silver dichromate and the time of heating. Experiments with benzaldehyde, salicylaldehyde, and cinnamaldehyde show that if one of these factors is changed, the other varies in the opposite sense. The author recommends the use of 4·0 g. of silver dichromate for each 0·2 g. of the substance to be oxidised and heating for 30 mins. at 100° or 12·0 g. and 4 mins., but recognises that the method is empirical. H. J. E.

Absorption of Carbon Monoxide. I. Critical Comparison of some Methods Employed in Gas Analysis. H. R. Ambler. **II. Advantages of Using Hot Reagent.** T. C. Sutton and H. R. Ambler (*Analyst*, 1925, **50**, 167—174).—Acid cuprous chloride solution was not satisfactory but ammoniacal cuprous chloride solution effected complete absorption of carbon monoxide, provided that it had not previously absorbed more than 5% of its volume of the gas. Cuprous oxide in sulphuric acid containing β-naphthol also brought about complete absorption, but at a slower rate. The time may, however, be reduced to 3 mins. by using the solution at a temperature of about 60°. [Cf. *B.*, May 29th.] D. G. H.

Separation and Determination of the Alkali Metals, using Perchloric Acid. I. Solubilities of the Perchlorates of the Alkali Metals in Mixed Organic Solvents. G. F. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 762—769).—The solubilities of sodium, potassium, rubidium, cæsium, and ammonium perchlorates, sodium perchlorate monohydrate, and lithium perchlorate trihydrate have been determined in various mixtures of methyl, ethyl, and *n*-butyl

alcohol with ethyl acetate. The salts fall into two groups, the readily soluble sodium, lithium, and ammonium salts, and the sparingly soluble potassium, rubidium, and cæsium salts. The solubility data are discussed from the point of view of the separation and determination of the alkali metals, and it is shown that the use of mixed solvents has many advantages over that of individual solvents (A., 1923, ii, 239). J. S. C.

Separation and Determination of the Alkali Metals Using Perchloric Acid. II. Precise Determination of the Insoluble Alkali Metal Perchlorates. G. F. SMITH and J. F. ROSS (*J. Amer. Chem. Soc.*, 1925, 47, 774—781; cf. preceding abstract).—The alkali chlorides, free from ammonium salts, are evaporated with perchloric acid and then taken twice to dryness on the hot plate. The soluble sodium or lithium salts are removed by extraction with one of the mixed solvents previously studied. The insoluble potassium, rubidium, or cæsium perchlorate is dried to constant weight at 350°. The evaporation of the chlorides with excess of perchloric acid results in the concentration of the latter to 72·5%, in which the perchlorates are freely soluble. Photomicrographs show that the perchlorates crystallise from such solutions in long, tubular crystals, in the hollow parts of which mother-liquor is frequently enclosed. The extent of acid occlusion is usually very small. Previous methods for the perchlorate separation are shown to have appeared exact as the result of a fortuitous compensation of errors. J. S. C.

Determination of Potassium in Potassium Salts as Perchlorate. A. VÜRTHEIM (*Chem. Weekblad*, 1925, 22, 138—140).—With suitable precautions, the method yields very accurate results. Potassium perchlorate is insoluble in 96% alcohol containing 3 c.c. of 50% perchloric acid per litre; the minimum quantity of neutral 96% alcohol must be used for the final wash-liquid, since if neutral alcohol saturated with the perchlorate be used the results are too high. Barium perchlorate is very soluble in 96% alcohol containing the above quantity of perchloric acid; 40 c.c. dissolve 28 g. Even in presence of other salts, the results are accurate if sulphates be carefully removed. S. I. L.

Reaction for Magnesium and Calcium and for Rubidium and Cæsium. E. MURMANN (*Oesterr. Chem.-Ztg.*, 1925, 28, 42—44; cf. A., 1924, i, 20).—The cæsium magnesium ferrocyanide precipitate is a fine white powder, practically insoluble in water; it is a mixture of composition approximately corresponding with the formula $Cs_3Mg_2Fe_2(CN)_{12},4H_2O$. The sensitiveness for varying proportions of the reagents is given. S. I. L.

Separation of Small Quantities of Calcium from Large Amounts of Magnesium. R. HEILINGÖTTER (*Chem.-Ztg.*, 1925, 49, 241).—For the determination of less than 5% of calcium oxide in commercial magnesites, the method of Dede (A., 1912, ii, 491) gives sufficiently accurate results in a shorter time than that of

Rodt and Kindscher (this vol., ii, 158), but no comparative figures of the two methods are given. A. R. P.

Oxalate Separation of Calcium and Magnesium. G. LUFF (*Z. anal. Chem.*, 1925, 65, 439—448).—The presence of ammonium chloride and too great an excess of ammonium oxalate tends to cause co-precipitation of magnesium from solutions containing much magnesium in the presence of little calcium. In the absence of ammonium chloride and by using only a very slight excess of ammonium oxalate and digesting the liquid for 1—2 hrs. on the water-bath, good separations of calcium from relatively large amounts of magnesium may be effected in one operation. In the usual course of analysis, the solution from which the calcium is to be precipitated generally contains a quantity of ammonium chloride; in such cases, the boiling, slightly ammoniacal solution is treated drop by drop with a saturated ammonium oxalate solution from a burette until a drop of the clear liquor shows the presence of an excess of the reagent in a spot test with calcium nitrate solution. The precipitate is collected after digestion for 1 hr. on the water-bath. From acetic acid solutions, considerable co-precipitation of magnesium takes place, even under the most carefully controlled conditions. A. R. P.

Fractional Crystallisation of Radioactive Substances. W. CHLOPIN (*Z. anorg. Chem.*, 1925, 143, 97—117; cf. A., 1924, ii, 42).—The fractional crystallisation of barium–radium salts by evaporation of the solution can be successfully replaced by fractional precipitation of the given solution by increasing the concentration of the anion. Acids or salts which contain the same anion as the barium–radium salt, and form no double or complex compounds with this, may be used. Precipitants which favour hydrate formation are of special value. It is found that the "coefficient of enrichment" is approximately only dependent on the relative mass of the precipitated barium salt in the case of chlorides, bromides, and nitrates. The fractional precipitation of the chlorides by means of hydrochloric acid has been utilised for the separation of radium from barium on the large scale. The fractional crystallisation or precipitation of the nitrates leads to a concentration of radium in the solid phase, and thus to a gradual separation of radium from barium. The distribution of radium between solid and liquid phases follows approximately the Nernst–Berthelot distribution law. The value of the "coefficient of enrichment" is different according as the fractionation is brought about by partial precipitation or by partial crystallisation of the barium–radium salt. L. L. B.

Volumetric Determination of Zinc. E. BEYNE (*Bull. Soc. chim. Belg.*, 1925, 34, 38—41; cf. this vol., ii, 69).—In the Schaffner method (for which the author suggests the unambiguous name "Vieille-Montagne" method), a small error is involved in the incomplete separation of zinc with iron, aluminium, and manganese hydroxides by ammonia in the presence of ammonium salts. [Cf. *B.*, 1925, 246.] J. W. B.

Separation of Zinc and Nickel by Hydrogen Sulphide. A. KLING and [MME.] A. LASSIEUR (*Compt. rend.*, 1925, **180**, 517—519).—The p_H values necessary for the precipitation of zinc and nickel by hydrogen sulphide are determined with a view to obtain a satisfactory separation of these two metals by this reagent. In the case of nickel, when hydrogen sulphide is passed for 45 mins., the minimum p_H value is 2·80, whilst the corresponding value for the quantitative precipitation of zinc is 2·4, and thus separation is not possible in a short time. If the gas be passed for 1 hr. and the solution left for a further 12 hrs., nickel is precipitated from solutions with $p_H > 2·0$, whilst zinc requires p_H 1·35 for complete precipitation; again, the margin is too small to allow the separation to be trustworthy. The presence of ammonium sulphate does not affect the precipitation of nickel, but in the case of zinc the presence of this salt (10 g. per litre) causes precipitation to commence at p_H 1·0, and to be quantitative at p_H 2·4. J. W. B.

Electroanalytical Determination of Cadmium in Sulphuric Acid Solutions. E. BÜTTGENBACH (*Z. anal. Chem.*, 1925, **65**, 452—455).—Cadmium may be deposited electrolytically on a stationary cathode from a solution containing 6 g. of potassium hydrogen sulphate in 200 c.c. by the use of a rotating anode and an *E.M.F.* of 3·8 volts. With small amounts of cadmium a cadmium-plated cathode should be used with a stationary anode. A. R. P.

Separation of the Rare-earths by Basic Precipitation. VIII. Preparation of Pure Yttrium Oxide. W. PRANDTL (*Z. anorg. Chem.*, 1925, **143**, 277—284).—The solubilities of yttrium oxide in *N*-, 2*N*-, 3*N*-, 4*N*-, and 5*N*-ammonium nitrate solutions, at temperatures up to 100°, alone and in presence of zinc and cadmium nitrates, are recorded. In absence of heavy metals, the solubilities are lower (one-third to one-half) than the solubilities of samaria, the weakest base of the ceria group. The presence of cadmium nitrate raises the solubilities considerably, that of zinc nitrate much more; in this, yttria behaves differently from the ceria earths, the solubilities of which in ammonium nitrate solutions are greater in presence of cadmium nitrate than of zinc nitrate. Yttrium is readily concentrated by taking advantage of these solubility differences; of three crude yttrium fractions obtained by this fractional basic precipitation, the most basic was further treated by bromate fractionation; yttrium from the most soluble fractions contained only a trace of holmium and gave an atomic weight 89·09. The middle and least basic fractions were treated by bromate fractionation, followed again by basic precipitation fractionation; the yttrium so obtained had an atomic weight 88·95, and its *X*-ray spectrum gave no rare-earth lines other than those of that element. The last traces of erbium in this yttrium were removed by the ferrocyanide method; the final product showed no absorption lines in a thickness of 20 cm. of the concentrated nitrate solution. The ferrocyanide precipitation is carried out in presence of ammonia or zinc nitrate to assist

filtration; the precipitate is dried and ignited, the residue extracted with nitric acid, and the earths precipitated as oxalates.

S. I. L.

Goppelsroeder's Reaction for Aluminium and its Application in Microchemistry. E. SCHANTL (*Mikrochem.*, 1924, 2, 174—185).—Aluminium salts in neutral solution yield a characteristic green fluorescence with alcoholic solutions of morin (tetrahydroxyflavonol) due to the formation of the neutral salt $Al(C_{15}H_9O_7)_3$. Mineral and organic acids, except acetic, reduce the sensitivity appreciably. If the test is carried out in a dark room and the solution viewed through a Tswett's luminoscope (*Z. physikal. Chem.*, 36, 450), as little as 0·0000001 mg. of aluminium in 10 c.c. of solution is readily detected; the method is therefore as delicate as the spectrographic test. Iron and chromium salts give dark-coloured, colloidal precipitates with the reagent, but these may be separated by filtration through a filter-candle and the filtrate tested for fluorescence in the luminoscope. Manganese, cobalt, nickel, and zinc salts do not interfere. Morinsulphonic acid, which is readily soluble in water, may be used in place of morin itself without appreciably affecting the sensitivity of the test and, in this case, the presence of mineral acids has a much less marked inhibiting power on the development of the fluorescence.

A. R. P.

Determination of Large Quantities of Manganese by Titration with Permonophosphoric Acid. T. HECZKO (*Z. anorg. Chem.*, 1925, 143, 129—142).—By the action of permonophosphoric acid, prepared from phosphoric acid, phosphorus pentoxide, and hydrogen peroxide, in acid solution on manganese salts, a stable complex compound of tervalent manganese is obtained in solution. After complete oxidation of the manganese, the excess of the oxidising agent decomposes in a short time. Iodometric titration is employed. [Cf. *B.*, May 29th.] L. L. B.

Certain and Exact Establishment of the End-point in the Titration of Manganese. O. HACKL (*Chem.-Ztg.*, 1925, 49, 257).—In the titration of manganese by Volhard's method, the end-point is often masked, especially if much iron is present, by the presence of finely-divided suspended particles which do not settle well. In these cases, a portion of the solution should be filtered by suction through an asbestos filter and the colour of the filtrate compared with a standard made by tinting with 0·1 c.c. of permanganate a volume of water equal to the volume of the solution being titrated. If the end-point is not yet reached, the filtrate is returned to the main solution and the process repeated. Before use, the asbestos should be ignited, then washed successively with hydrochloric acid, water, dilute permanganate, and water again to ensure the absence of reducing compounds. A. R. P.

Reaction between Potassium Permanganate and Hydrogen Peroxide in Presence of Ammonium Sulphate. N. A. TANANAEV (*Z. anorg. Chem.*, 1925, 143, 118—124).—Potassium

permanganate is reduced by hydrogen peroxide in the presence of ammonium sulphate: $2KMnO_4+3(NH_4)_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2+6NH_3$. The ammonia set free can be determined with standard sulphuric acid, and the titre of the permanganate thus calculated. For an exact determination of the end-point of the reaction the use of methyl-red is recommended. L. L. B.

General Application of the Alloxantin Reaction for Ferric Iron. G. DENIGÈS (*Compt. rend.*, 1925, **180**, 519—520).—The blue colour produced by the action of ferric salts on alloxantin in alkaline solutions serves as a sensitive test for ferric iron and as a means for its colorimetric determination. The reagent consists of 0·1 g. of alloxantin dissolved in 10 c.c. of *N*-sodium hydroxide solution (if rose-coloured the solution is first boiled to destroy the colour and rapidly cooled). A distinct blue colour is developed on adding 1 c.c. to 2 c.c. of a solution containing 0·001 g. of ferric iron per litre. By using five times these quantities and examining the colour through a long column, a few tenths of 1 mg. per litre can be detected. The presence of tartaric and citric acids, which prevents the use of salicylic, thiocyanic, and even Prussian-blue tests, seems favourable to the alloxantin reaction. J. W. B.

Electrometric Titrations. Use of Titanous Chloride for Ore Analysis. A. MCMILLAN and W. C. FERGUSON (*J. Soc. Chem. Ind.*, 1925, **44**, 141—142T).—In the analysis of iron ore, ferrous iron is oxidised with bromine; manganese is determined by oxidising the solution of the ore with ammonium persulphate, adding ammonia in excess, dissolving the precipitate containing manganese dioxide in the least possible quantity of acid ferrous ammonium sulphate solution, and determining the amount of iron oxidised by electrometric titration. The results agree with those obtained by more tedious methods. F. B.

Separation of Nickel and Iron in Presence of Chromium by Electrolysis. E. ROUSSEAU (*Chim. et Ind.*, 1925, **13**, 199—201).—The electrolytic deposition of nickel from an alkaline solution of its salts is prevented, in presence of chromium, by the simultaneous formation of ammonium chromate. This can be avoided by the addition of ammonium oxalate to the solution before electrolysis together with ammonium citrate to retain iron in solution. With this and other precautions, the electrolytic method is accurate when applied to the analysis of chromium alloys or their solutions. [Cf. *B.*, 1925, 341.] C. I.

Determination of Thorium-*X*. F. GAZZONI (*Compt. rend.*, 1924, **179**, 963—965).—The precipitating reagent used for other substances which may be present is either hydrogen peroxide or ammonia; both leave the thorium-*X* in solution but accompanied in the former case by its active deposit. The thorium-*X* is in part carried down by the precipitate and four or five precipitations are necessary to effect a good separation; this is more difficult when using hydrogen peroxide. The vessels containing the original

mixture and the thorium-*X*, evaporated to dryness, are compared in an ionisation chamber protected by lead. The results obtained for the thorium-*X* are modified by the factor 0·88, which is calculated from the increase and subsequent decrease of the radiation from the separated product, which attains a maximum after 2·50 days. H. J. E.

Germanium. X. Determination of Germanium. E. B. JOHNSON and L. M. DENNIS (*J. Amer. Chem. Soc.*, 1925, **47**, 790—793).—The metal is precipitated from acid solutions as the disulphide, the precipitate dissolved in ammonia, oxidised with 3% hydrogen peroxide, and weighed as the dioxide. J. S. C.

Diphenylamine as Indicator in the Reduction of Vanadic Acid. N. H. FURMAN (*Ind. Eng. Chem.*, 1925, **17**, 314—316).—In titrating vanadic acid with ferrous sulphate, diphenylamine can be used as indicator, as in the analogous determination of chromic acid (cf. Knop, A., 1924, ii, 351). A small correction must be made for the vanadic acid consumed in oxidising the diphenylamine to the blue compound that actually serves as indicator. Vanadium in ores and steels may be determined by Willard and Fenwick's methods (A., 1923, ii, 187) using this indicator. W. A. S.

Use of Pyrogallol in the Gravimetric Determination of Bismuth and its Separation from Lead. F. FEIGL and H. ORDELT (*Z. anal. Chem.*, 1925, **65**, 448—451).—The solution of the two metals as nitrates is treated with ammonia until a faint turbidity is produced, heated to boiling, and treated with a slight excess of pyrogallol. The heavy, yellow, crystalline precipitate having the composition $C_6H_3O_3Bi$ is collected on a Gooch crucible, washed with very dilute nitric acid, then with cold water, dried at 110°, and weighed; it contains 62·84% Bi. The lead is recovered from the filtrate by saturation with hydrogen sulphide and is converted into sulphate for weighing. A. R. P.

Electrometric Titration of Bismuth alone and together with Lead. E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1924, **139**, 397—410).—Bismuth solutions can be readily titrated by reduction from the tervalent condition to metal by means of titanous chloride solution, the end-point being determined electrometrically in the usual way. The best results are obtained in 3% hydrochloric acid or in acetic acid solution, the precipitation of basic bismuth chloride being prevented by the addition of sodium chloride, and titanic acid by the addition of tartaric acid. Sulphates are without influence, but nitrates must be absent. The operation can be carried out in the same way in the presence of lead. Owing to the ease of oxidation of the finely-divided bismuth, the titration must be carried out in an inert atmosphere. H. T.

Precipitation of Tantalum and Niobium by "Cupferron" and their Separation from Iron. H. PIED (*Compt. rend.*, 1924, **179**, 897—899).—The method of Weiss and Landecker (A., 1909, ii, 942) for separation of iron may be used in the case of

tantalum and niobium by dissolving the freshly-precipitated hydroxides in oxalic acid and adding tartaric acid to the solution. It is then boiled and the iron precipitated as sulphide in the manner recommended (*loc. cit.*). The precipitate is filtered off, the filtrate acidified with sulphuric acid, boiled, and again filtered. When quite cold, the filtrate is shaken vigorously with "cupferron," the end of the reaction being indicated by the appearance of a white film at the surface of the liquid. The precipitate, which contains all the tantalum and niobium, also titanium if present, is filtered off, washed with water containing a little sulphuric acid, dried, and calcined. This method as compared with that of Thornton (A., 1914, ii, 583) gives a more complete separation, and does not necessitate prolonged boiling. H. J. E.

Determination of Palladium. H. E. ZSCHIEGNER (*Ind. Eng. Chem.*, 1925, **17**, 294).—The sample, *e.g.*, of technical platinum, is dissolved in aqua regia and evaporated to dryness; the chlorides obtained are dissolved in water and treated at 80° with sodium nitrite in excess. The cooled solution is made just alkaline with sodium carbonate; gold, silver, and base metals are so precipitated. The palladium in the cold filtrate is now precipitated as the compound with dimethylglyoxime. [Cf. *B.*, 1925, 341.] W. A. S.

Ruthenium Pentafluoride. Separation of Platinum and Ruthenium. O. RUFF and E. VIDIC (*Z. anorg. Chem.*, 1925, **143**, 163—182).—A solution containing platinum and ruthenium, when made alkaline with sodium hydroxide solution containing glycerol, boiled, then kept 1 hr. after addition of sodium hydroxide and bromine, and finally warmed, deposits the platinum quantitatively; the ruthenium is precipitated from the filtrate as sulphide. By a modification of the method, fluorine may also be determined. In the preparation of pure ruthenium pentafluoride, the powdered metal, prepared from ruthenium tetroxide, is heated with fluorine at about 280° in an apparatus previously used by Ruff and Tschirch (A., 1913, ii, 416). It is a dark green, transparent mass, m. p. 101°, b. p. 270—275°; $d^{16\cdot5}$ 2·963. It is readily decomposed by water, yielding the tetroxide. Concentrated hydrochloric acid yields first the tetrachloride; on boiling, further evolution of chlorine takes place. Vigorous interaction takes place with chloroform and carbon tetrachloride. L. L. B.

Determination of Ethyl Alcohol. A. ASTRUC and RADET (*Ann. Falsif.*, 1925, **195**, 165—171).—Small proportions of ethyl alcohol (0·15—0·25 c.c.%) may be accurately determined by oxidation with alkaline permanganate solution. The active oxygen content of the hot alkaline permanganate solution is first determined by addition of excess of oxalic acid, followed by sulphuric acid and titration with permanganate; the process is then repeated on another sample after addition of the alcoholic liquid. [Cf. *B.*, May 29th.] D. G. H.

Cinchonine as a Tannin Precipitant, with Special Reference to the Analysis of Cutch and Gambier. D. HOOPER (*Analyst*, 1925, **50**, 162—166).—The cinchonine method for the determination

of tannin (Chapman, *J. Inst. Brewing*, 1907, **13**, 646—667; 1909, **15**, 360—374; *J. Soc. Chem. Ind.*, 1908, **27**, 135; 1909, **28**, 619) may be used to differentiate the proportion of catechin and tannin in commercial samples of cutch and gambier, since the catechin is not affected by the addition of cinchonine sulphate whereas it is largely absorbed by hide powder. [Cf. *B.*, May 29th.] D. G. H.

Use of Mitchell's Ferrous Tartrate Reagent in Qualitative Analysis. A. H. WARE (*Analyst*, 1925, **50**, 127—130).—A practical method of classifying pyrogallol-tannin substances is based on the colorations formed after either adding acetic acid subsequently to the addition of Mitchell's ferrous tartrate reagent (A., 1923, ii, 188), boiling, and cooling, or making the solution or extract in the presence of acetic acid, cooling, and adding the ferrous tartrate reagent. Gallic acid, the bark and leaves of *Hamamelis virginica*, logwood, bearberry leaves, and commercial cloves give no definite blue or violet colours; certain ellagitannin extractives give colloidal black precipitates or green colorations, whilst a bluish-violet colour is given by commercially pure gallotannic acid, certain galls, divi-divi, valonia, true sumach, etc. Ordinary gallotannin may thus be detected in gallic acid. [Cf. *B.*, 1925, 302.] D. G. H.

Differentiation of the Naphthols, and Condensation Product of α-Naphthol with Formaldehyde. A. ZAMPARO (*Boll. Chim. Farm.*, 1925, **64**, 97—100).—The two naphthols may be differentiated by means of their colour reactions with (i) sulphuric acid in alcoholic solution containing hydrogen peroxide, and (ii) formaldehyde in presence of hydrochloric acid.

The di-α-naphthylmethane obtained by the condensation of α-naphthol in alcoholic solution with formaldehyde in presence of hydrochloric acid readily undergoes oxidation to α-naphthylnaphthylidenemethane (?), which is a red compound turned blue by alkali and may be used as an indicator. [Cf. *B.*, 1925, 278.]

T. H. P.

Detection and Determination of Small Amounts of α-Naphthol in β-Naphthol. T. CALLAN (*J. Soc. Chem. Ind.*, 1925, **44**, 125—127T).—An examination of the sensitiveness of the various tests for α-naphthol shows that it can be detected when present to the following minimal extents in β-naphthol:—Dané's test (*L'Union pharm.*, 1909, **50**, 1), 5%; Driver's test (*J. Soc. Chem. Ind.*, 1924, **43**, 206T), 1%; Leger's test (A., 1897, ii, 526), 0·5%; a modified B.P. test (cf. *Annalen*, **152**, 281), the Volcy-Boucher test (A., 1908, ii, 990) and the Artzberger test (*Pharm. J.*, 1903, **70**, 89), 0·2%; and the Liebmann and Prochazka tests (A., 1899, ii, 65; 1924, ii, 70), 0·1%. The two last-named methods may also be employed for the determination with the same limiting concentration of not less than 0·1% of α-naphthol present. L. F. H.

Determination of the Iodine Number of Cholesterol. H. DAM (*Biochem. Z.*, 1924, **152**, 101—110).—A comparative investigation of various methods of determining the iodine number of cholesterol. The methods of Hanuš, of Winkler, and the pyridine

sulphate–dibromide method are preferred to those of Hübl, Waller, Wijs, and Obermüller. The most trustworthy is the pyridine sulphate method, the least so those of Obermüller and Wijs—the latter giving values which may vary greatly with the excess of iodine used. J. P.

Preparation of Fehling's Solution for the Volumetric Determination of Reducing Sugars. J. H. LANE and L. EYNON (*J. Soc. Chem. Ind.*, 1925, 44, 150—152T).—In the determination of reducing sugars, using the method and tables previously published (A., 1923, ii, 193), a control titration with invert-sugar is desirable, since errors up to 0·7% may be incurred owing to the copper sulphate pentahydrate containing excess of moisture. F. B.

Volumetric Determination of Invert-sugar by Reduction in Presence of Sucrose. M. A. H. VAN DEN HOUT, P. A. NEETESON, and E. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1925, 22, 126—132; cf. this vol., ii, 74).—The reduction of cupric compounds in alkaline solution by sucrose reaches a maximum at a concentration of 4 g. of sucrose in 100 c.c. of reaction liquid and then rapidly diminishes; if tartrates are present, the maximum is at 8 g. of sucrose per 100 c.c., and with increasing concentration of sucrose the diminution is very gradual. Theoretical explanations are advanced. This behaviour is altered by the presence of invert-sugar; the cuprous oxide precipitated by a given quantity of invert-sugar in presence of tartrate increases continuously with the amount of sucrose present, the increase being very great at high concentrations of invert-sugar, but in absence of tartrate the effect is reversed; the influence of sucrose in absence of tartrate disappears at a definite concentration of invert-sugar. The methods in use are reviewed in the light of these results, and a procedure is laid down by which a control test, a titration with the sample, which must contain sucrose in specified concentration, and a titration with sucrose free from invert-sugar, are carried out, the results being obtained from tables. S. I. L.

Determination of Invert-sugar in Presence of Sucrose, and Development of Invert-sugar in Sucrose Solutions. N. SCHOOREL (*Chem. Weekblad*, 1925, 22, 132—134; cf. preceding abstract).—Luff's solution of copper sulphate, citric acid, and sodium hydrogen carbonate is much less readily reduced by sucrose than Fehling's solution; the reduction by sucrose is proportional to the time of boiling and a constant correction may therefore be applied. Using this reagent, the inversion of sucrose in distilled water of p_H 5 observed by van den Hout and others (this vol., ii, 74) could not be confirmed. S. I. L.

Detection of Small Quantities of Formaldehyde in Cases of Poisoning. C. GHIGLIOTTO (*Ann. Chim. Analyt.*, 1925, [ii], 7, 39).—Tests for formaldehyde may be applied directly to pieces of stomach wall since the combination formed by the protein material and the formaldehyde retains properties of the latter. D. G. H.

Gravimetric Determination of the Iodine-Bromine Number. L. W. WINKLER (*Pharm. Zentr.*, 1925, 66, 241—244).—A rapid gravimetric method of determining the iodine-bromine number of oils and fats is described (cf. Winkler, A., 1922, ii, 534; Becker, A., 1923, ii, 886; Sabalitschka and Dietrich, A., 1924, ii, 707; Oestermann, B., 1924, 719; Köpke, A., 1925, ii, 246). Bromine dissolved in a mixture of acetic acid and carbon tetrachloride is added to a weighed amount of the material in a shallow dish and the mixture is evaporated to dryness. In some cases one or, in others, two repetitions of this process are necessary. The evaporations are conducted in the dark, and, on the average, 1/15th of the bromine is used for substitution in place of addition. The iodine-bromine value is calculated from the increase in weight of the material. The results obtained in the case of forty oils, fats, waxes, and fatty acids are tabulated. L. F. H.

Determination of the Acetyl Value of Fats. E. ANDRÉ (*Bull. Soc. chim.*, 1925, [iv], 37, 335—339).—The author defines the acetyl value of an oil or fat as the number of mg. of acetic acid taken up in acetylation by 1 g. of the oil. The sample is heated with excess of acetic anhydride and xylene, the distillation of the excess being repeated twice at 175° by the addition of xylene. A control sample is similarly heated with xylene alone, and the difference between the saponification values of the acetylated sample and the control, multiplied by 1·071, gives the true acetyl value of the oil. The values obtained agree with those obtained by the method previously described (A., 1921, ii, 419). R. B.

Micro-determinations of Acetyl Groups. K. FREUDENBERG and E. WEBER (*Z. angew. Chem.*, 1925, 38, 280—285).—The compound is decomposed in absolute alcohol with toluenesulphonic acid, and the ethyl acetate distilled off and determined by hydrolysis and titration; 0·05*N*-solutions of sodium hydroxide and sulphuric acid are employed, the former being standardised with succinic acid. About 20 mg. of the acetyl compound, 0·1 g. of toluenesulphonic acid, and 5 c.c. of absolute alcohol are required. The receiving flask is cooled with ice. If halogens are present, 10—30 mg. of silver toluenesulphonate are added. The apparatus and procedure are described minutely. S. I. L.

Detection of Methylamine in Presence of Excess of Ammonia. P. A. VALTON (*J. Chem. Soc.*, 1925, 127, 40—41).—The solution is treated with 30 c.c. of 2*N*-sodium hydroxide, diluted to 80 c.c., and distilled through a Kjeldahl trap into 10 c.c. of a 0·5% alcoholic solution of chloro-2 : 4-dinitrobenzene. When the distillate has increased this volume to 20 c.c., distillation is stopped. On keeping for 20 hrs., 2 : 4-dinitromethylaniline separates, is recrystallised from alcohol, and identified by the method of mixed m. p. No dinitroaniline separates in this time. By this method 0·02 g. of methylamine hydrochloride was detected in the presence of 20 g. of ammonium chloride. L. J. H.

Determination of Aniline in Aqueous Solutions. C. M. CARSON (*Ind. Eng. Chem.*, 1925, **17**, 62—63).—Aqueous solutions containing from 0·1 to 2·0% of aniline are titrated with 0·1*N*-sulphuric acid, the best indicators being (in the order named) bromophenol-blue, *p*-dimethylaminoazobenzene, and Congo-red. The end-point is found by comparing the colour with that of a standard solution of aniline which has been exactly neutralised with 0·1*N*-sulphuric acid and contains exactly the same quantity of indicator as is used in the titration. For solutions containing less than 0·1% of aniline, the colorimetric methods are preferable. *o*-Toluidine can be thus determined with fair accuracy, but less favourable results are obtained with *p*-toluidine owing to its small solubility in water.
W. T. K. B.

Colorimetric Determination of Thiocyanates and Cyanates. K. C. BAILEY and D. F. H. BAILEY (*Proc. Roy. Irish. Acad.*, 1924, **37**, [*B*], 1—6).—The method of Spacu (A., 1923, ii, 40) for the detection of copper by formation of the compound $Cu(SCN)_2,(C_5H_5N)_2$, and Werner's application thereof (T., 1923, **123**, 2577) to the detection of cyanates are adapted for the colorimetric determination of thiocyanates and cyanates under comparable conditions. Ammonium cyanate may be determined in the presence of carbamide, but the method fails if disodium hydrogen phosphate, sodium hydrogen tartrate, sodium nitrite, sulphate, or cyanide, or thiocarbamide is present. [Cf. *B.*, 1925, 313.] D. G. H.

Determination of the Composition of Phenol Nitration Products. L. DESVERGNES (*Ann. Chim. Analyt.*, 1925, [ii], **7**, 35—38).—After removal of any substances insoluble in 10% sodium carbonate solution at 50°, the amount of bromine absorbed by the mono- and di-nitrophenols is determined by the Callan and Henderson method (A., 1922, ii, 524) and trinitrophenol as nitron picrate. The nitrated product is dissolved in a dilute solution of sodium carbonate, sulphuric acid added in slight excess, and the mixture cooled. Any crystals of dinitrophenol are filtered off, 10% nitron acetate solution is added, and the precipitate of nitron picrate left to form at 0°. [Cf. *B.*, 1925, 199.] D. G. H.

Gravimetric Determination of Trinitrophenol and a Mixture of Picric Acid and Trinitrocresol. L. DESVERGNES (*Ann. Chim. Analyt.*, 1925, [ii], **7**, 65—66).—The material may be dissolved in a saturated solution of picric acid of known concentration and either kept for 5 days and the crystals of picric acid collected and weighed, or the total weight of trinitrophenol and trinitro-*m*-cresol determined in the filtered liquid. [Cf. *B.*, 1925, 339.]
D. G. H.

Micro-determination of Carbamide and Ammonium Salts. J. GOLSE.—(See i, 609.)

Determination of Uric Acid in Blood. F. M. R. BULMER, B. A. EAGLES, and G. HUNTER.—(See i, 605.)

Grant's Test for Sparteine. J. F. COUCH (*Amer. J. Pharm.*, 1925, 97, 38—39).—Grant's test for sparteine (A., 1921, ii, 71) is very specific, exciting no response from lupinine, spathulatine, *d*-lupanine, *dl*-lupanine, hydroxylupanine, or nicotine. The test is conveniently modified thus: a strip of filter-paper is moistened with the chloroform extract of the ammoniacal solution of the alkaloid, allowed to dry, exposed to bromine fumes, then to ammonia fumes, and finally warmed, when the characteristic bright pink colour appears. B. F.

Extraction and Determination of Lipoids in Cereal Products. O. S. RASK and I. K. PHELPS (*Ind. Eng. Chem.*, 1925, 17, 187—189).—Determination of the fat content of cereal materials by direct extraction with ether yields less than one-half of the lipoid or ether-soluble material obtained by the ammoniacal extraction method proposed. [Cf. *B.*, 1925, 224.] D. G. H.

Determination of the Tyrosine Content of Proteins. III. O. FÜRTH and A. FISCHER (*Biochem. Z.*, 1924, 154, 1—23).—It is confirmed that the methods previously described (A., 1924, ii, 575) are unsatisfactory for tyrosine determination in protein. The Pierre-Thomas modification of the Millon reaction and the mercuric sulphate and nitrate precipitation methods are also unsuitable. By successive treatment of the sulphuric acid hydrolysates with phosphotungstic acid, quinine sulphate, and sodium hydroxide solutions, a filtrate is obtained in which, after neutralisation, the tyrosine is determined by the Millon colorimetric method. Tyrosine can also be determined by addition of bromine, but this must be regarded only as confirmatory. The hydrolysis of casein and fibrin by trypsin and alkali has been followed, and it is shown that the liberation of tyrosine considerably precedes the complete disintegration of the protein molecule, thus differing from tryptophan (A., 1924, i, 64). P. W. C.

Colorimetric Determination of Tryptophan and Its Separation from Indole and Skatole. I. KRAUS (*J. Biol. Chem.*, 1925, 63, 157—178).—The blue condensation product with vanillin given by tryptophan in presence of concentrated hydrochloric acid was used for the colorimetric determination of the amino-acid; interference by indole and skatole could be prevented by preliminary extraction of these substances with toluene. It was not, however, found possible to recover tryptophan quantitatively from the products of the hydrolysis of protein by barium hydroxide or trypsin, nor after incubation of mixtures of the amino-acid with trypsin and the mixed diamino-acids of casein or with trypsin and glucosamine. Pure tryptophan heated on a water-bath for 40 hours with 14% barium hydroxide is destroyed to the extent of 20%; the use of the phenol reagent of Folin and Looney (A., 1922, ii, 539) involves a loss of about 7% of tryptophan. The vanillin method gave a positive test for tryptophan with gelatin and with zein. C. R. H.

General, Physical, and Inorganic Chemistry.

Sommerfeld's Theory of Fine Structure [of Spectral Lines] from the Point of View of General Relativity. M. S. VALLARTA (*J. Math. Phys. Mass. Inst. Tech.*, 1925, **4**, 65—83).—A mathematical paper in which it is shown that, keeping in mind the relations between the magnitudes of the electronic mass and charge, on the one hand, and the nuclear mass and charge on the other, it is possible to obtain the relativistic Keplerian conditioned-periodic orbits of Sommerfeld's theory (*Ann. Physik*, 1916, [iv], **51**, 53) from considerations of general relativity. For the hydrogen atom and hydrogenic ions, of the type He^+, Li^{++}, Be^{+++}, etc., the material field of the nucleus is almost Euclidean and almost static. J. S. C.

S-Term. F. J. VON WIŠNIEWSKI (*Physikal. Z.*, 1925, **26**, 255).—The energy level E_s corresponding with the s-terms in the arc and spark spectra of elements belonging to the 1st, 2nd, 3rd, and 8th periodic groups can be expressed as :—$E_s=-Nh/[n+\beta+\sigma_p]^2$, where $n=1, 2, 3, 4 \ldots$, σ_p =the correction in p-spectral terms, β is a constant differing for different groups but the same for elements in the same vertical row, N and h are the Rydberg and Planck constants respectively. Thus $\sqrt{13{\cdot}53/V_{ion}}=n+\beta+\sigma_p$, where V_{ion} is the ionisation potential; σp is given by the expression $2+\sigma_p=(13{\cdot}53/V_{ion}-V_{res.})^{\frac{1}{2}}$, where $V_{res.}$ is the resonance potential. The values of β are: 1st group, 0·50; 2nd group arc (*a*) 0·682, (*b*) 0·608, spark 0·634; 3rd group, 0·679, 8th [He, Ne]—0·324. Hence $E_s=-Nh/(n+\sigma_s)^2$, where $n=1, 2 \ldots$, σ_s being the s-spectral term correction, so that $\sigma_s=\beta+\sigma_p$. It follows that $\sigma_s-\sigma_p$=constant for the elements of the same vertical column. R. A. M.

Simple Demonstration Screen for Ultra-violet Radiations. W. STEUBING (*Physikal. Z.*, 1925, **26**, 329—331).—For the visual perception of spectral lines in the ultra-violet a thinner layer of fluorescent material than the usual uranium glass is desirable. A suitable screen is made as follows: on a desilverised photographic plate, of which the edges have just been allowed to dry out, finely-powdered ammonium uranyl fluoride is uniformly sprinkled from a lawn sieve. The powder is rubbed into the damp gelatin, which on drying assumes a fine-grained matt aspect. W. A. C.

Hydrogen Balmer Series. L. JANICKI (*Ann. Physik*, 1925, [iv], **76**, 561—566).—Shrum's measurements of the fine structure of the hydrogen lines (A., 1924, ii, 282) require correction for errors arising from physiological and photographic effects, which lead to too high values for the doublet separations. Values smaller and more probable than Shrum's were obtained by an objective photometric examination of the reproductions of Shrum's photographs

by the Koch–Gooschen recording photometer. The most probable values for the separation of the α, β, and γ lines are 0·130, 0·076, and 0·060 Å., respectively. F. G. T.

Spectroheliograms with Different Parts of the H_α Line. T. Royds (*Month. Not. Roy. Astr. Soc.*, 1925, **85**, 464—466).—Spectroheliograms obtained when a slit of about 0·5 Å. width is set on either the red or violet edge of the H_α line show a bright spot ring, often complete and unbroken, round nearly all sunspots of medium size. At the same time, dark flocculi are produced outside the bright ring, where the H_α line is wider than normal. A less striking feature is a bright surround intervening between the dark flocculus and the coarse network of the general body of the sun. F. G. T.

Intensities in the Many-lined Spectrum of Hydrogen. G. H. Diecke (*Z. Physik*, 1925, **32**, 180—185).—The intensities of the lines and their grouping are discussed, particularly with regard to the effect of temperature and pressure on the relative intensities. E. B. L.

Variations in the Structure of the Lithium Red Line 6708 Å. D. S. Ainslie (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 137—143).—Using both a glass Lummer plate and a 30-plate echelon grating as resolving instruments, the fine structure of the red lithium line, 6708, has been investigated. Several photographs were taken using various lithium compounds and metallic lithium in the vacuum arc. With a current of 4—6 amp., a simple doublet is obtained. With currents of 7 amp., both components appear as double, giving a close quadruplet pattern. This pattern is easily changed into a triplet, the components of which vary considerably in relative intensity. The measured separations between the components are given for various current-strengths and lithium salts. The suggestion that each lithium isotope gives rise to a pair of lines in the quadruplet (A., 1922, ii, 541) must be modified. The absorption spectrum of lithium vapour shows 12 bands between 3966 and 3387. J. S. C.

Ground Term of the Neon Spectrum. S. Goudsmit (*Z. Physik*, 1925, **32**, 111—112).—Reasons are given for concluding that the ground term is simple, with the quantum numbers $k=2$ and $J=\frac{1}{2}$. E. B. L.

Low-voltage Arcs in Sodium and Potassium Vapours. F. H. Newman (*Phil. Mag.*, 1925, [vi], **49**, 1057—1064).—Details are given of the construction of a tube for producing low-voltage arcs in metallic vapours. The potentials necessary to strike and maintain arcs in sodium and potassium vapours depend primarily on the density of the vapour and temperature of the cathode, the potentials decreasing as these increase. At a very high cathode filament temperature, an arc, struck at 3·8 volts, may be maintained at 2·8 volts in sodium vapour at 450°. Slightly higher voltages are necessary for potassium, and the arcs are less steady. The differ-

ence between the striking and maintenance voltages becomes less as the density of the vapour decreases. With intensely hot cathodes arcs may be struck and maintained with potentials less than the ionising potentials of the vapours. The ionisation in these cases probably arises through the absorption of radiation emitted from atoms already excited, but not ionised. This ionisation by photo-impact (*Physical Rev.*, 1922, [ii], **20**, 296) results in complete ionisation of the vapour atoms by electrons, none of which has a velocity greater than that corresponding with the resonance potential. F. G. T.

Arc Spectrum of Sodium. F. J. VON WIŠNIEWSKI (*Physikal. Z.*, 1924, **25**, 480—482).—A mathematical theory of the arc spectrum based on an analogy between the structure of a neutral sodium atom and that of a doubly-ionised aluminium atom. The analogy is extended to the structure of the neon atom, and on the basis of theory the difference between the ionisation potential (21·5 volts) and the second excitation potential (18·45 volts) is calculated to be −2·98 volts whilst the observed value is −3·05 volts. R. W. L.

Extreme Ultra-violet Spectra of the Alkali Metals. W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 23—34).—The spectra of the electrodeless discharge in the vapours of sodium, potassium, rubidium, and cæsium have been investigated using a fluorite spectrograph, the frequencies and wave-lengths of the lines being recorded. The results with sodium were negative in character, but it is thought that at a higher temperature a second spectrum would appear corresponding with the many-lined spectra of the other metals. The spectra of the electrodeless discharge in the vapours of rubidium and cæsium were investigated in the region between 1850 and 2300 Å. and a number of lines in addition to those discovered by Dunoyer (A., 1922, ii, 729) were obtained. A number of frequencies in the potassium spectrum agreed with values predicted from energy levels calculated by Nissen (A., 1923, ii, 671) for the singly-ionised potassium atom. J. S. C.

Double Excitation Spectra of Magnesium and Related Elements. J. B. GREEN and M. PETERSEN (*Astrophys. J.*, 1924, **60**, 301—312).—The occurrence of the pp' group of five strong lines at about 2780 Å. in the spectrum of magnesium is not correlated with the strength of the spark spectrum; thus the origin of the p' terms cannot be related to the ionised state of the atom. The p' and d' terms of magnesium and the alkaline earths are proposed as designating doubly excited states of the neutral atoms independent of metastable ionised states. A. A. E.

Theory of the Spark Spectra of Aluminium. F. J. VON WIŠNIEWSKI (*Physikal. Z.*, 1924, **25**, 477—480).—The arguments concerning the atomic structure of helium and lithium (A., 1924, ii, 361, 637) are now applied to a deduction of a theory of the core structure of doubly-ionised aluminium atoms. R. W. L.

Series, Ultra-violet, and Infra-red Spectra of Silicon. J. C. McLennan and W. W. Shaver (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 1—22).—The wave-lengths and frequencies of 50 new lines in the extreme ultra-violet spectrum of the silicon vacuum spark in the region between 2000 and 458 Å. are recorded; 21 lines belonging to the Si IV series spectra as worked out by Fowler (A., 1923, ii, 447) were recorded on the vacuum spark spectrogram. The spectrum of the silicon arc and spark in air have been investigated with a quartz spectrograph and a large number of new lines between 2300 and 1842 obtained. The vacuum arc spectrum was studied, using a fluorite spectrograph, in the region between 1850 and 1500. In an examination of the Si I spectrum for series relations a scheme of constant frequency differences has been worked out and energy levels accounting for a number of the lines have been calculated. Thirty-three wave-lengths in the hitherto unstudied infra-red spectrum were observed and measured in the region 6300—11235 Å. J. S. C.

Spectrum of Silicon at Successive Stages of Ionisation. A. Fowler (*Phil. Trans.*, 1925, **A**, **225**, 1—48).—Lines in the spectrum fall into four groups, Si I=neutral atoms, Si II or Si^{+}= singly-ionised atoms, Si III or Si^{++} = doubly-ionised atoms, Si IV or Si^{+++}=trebly-ionised atoms. In these classes, the series constant changes from Rydberg's R to $4R$, $9R$, $16R$, and the series systems consist alternately of triplets and doublets in accordance with the displacement law of Kossel and Sommerfeld. Notation is reviewed and the various series are dealt with in detail, a catalogue of wave-lengths is given, with plates showing photographs of the progressive spectra. E. B. L.

Low-voltage Arcs in Phosphorus Vapour. O. S. Duffendack and H. Huthsteiner (*Physical Rev.*, 1925, [ii], **25**, 501—508).—The minimum arcing potential for phosphorus vapour is 10·3 volts, which is regarded as the ionising potential of the phosphorus atom. The low-voltage arc spectrum contains arc lines and bands. A. A. E.

Continuous Spectra of the Halogens. W. Steubing (*Z. Physik*, 1925, **32**, 159—162).—As considerable doubt has recently been thrown on the interpretation of the continuous spectrum of iodine and the other halogens as due to the acquisition of an electron by a neutral atom (electron affinity spectrum), it is suggested that the peculiarities are due to instability in the outer shell of electrons. E. B. L.

Intensities in the Argon Spectrum. P. Lowe and D. C. Rose (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 313—323).—Fifty-one lines in the argon spectrum were identified and measured. Quantitative measurements of intensities show that the red spectrum may be divided into two groups: (I) lines showing no maximum intensity at any voltage, which after 40 volts are sensibly constant; (II) those which have a maximum intensity at 27 volts and decrease continually. The lines of the blue spectrum are listed in a third

group, the more intense of which appear at 39 volts, others appearing and increasing in intensity as the applied voltage is increased, reaching a maximum at 65 volts. J. S. C.

Absorption Spectrum of Potassium Vapour at High Temperatures. N. K. Sur and R. N. Ghosh (*Phil. Mag.*, 1925, [vi], **49**, 60—64).—The absorption spectrum of potassium vapour was investigated at different temperatures. The temperature most suitable for obtaining reversals of lines of the subordinate series is 1300°. Above this, lines were obtained which could not be identified with known potassium lines, or placed in any series relation. Between 500° and 1000° channelled bands were obtained. The line 4641 was obtained and supports the views of Foote, Meggers, and Mohler (A., 1922, ii, 4). C. W. B.

Extreme Ultra-violet Spectrum of Germanium and Scandium. H. J. C. Ireton (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 103—109).—The spark spectrum of germanium has been extended from 2138·7 to 319·7 Å., 64 new lines being recorded. The spark spectrum of scandium has been extended from 2233·7 to 507·0, 45 new lines being observed. J. S. C.

Electric Furnace Spectra of Vanadium and Chromium in the Ultra-violet. A. S. King (*Astrophys. J.*, 1924, **60**, 282—300).—The temperature classification and relative intensities are tabulated for 515 vanadium lines between 2340 and 3185 Å., and for 640 chromium lines between 2362 and 3575 Å., new wave-lengths being ascribed to 133 vanadium lines and 94 chromium lines. Initial temperatures for the appearance of enhanced lines of vanadium and chromium are 2200° and 2600°, respectively. A. A. E.

Absorption Spectra of Copper, Silver, and Gold Vapours in the Ultra-violet. R. V. Zumstein (*Physical Rev.*, 1925, [ii], **25**, 523—526).—The metals were vaporised in a carbon tube by external heating, the absorption spectra being observed without the use of windows. Copper gave lines at 3273·9, 3247, 2225, 2182, 2178·9, 2165, 2024·3, and 2244 Å., silver at 3382, 3280, 2070·0, and 2061·2 Å., and gold at 2675·9 and 2427·9 Å. The component of the doublet having the shorter wave-length is always the stronger, as in the case of the alkali metals. There is also similarity in the increase in the separation of the doublets with increasing atomic weight. A. A. E.

Arc Spectra of Silver and Copper. A. G. Shenstone (*Phil. Mag.*, 1925, [vi], **49**, 951—962; cf. *Nature*, 1924, **114**, 501).—The spectra of un-ionised silver and copper atoms may be obtained by bombarding the vapour of the metals by hot filament electrons, accelerated by the application of low voltages. Measurements of the silver lines confirm the accepted energy levels of that atom. A table is given of the intensities and wave-lengths of copper lines excited by this method. The direct absorption of copper lines by copper vapour was measured, definite absorption occurring in the

case of the lines 2165·06, 2225·665, 2244·24, 2441·625, 2492·142 Å. From these data and from the low-voltage arc lines combinations were calculated for 64 of the lines found. F. G. T.

Absorption and Series Spectra of Tin. J. C. McLennan, J. F. T. Young, and A. B. McLay (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 57—75).—The tin arc spectrum has been re-investigated in the region between 2251 and 1850 Å. and a number of new wave-lengths are recorded. Seventeen new lines have been observed in the absorption spectrum of tin vapour at 1200°. By means of an arc-reversal method in an atmosphere of hydrogen, about 40 new wave-lengths have been added to the tin arc spectrum in the Schumann region. Tables of groups of constant frequency differences are given for the arc spectrum and two possible multiplets of the pp' type have been found. Six limits in the arc spectrum have been evaluated and the sharp and diffuse subordinate series arising from them built up. The ionisation and resonance potentials are calculated to be 7·3 and 4·3—4·8 volts, respectively. J. S. C.

Spectral Series of Lead and Tin. H. Sponer (*Z. Physik*, 1925, **32**, 19—26).—In the arc spectra of these metals the ground terms are p-terms with inner quantum numbers 0, 1, 2, 2, and possibly also 0 for lead and 0, 1, 2, 2, 0 for tin. The ground terms in Thorsen's series for lead are p_0, p_1, p_2. E. B. L.

Determination of the Terms in the Lanthanum Spectrum. S. Goudsmit (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 23—31).—Measurements of the Zeeman effect in certain spectra are insufficient for the application of Landé's rules for the arrangement of the lines (cf. *Z. Physik*, 1923, **15**, 189). Previous measurements by Paulson (*Ann. Physik*, 1914, [iv], **45**, 1203) enabled a number of lines in the lanthanum spectrum to be arranged in a term system, and the inner quantum number, J, and factor of resolution, g, could be found for every term. From these data it is usually possible to determine also the quantum numbers K and R with the aid of Landé's formulæ, and the term system can also be found. For certain terms in the lanthanum spectrum, however, this has been found to be inapplicable. Tables of spectra are given in illustration of this. L. L. B.

Spark Spectrum of Tungsten in a Helium Vacuum Arc. H. B. Lemon (*Nature*, 1925, **115**, 802).—A hot tungsten cathode used in the operation of an arc at low pressure in helium is capable of developing the spark spectrum of tungsten. The relative intensities of the lines are modified from those given in the standard tables of wave-lengths. A. A. E.

Platinum Metals. VII. Arc Spectra of the Platinum Metals (4500—9000 Å.). W. F. Meggers (*U.S. Bur. Standards, Sci. Papers* No. 499, 1925, **20**, 19—45).—Grating measurements were made of the arc spectra of the six platinum metals over the above range. Tables are given of the wave-length and estimated

relative intensity of 1260 lines for ruthenium, 572 for rhodium, 172 for palladium, 942 for osmium, 605 for iridium, and 239 for platinum. These were measured with an accuracy of 0·01 Å., and include several hundred new lines in the visible and infra-red. Tables are given of lines recorded by earlier observers and here shown to be due to impurities. One or more bands converging to heads toward short waves were found in the spectra of ruthenium, rhodium, osmium, and platinum. In the group VIII metals the general tendency within any triad as well as between triads is for the number of lines to decrease as the atomic number increases.

F. G. T.

Absorption of the Green Line of Thallium Vapour. K. R. Rao (*Proc. Roy. Soc.*, 1925, **A**, **107**, 762—765; cf. this vol., ii, 5).—Work on the absorption of 5461 of mercury (cf. Metcalfe and Venkatesachar, A., 1924, ii, 439) suggested a study of the green line 5350 of thallium. The structure of the line was examined, using a glass Lummer–Gehrcke plate of resolving power about 300,000 for 5350, and a Fabry–Perot étalon (thickness of air layer, 10·016 mm.). The source was the radiation from a vacuum tube through which was passed a condenser discharge from an induction coil between thallium electrodes. The main line is a close doublet accompanied by a satellite with separation 0·116 Å., the existence of the other satellite being shown by the étalon. In the absorption experiments, the column of absorbing vapour was contained at low pressure in a tube 2 ft. long. As the temperature was raised, gradual absorption of the central doublet began at 600° and was complete at 800°; absorption of the satellite began when that of the main line was complete, and was itself complete at about 950°. This is discussed theoretically. The intensities of the satellites relative to the main line are 0·2 and 0·75 for 0·024 and 0·116 Å., respectively. L. L. B.

Absorption and Series Spectra of Lead. J. C. McLennan, J. F. T. Young, and A. B. McLay (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 77—88).—The Thorsen scheme for the lead arc series (*Naturwiss.*, 1923, 78) and its extension by Grotrian (A., 1923, ii, 710) are discussed and converted into vacuum frequencies. The lead arc spectrum has been re-measured in the region 2250—1850 Å. and many new lines are recorded. The arc-reversal spectrum of the lead arc in hydrogen has been investigated and 12 new wave-lengths were observed. The results are shown to confirm and extend the Thorsen–Grotrian arrangement. J. S. C.

J-Phenomena and the Quantum Theory of Scattering of X-Radiation. R. T. Dunbar (*Phil. Mag.*, 1925, [vi], **49**, 210—236).—Experiments on the relative absorptions of *X*-rays by copper, aluminium, and paper show that under the stated conditions the *J*-discontinuities of Barkla and White (*ibid.*, 1917, [vi], **34**, 270) do not appear. Absorption associated with scattering agrees with that calculated on the quantum theory by Compton (*Physical Rev.*, 1923, [ii], **21**, 483). Using the ionisation of sulphur dioxide

and ethyl bromide, evidence was obtained of abnormal corpuscular emission from air. Measured by ionisation of hydrogen, corpuscular emissions from paper, aluminium, copper, and lead show that the lighter elements emit an additional corpuscular radiation for short wave-lengths of incident radiation, the energy required giving no discontinuity in the absorption curve for paper. Compton's theory of the change in quality and intensity of scattered radiation is supported by results with filter-paper, over a considerable range of wave-lengths, for scattering at right angles to the primary. It is deduced that the scattered X-rays carry only a fraction of the energy absorbed in association with scattering. C. W. B.

J-Transformation of Scattered X-Rays. C. G. Barkla and S. R. Khastgir (*Phil. Mag.*, 1925, [vi], **49**, 251—256).—Differences between the primary and secondary radiations are described in a previous paper (*Nature*, 1923, **112**, 723). Compared by their power of penetrating thin sheets they appear to be identical, but a big difference is observed with thicker sheets. At a critical thickness, an abrupt absorption of the secondary occurs, and the transmitted radiation is subsequently more readily absorbed than the primary transmitted through the same thickness of absorbing sheet. The experiments show that the transformation in the secondary radiation is not produced by scattering. C. W. B.

J-Phenomenon in X-Rays. C. G. Barkla (*Phil. Mag.*, 1925, [vi], **49**, 1033—1056).—A general account of the J absorption discontinuities, supplemented by additional experimental evidence. As the penetrating power of a radiation is increased there occur sudden increases in its absorption by any particular substance. Absorption discontinuities have been observed directly in the cases of carbon, oxygen, aluminium, copper, platinum, and gold, and indirectly in those of nitrogen, sulphur, and lead. They fall into several series, J_1, J_2, J_3, and possibly J_4 and J_5. The increase in absorption is accompanied by the emission of slowly moving electrons from the absorbing substance, producing, when that substance is in a gaseous state, an even more strongly marked discontinuity in ionisation. From experiments quoted, it is concluded that the activity of an X-ray radiation is dependent on factors which have not hitherto been considered, and that alternative absorptions are possible for what are apparently identical radiations. Two levels of activity are definitely, and others probably, indicated. F. G. T.

Characteristic X-Rays from Light Elements. (Miss) M. Levi (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 159—176).—The minimum potential necessary for the excitation of the characteristic radiation was determined experimentally, the wave-length of the radiation being then computed from the quantum relation. The critical K- and L-absorption limits of lithium, beryllium, boron, and carbon, the critical L-absorption limit of fluorine, sodium, silicon, and vanadium, the L- and M-absorption limits of chlorine, scandium, titanium, and nickel, and the M-absorption limits of chromium, manganese, and cobalt have been determined.

J. S. C.

K-Series of X-Rays. A. LEIDE (*Compt. rend.*, 1925, **180**, 1203—1204).—Accurate measurements are recorded of α_1 and β_1 lines for copper, α_1, α_2, β_1, β_2, β_3, and β_4 for molybdenum and palladium and, omitting β_4, for silver, cadmium, indium, and tin. The α_1, α_2, β_1, β_2 lines for all the elements of atomic number 29 (copper) to 53 (iodine) have been measured with the exceptions 36 (krypton) and 43 (unknown). The standard lines chosen were Cu$K\alpha_1$ 1537·29, Mo$K\alpha_1$ 707·80, W$K\alpha_1$ 208·71. R. A. M.

K-Series of Heavy Elements. G. RÉCHOU (*Compt. rend.*, 1925, **180**, 1107—1108).—Wave-lengths of α_2, α_1, β, and γ lines of K-series have been determined with an accuracy of $0{\cdot}1\times10^{11}$ cm. for the following elements: tantalum, tungsten, osmium, iridium, platinum, gold, thallium, lead, bismuth, and uranium. Experimental difficulties are as yet too great for determinations with mercury and thorium. For tungsten, the values agree with those found by other investigators. Rogers' recent work on platinum is confirmed and de Broglie's values are accurate except for the γ line. R. A. M.

Dependence of the $K\alpha$ Doublet with Different Chemical Compounds. B. B. RAY (*Phil. Mag.*, 1925, [vi], **49**, 168—170).—For chlorine, potassium, vanadium, and iron, the value of $\Delta\lambda$ for the $K\alpha$ doublet decreases with increasing valency of the element, in the chemical compounds investigated. Mean values of the distance between the two $K\alpha$ lines are obtained correct to 1%. C. W. B.

Absorption Limits of K-Series. F. J. VON WIŠNIEWSKI (*Z. Physik*, 1924, **28**, 231—235).—The explanation of the K-absorption limit which was developed for light atoms in a previous paper (A., 1924, ii, 639) has been extended to heavier elements. The arrangements of the electrons in the K-systems of the atoms are deduced on the basis of the theory. S. B.

L-Absorption Spectra of the Elements from Sn(60) to W(74) and their Relation to Atomic Constitution. Y. NISHINA (*Phil. Mag.*, 1925, [vi], **49**, 521—537).—The L-absorption spectra of all the elements from tin (50) to tungsten (74) are measured. Evidence of fine structure is obtained in the case of the L_{III} absorption spectra. The values of different energy levels of different atoms are calculated by means of the frequency values of the emission lines. The curves showing the relation between energy levels and atomic number are discussed with special reference to the development of electronic groups due to the appearance, as atomic weights increase, of orbits of new type. C. W. B.

Semi-optical Lines in the X-Ray Spectra. E. BÄCKLIN, M. SIEGBAHN, and R. THORÆUS (*Phil. Mag.*, 1925, [vi], **79**, 513—517).—Peculiarities found in the $K\beta_1$ line of sodium and magnesium are explained by an atomic model proposed by Stoner (this vol., ii, 85). The $K\beta_1$ line of sodium and magnesium is not a true X-ray line of the K-spectrum, since with these elements there is no electron in

the M_{II} level. The $K\beta_1$ line is a semi-optical line produced by a transition from a free level of the atom to the K level. A similar phenomenon is found in the case of the $K\beta_2$ line for potassium.

C. W. B.

Semi-optical Lines in the X-Ray Spectra. L. DE BROGLIE and A. DAUVILLIER (*Phil. Mag.*, 1925, [vi], **49**, 752—753; cf. preceding abstract, also A., 1924, ii, 369).—A claim for priority. The views of the authors on the relations between X-ray lines, the periodic system, and the electronic structure of the elements are illustrated. R. A. M.

Absorption of Superposed X-Radiations. W. H. WATSON (*Proc. Roy. Soc. Edin.*, 1924—5, **45**, 48—58).—Attempts have been made to determine whether the sudden increase in absorption of X-rays, by aluminium, as the rays are hardened and a certain value of the mass-absorption coefficient is reached, is due to some temporary transformation of the aluminium. The influence on the absorption of a second beam of X-rays, when this passes through the affected aluminium at the same time as the original beam, has been studied. No effect of superposition in the first series of experiments was observed, but the results are not conclusive. A second similar series of investigations, suggested by Wilson's photographs of paired β-ray tracks obtained by the passage of X-rays through the air (*Proc. Roy. Soc.*, 1923, **A**, **104**, 1, 190), gave effects very much smaller than were to be anticipated.

M. S. B.

Suitability of the Seemann "Edge-method" for Measurements of X-Ray Standards. A. P. WEBER (*Z. wiss. Phot.*, 1925, **23**, 149—183).—The Seemann "edge-method" is quite suitable for precision measurements, and with other methods, is suitable for use in setting up the planned standard system of X-ray wave-lengths. The sources of error in the "edge-method" were fully examined and results compared with results obtained by other methods. This showed that Bragg's method must give a systematic error due to the penetration of the rays in the crystal. The apparatus used was of improved design, giving greater precision, but not suitable for absolute measurements. An instrument for absolute measurements of wave-length has been designed, combining the author's principle of crystal rotation with the arrangement used by Vogel, which is considered to be particularly suitable for absolute measurements. W. C.

Energy Levels of X-Ray Spectra of Chemical Elements. D. COSTER (*Z. Physik*, 1925, **31**, 898—900).—Critical of the conclusions of Walter (*ibid.*, 1924, **30**, 357), who found no irregularities in the energy levels for the iron and palladium groups such as had been suggested as probable by Bohr and Coster (*ibid.*, 1923, **12**, 342). E. B. L.

Intensity of Multiplets and their Zeeman Components. R. DE L. KRONIG (*Z. Physik*, 1925, **31**, 885—897).—The conditions

arising from the application of the principle of correspondence are studied and deductions made which enable the intensities to be calculated in magnetic fields either strong, weak, or vanishingly small. The formula obtained is in agreement with experiment.
E. B. L.

Glow Electronic Emission at Transition and Melting Points. A. GOETZ (*Physikal Z.*, 1925, **26**, 206—207; cf. *ibid.*, 1923, **24**, 377; 1924, **25**, 570).—The Richardson emission equation requires a linear relationship between the logarithms of the intensity of electronic glow and of the reciprocal of temperature. The slope of this line is determined by the work of emission, and its position by the number of conducting electrons. A change in the former at a transition or melting point would correspond with a change of direction, and of the latter to a parallel displacement of the intensity–temperature curve. Change of direction, but no displacement, is found at these points. According to the above equation, a displacement is to be expected at the A_4 point of iron owing to the increase of conducting electrons consequent on the change from a face-centred to a space-centred lattice. F. G. T.

Absorption of Cathode Rays in Aluminium. B. F. J. SCHONLAND (*Nature*, 1925, **115**, 497).—Polemical (cf. *Proc. Roy. Soc.*, 1923, **A**, **104**, 235; Terrill, this vol., ii, 79). A. A. E.

Primary and Secondary Products of Ionisation in Hydrogen. H. D. SMYTH (*Physical Rev.*, 1925, [ii], **25**, 452—468).—A discussion in greater detail of results already reported (A., 1923, ii, 455). Atomic hydrogen ions are produced by secondary dissociation of diatomic ions, and triatomic ions also appear when the voltage is above 16. The probability of dissociation is considered theoretically. A. A. E.

Single and Double Ionisation of Argon by Electron Impacts. H. A. BARTON (*Physical Rev.*, 1925, [ii], **25**, 469—483).—Using Smyth's magnetic deflexion method (cf. preceding abstract), the minimum potentials for the production of singly and doubly charged argon ions are 15·2 volts (assumed) and 45·3±1·5 volts, respectively. No trebly charged argon ions or singly charged argon molecules were observed. Possible ways of reconciling the results with spectroscopic evidence for the production of doubly charged ions at 34 volts are discussed. A. A. E.

Total Ionisation Produced in Air by Electrons of Various Energies. G. A. ANSLOW (*Physical Rev.*, 1925, [ii], **25**, 484—500).—An account of the experimental and theoretical basis of results already published (this vol., ii, 343). The voltages at which the total ionisation shows peaks are interpreted as the ionisation potentials of the *L*-electrons of argon (250) and the *K*-electrons of nitrogen (375) and oxygen (494). A. A. E.

Ionisation of Potassium Vapour by Light. R. SAMUEL (*Z. Physik*, 1924, **29**, 209—213).—A reinvestigation of the minimum

frequency necessary to excite ionisation, using an apparatus which eliminates secondary effects under the conditions prescribed for its operation. The light source is the arc spectrum of magnesium which contains two unusually strong lines in 2852 and 2804 in the range of the convergence frequency of potassium 2857 Å. By the use of suitable filters, and by using fields too small to produce ionisation by collision, it is established that potassium vapour is ionised by radiation in the range 2893—2804 Å. R. W. L.

Ionisation of Potassium Vapour under the Influence of Visible Light. A. ARNULF (*Compt. rend.*, 1925, **180**, 1259—1262).—A discharge tube with a tungsten filament and a plane plate is kept evacuated by a mercury pump, and a little potassium is distilled into the tube. The plate is given a positive potential with respect to the filament. When the filament is heated to incandescence the ammeter registers I_1 milliamp. If now a beam of visible light is allowed to fall on the plate or anywhere inside the discharge tube a higher current is found. With a varying voltage, the following extreme readings are obtained: (*a*) $V=3$, $I_1=13{\cdot}2$, $I_2=15$, $\Delta I/I_1=0{\cdot}136$; (*b*) $V=110$, $I_1=650$, $I_2=826$, $\Delta I/I_1=0{\cdot}271$. If now the potential difference between plate and filament is reversed, the beam of light exerts no influence on the current. When the plate is again made positive and the beam falls midway between plate and filament, lateral displacement of the pencil of light causes ΔI to diminish.

The work indicates that potassium vapour is ionised by visible light and a small number of electrons and positive ions are liberated. The considerable increase in current is due to the accumulation of positive ions until the number of ions recombining every second plus the number per second reaching the filament is equal to the number of ions formed per second under the influence of visible light. Possible objections to this explanation are discussed.

R. A. M.

β-Rays produced in Air by Short-wave *X*-Rays. H. IKEUTI (*Compt. rend.*, 1925, **180**, 1257—1259).—Monochromatic *X*-rays, 0·21 Å., were allowed to enter a Wilson chamber and stereoscopic photographs taken. The β-rays were of two kinds, those arising from high-speed photo-electrons and the fish and sphere tracks from low-velocity electrons. The mean length of trajectory of the first kind was 76 mm. (air pressure 570 mm.); corrected to 18°/760 mm. the value is between 57 and 65 mm. Wilson's data extrapolated according to Whiddington's law lead to a higher value, namely, 67 mm. The maximum trajectory of the (slow electron) fish tracks lay between 3·3 and 3·7 mm. The fish tracks are not due to *J*-electrons, but to a new type of radiation. Compton's formula for calculating the energy of recoil electrons arising from the diffusion of *X*-rays leads to a value 2·9 mm., lower than that found. The trajectory (on the basis of recoil) corresponding with an initial angle θ with the direction of exciting rays can be calculated from $E_m=E(1+1{\cdot}01\tan^2\theta)$ for $\lambda=0{\cdot}2$ Å.,

where E_m is the maximum energy and E the energy of a recoil electron projected at an angle θ. This expression of Compton is approximately verified, but there are a few completely anomalous trajectories.

If the small trajectories are due to recoil effects the ratio of absorption coefficients by diffusion and by fluorescence should correspond with the ratio of the number of short with long trajectories. This is 11·0 in both cases. Wilson's work leads to equally good agreement, so that the view that the small trajectories are due to the recoil of diffusing electrons is completely justified. Compton's theory gives 1·3 for the ratio of the number of sphere tracks to fish tracks. Regarding as sphere tracks all below 0·2 mm., experiment leads to a value of 1·1 for this ratio. R. A. M.

Radiation given out by Gases through which Electric Discharges are passing. (Sir) J. J. Thomson (*Phil. Mag.*, 1925, [vi], **49**, 761—786).—The suggestion (A., 1924, ii, 646) that ionisation in the negative glow of a discharge tube is due to radiation excited by the cathode rays in the gas through which they pass is confirmed by experiments of several types. The rays so generated have low penetrative powers, less than 1% from the negative glow produced by 3000 volts passing through a celluloid film 3×10^{-5} cm. thick. From measurements of the absorption of these rays by different materials, it is shown that they may have far higher frequencies than any characteristic of the gas from which they are derived. Thus the most penetrative rays generated in hydrogen by the electrons produced by a potential of 1500 volts were of wave-length $8{\cdot}1\times10^{-8}$ cm. The frequency of these rays thus corresponds with an ionising potential of 1500 volts. These results and the variations of the radiations in their path through the discharge tube indicate that they constitute a continuous spectrum with a maximum frequency proportional to the energy of the exciting electrons. It is concluded from the fact that some of this radiation is absorbable by two or three centimetres of air at 0·01 mm. pressure that the volume in which the energy of this type of radiation is concentrated must be considerably larger than the volume of a molecule of the gas (cf. *ibid.*, 1924, [vi], **48**, 737). At a polished zinc surface, up to about 5% of the rays suffer reflexion. An expression is derived for the distribution of energy in a continuous spectrum produced by the passage of electrons through a gas, and it is shown how this continuous spectrum, with a concentration of energy in the longer wave-lengths, may be brought about by the degradation of a homogeneous radiation, the frequency of which fixes the upper limit of the continuous spectrum. F. G. T.

Electrical Conductivity of Heated Gas. R. N. Ghosh (*Z. Physik*, 1925, **32**, 113—118).—The conductivity is calculated from estimates of the life-period of electrons in heated gases; in the case of stellar material, the value is about 100 times that of copper. E. B. L.

Gas Ion Mobilities. L. B. Loeb (*Phil. Mag.*, 1925, [vi], **49**, 517—519).—The ionic mobility equation originally published

(*ibid.*, 1924, [vi], **48**, 446) should be multiplied by $\sqrt{2}$. The corrected equation is: $K=(0{\cdot}104\sqrt{(1+b)/b})/(p/760\sqrt{(D-1)M_0})$ cm./sec./volt/cm. C. W. B.

The Permanent Electret. M. EGUCHI (*Phil. Mag.*, 1925, [vi], **49**, 178—192).—Disc electrets are prepared by solidifying molten mixtures of equal parts of carnaüba wax and resin in a strong electric field. The nature of the free charge is shown to be a permanent internal electrisation, the surface density of which is calculated by $\sigma=CV/\pi r^2$, where C is the capacity of condenser system, V the potential recorded by electrometer, and r the effective radius of the induction plate. The free charge remains the same over a period of some years, and is only temporarily affected by exposure to X-rays, solvents, planing with a knife, application of electric forces, etc. Under such treatment, the free charge temporarily disappears and then recovers exponentially according to the law $V'-V=(V'-V_0)e^{-\lambda t}$, where V is the potential at time t, and V' the final potential. The intensity of electrisation $E=4\pi\sigma$ is such that the electric intensity in air in front of the electret takes almost the greatest sustainable value. C. W. B.

Periodic Classification of the Elements from the Point of View of the Study of Isotopes. S. SCHTSCHUKAREV (*Neue Anschaungen in der Chemie*, 1924, **9**, 61—120; from *Chem. Zentr.*, 1924, ii, 1877—1878).—All elements are derived from the disintegration of four parent elements, of which two, namely, thorium and uranium, are known. The nuclei of elements consist of protons, electrons, α-particles, and helium atoms. The α-particle is given off as such: the helium atom is given off in three stages, namely, an α-radiation and two successive β-radiations (the α,β,β-transformation which thus results in the formation of isotopes). The α- and α,β,β-transformations can be so arranged as to give all known and some unknown isotopes. There are, for example, between niton and xenon 16 α- and 6 α,β,β-transformations, between xenon and krypton 9 α- and 3 α,β,β-transformations, between krypton and argon 9 α- and 3 α,β,β-transformations, between argon and neon 4 α-transformations, and between neon and lithium 3 α- and 1 β-transformations.

The existence of isobares is explained on the theory expressed. It is shown that the outer periodicity of the electron structure appears to be superimposed on the inner periodicity of the nuclear structure. The different changes are represented in tabular form. G. W. R.

Attempted Electrolytic Separation of the Isotopes of Chlorine and Magnesium. J. E. G. PHILEY (*Phil. Mag.*, 1925, [vi], **49**, 889—899).—By considering the migration velocity of an ion as made up of a large number of free paths over which there is a component of acceleration due to an electrical force, an expression is deduced for the variation of mobility with the mass of ions otherwise identical. For the isotopic chlorine ions, provided neither

hydration nor association of water molecules occurs, a difference of mobility of between 0·3 and 0·7% is to be expected, according to the value of the coefficient of restitution in the ionic collisions. If the ions are hydrated, and the water molecules polymerised, these limiting differences become 0·2 and 0·4%. The differences for the magnesium ions should be of the same order. Unsuccessful attempts were made to detect such differences in the diffusion of these ions through long tubes filled with agar gel under a potential difference of 300 volts. Careful atomic weight determinations on different layers of the gel after the experiments showed no indication of a separation of the isotopes. Probable causes of the failure of this method are discussed. F. G. T.

Rare Earths. XVI. Purification and Atomic Weight of Holmium. F. H. Driggs and B. S. Hopkins (*J. Amer. Chem. Soc.*, 1925, **47**, 363—369).—Purification was effected by fractionation of the bromates, dividing the series into fractions containing neodymium but no erbium and those containing erbium but no neodymium, followed by partial decomposition of the nitrates. Freedom from yttrium and dysprosium was established by comparison of the observed magnetic susceptibility with that calculated from the equivalent weight. From the ratio chloride : silver the atomic weight of holmium is 163·47. L. J. H.

Period of Mesothorium-2. W. P. Widdowson and A. S. Russell (*Phil. Mag.*, 1925, [vi], **49**, 137—140).—The separation of mesothorium-2 from its parent substance by addition of thorium and precipitation with ammonia is described. From a preparation with γ-ray activity equal to that of 6 mg. of radium bromide, mesothorium-2 is obtained and its half-period determined. Exponential decay to zero is observed and the half-period values are 360, 352, 359, 361, 356, 354, and 356, giving a mean of 357 mins. The period of average life is consequently 8·58 hrs. and the disintegration constant λ=0·116 per hr. The half-value period, having a probable error of 1%, is 4% lower than that obtained by Hahn (A., 1908, ii, 454). No product with a less period is detectable, and the experiments point to the unlikelihood of a product with greater period. C. W. B.

Constancy of the Rate of Transformation of Radium Emanation at Different Concentrations. (Mme.) P. Curie (*Ann. Physique*, 1924, **11**, 405).—The rates of decay of the γ-radiation from similar samples of radium emanation enclosed in small spherical vessels are found to be constant to within 1 part in 10,000 parts. At pressures of about 0·5 atm. the emanation gives γ-rays the rate of decay of which differs by less than 1 part in 2000 parts from that of samples at lower concentrations. R. W. L.

Determination of the Ratio of the Velocities of the Two Groups of α-Particles Emitted from the Active Deposit of Thorium. S. Rosenblum (*Compt. rend.*, 1925, **180**, 1332—1334).—A new experimental arrangement of the photographic method of measuring deflexion in a magnetic field of varying in-

tensity (15,000—18,000 gauss) is described. The distance from radioactive source to photographic plate was also varied. The ratio of the velocities of α-particles from thorium-*C* and thorium-*C*′ is 1·209±0·001. The value obtained after correction for the increase in mass of high-velocity α-particles is 1·210, so that the experimental error and the correction are of the same order. The most recent values for the ranges of α-particles from thorium-*C* and -*C*′ are 8·62 cm. and 4·72 cm., respectively, at 15° and 760 mm. (Henderson, A., 1921, ii, 617; Geiger, *Z. Physik*, 1922, **8**, 45). The cube root of the ratio of these numbers is 1·217, agreeing with the ratio of velocities to within 0·6%. R. A. M.

Increase of the Heating Effect of Radium Preparations Due to Growth of Polonium. (MME.) M. CURIE and D. K. YOVANOVITCH (*J. Phys. Radium*, 1925, [vi], **6**, 33—35).—The heating effect of a preparation of radium chloride, purified 16¾ years ago, has been compared with that of a preparation recently prepared, the actual masses of radium in each preparation being compared by their γ-radiations. The results show that the heating effect has increased by 11% in this period. This is due to the formation of polonium and is very approximately the amount to be expected on present knowledge of the heating effects of radium with its short-lived products, and of polonium, and of the periods of radium, radium-*D*, and polonium. The growth of polonium in preparations of radium is consequently at the rate to be expected on present theory. The calorimetric measurements are not sufficiently accurate to give at this stage a more exact value of the period of radium-*D* than that accepted at present. A. S. R.

Quantity of Heat Set Free as γ-Radiation in Radioactive Disintegration. J. THIBAUD (*Compt. rend.*, 1925, **180**, 1166–1169).—The total heat set free per hr. by 1 g. of radium in radioactive equilibrium is 135—137 cal. (Rutherford and Robinson, A., 1913, ii, 269). The kinetic energy of α-particles and the recoil effects are calculated to be 117·7 cal., or, including the energy of β-radiation, 129·8. The discrepancy is due to the effect of penetrating γ-rays. Kovarik (A., 1924, ii, 447) suggests that each α-particle emission is accompanied by a single γ-quantum. The complexity of γ-spectra implies that nuclear emission need not be followed by emission of a γ-quantum of constant energy. Radium-*B* would emit several frequencies, some of which would be more likely to occur than others. Their intensities supply a measure of the probability of occurrence. Summation of energy and intensities indicates values for the mean quanta of the γ-radiations of radium-*B* (302,000 volts), radium-*C* (1,010,000 volts) and radium (187,000 volts). Thus, $\Sigma h\nu = 1{\cdot}49 \times 10^6$ volts and $E\gamma = Z.\Sigma h\nu = 0{\cdot}841 \times 10^5$ ergs (Z is $3{\cdot}57 \times 10^{10}$, the number of atoms disintegrating per second). This corresponds with 7·25 g.-cal. per hr., accounting quantitatively for the low calculated heat evolution given above.

The heat in cal./hr. is distributed as follows: α-particle emission and recoil effect 117·7, primary β-emission 12·1, γ-emission 7·2, total, 136·9. The energy due to γ-rays is by no means negligible;

for radium-B+-C, it attains 16% of the total heat. The success of these calculations supports the hypothesis that each α-particle emission from the nucleus is followed by emission of a single γ-entity the quantum of which may be variable. R. A. M.

Separation of the Total Radiation of Radium into Groups by Absorption in Platinum. J. S. LATTÈS (*Compt. rend.*, 1925, **180**, 1023—1026).—The radiation from radium and its disintegration products, which is of four main types, namely, primary β- and γ-radiations and the secondary γ- and β-radiations derived from them, is further divided into ten groups, according to their various coefficients of absorption by platinum. The distributions of the radiation in the various groups are tabulated for thicknesses of platinum up to 1·5 mm. The bearing of the results on medical applications is discussed. G. M. B.

Gold in the Mercury Lamp. T. RETSCHINSKY (*Physikal. Z.*, 1925, **26**, 280—281).—Since the potential gradient in the Heraeus high-pressure lamp is slightly greater than in the Jaenicke lamp, conditions in the former are more favourable for the penetration of the atomic nuclei by electrons. Slightly modified Heraeus lamps have been constructed to work at a potential gradient of 21 volts/cm. and 150 cm. mercury pressure. F. G. T.

Quantum Radiation. (SIR) O. LODGE (*Nature*, 1925, **115**, 798).

Electrical Behaviour of Radioactive Colloidal Particles of the Order of 10^{-5} cm. as Observed Separately in a Gas. F. EHRENHAFT (*Phil. Mag.*, 1925, [vi], **49**, 633—648).—Largely polemical against Millikan, with a claim for priority in the method of determining the electric charge on individual particles. The author contends that he has proved the existence of fractions of an electronic charge. Microscopic spherical particles of silver of the order of 10^{-5} cm. were examined under a variable electric field E between two horizontal metal plates. A test-body of constant charge e would move with a velocity $(Ee-mg)B$, where B is the mobility. Since the observed speed varies linearly with field strength, the mobility is constant and concordant values are given on the basis of Stokes' law, the colour of the light scattered, and the photophoretic maximum. The Einstein theory of Brownian movement in gases leads to an anomalous and untrustworthy value. It was found that for particles of radius less than 3×10^{-5} cm. charges smaller than that on an electron were often carried, the fraction falling below 1/10 and 1/20 of the elementary quantum.

The subdivision of the electron charge has been criticised on the grounds (*a*) that the test-bodies are not spheres, (*b*) that the density of the particle is not the same as that of the substance in bulk, (*c*) that the test-body is surrounded by a gas layer, (*d*) that the exact form of the law of resistance for small spheres in a gas is not known. The author claims that these objections are all either untenable or irrelevant. If (*b*) is valid, the density of platinum must fall from 21·4 to 0·2.

Small, spherical, colloidal test-particles of selenium and mercury can be made radioactive by contact with niton or polonium. In a constant electric field they move so as to give the impression of a continuous change of electric charge, whilst the movement of non-radioactive particles is uniform. The radioactive test-bodies must therefore gain or lose charges which are only small fractions of the supposed indivisible electronic charge. These results have an important bearing on the fact that there is no theory to account for the cohesion and stability of the electron.

Observations consistent with subdivision of the electronic charge have been made by other workers and discrepancies are due to interpretation rather than experiment. Lodge adds a note to the effect that Millikan ("The Electron," 1917) has discussed carefully and rejected Ehrenhaft's views, but that, nevertheless, a serious attack on so fundamental a question cannot be ignored.

R. A. M.

Law of Force within the Atom. G. GREEN (*Phil. Mag.*, 1925, [vi], **49**, 1020—1028).—A law of force is suggested which gives rise to an atomic system essentially in conformity with the Bohr theory of the atom and with quantum theory. The proposed law of force between a positive charge e and an electron e is of the form $f=(e^2/r^2).\cos(\rho/r)$, where ρ represents a radius drawn from the centre of an atom, such that for all distances exceeding a small multiple of ρ the inverse square law of attraction holds. According to this law, an electron within an atom could remain at rest in stable equilibrium at values of r given by $\rho/r=(2n+\frac{1}{2})\pi$, where n is an integer. Consideration of the amount of energy radiated in the movement of an electron from one stable position to another shows that this law provides a system in which energy would be radiated in a manner conforming closely to that obtaining for change of orbit in the Bohr atom. By choosing a system of stable states such that $n=25$, 16, 9, 4, 1, the Rydberg constant may be derived. It is further shown that, in agreement with the Bohr theory, an orbital motion established by an electron in any one of the stable positions would be nearly permanent, provided the natural radiation loss was small.

F. G. T.

Problem of the Quantitative Formulation of Bohr's Correspondence Principle. R. C. TOLMAN (*Phil. Mag.*, 1925, [vi], **49**, 130—136).—Six methods of averaging the light intensities emitted by states intermediate between the initial and final quantum states used by Hoyt (A., 1924, ii, 433) are employed to calculate the probability of transitions in three simple quantum systems: the harmonic oscillation, the rotating dipole, and the simplified hydrogen atom. The only method giving zero probability for an electron falling into the hydrogen nucleus from the innermost orbit, is that expressed by $\log(Q\nu^2)=\int_0^\infty \log(C_\tau r^2\omega^2)d\lambda$. This treatment assumes the validity of the inverse square law down to zero distance between nucleus and electron, contrary to the finite mass and energy of the hydrogen atom.

C. W. B.

Possible Reconciliation of Bohr's Interpenetration Ideas with Sommerfeld's Relativistic Treatment of Electron Orbits. R. A. MILLIKAN and I. S. BOWEN (*Phil. Mag.*, 1925, [vi], **49**, 923—935; cf. A., 1924, ii, 710).—A third possibility is suggested as a solution of the dilemma previously discussed. An examination of the data of doublet separation shows that whilst the Sommerfeld relativity equation predicts the fine structure of hydrogen and ionised helium as accurately as is attainable in experimental work, for lithium to nitrogen, and sodium to chlorine series, even for remote orbits which ought to obey the laws of a simple nucleus-electron system, greater discrepancies are obtained by the use of the equation than can be accounted for by experimental error. It is suggested that whilst the fine structure in the cases of hydrogen and ionised helium is due entirely to the relativity effect, in the heavier atoms there is some cause acting by virtue of the difference of the orientation of the two circular orbits L_{II} and L_{III}, which increases the energy of the circular orbit L_{II} to about the amount which it would have had by virtue of relativity, had it been a 2_1 orbit. To account for the approximate validity of the relativity equation for these atoms, this postulated force, which may be magnetic or electrostatic or a combination of the two, must demand the same variation with nuclear charge, and with total and azimuthal quantum number, as is required by the relativity principle. The difference of behaviour in weak magnetic fields of hydrogen and helium as compared with lithium and other atoms is adduced in support of this suggestion. The appearance of the Paschen–Back effect in hydrogen is, however, contrary to expectation. F. G. T.

Quantum Defect and Atomic Number. D. R. HARTREE (*Phil. Mag.*, 1925, [vi], **49**, 390—396; cf. Turner, *ibid.*, 1924, **48**, 384).—The proposal to alter the assignment of the principal quantum numbers to certain terms of atomic number greater than 28 is discussed. It is maintained that the reasons for the change are scarcely adequate. An objection to the newly-proposed scheme of quantum numbers is pointed out. Fresh evidence, afforded by X-ray spectra, which seems to be definitely in favour of Bohr's assignment, is put forward. C. W. B.

Quantum Numbers of the Bohr Orbits in the Alkali Atoms. R. B. LINDSAY (*Science*, 1924, **60**, 475—476).—Polemical against Turner (A., 1924, ii, 797), whose assignment of quantum numbers 6 and 8 to the outermost orbits of rubidium and cæsium, respectively, is held to be unjustified. A. A. E.

Quantum Theory of Red Displacement of Spectral Lines. J. KUDAR (*Physikal Z.*, 1925, **26**, 207—211).—Mathematical. The Einstein red displacement of the hydrogen series and the Deslandres–Schwartzchild band spectra are deduced on the basis of the equations of electron movement of the general relativity theory, the Sommerfeld quantum condition for hypothetical periodic systems, and the Bohr frequency relation. F. G. T.

Balmer Law as an Equation of Motion. L. PAGE (*Physical Rev.*, 1925, [ii], **25**, 429—443).—An attempt to develop a form of dynamics in which the intra-atomic motions are unifrequentic, the dynamical frequency coinciding with the optical frequency as calculated on Bohr's theory. A. A. E.

Intensity of Multiplet Lines. A. SOMMERFELD and H. HÖNL (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 141—161).—A formula is suggested by which the intensity of multiplet lines arising from a given electron transition may be calculated. Where data are available for comparison the agreement is good. The expression embodies the correspondence principle and the summation rule of Burger and Dorgelo (*Z. Physik*, 1924, **23**, 258). F. G. T.

Rectilinear Diameter of Helium. E. MATHIAS, C. A. CROMMELIN, H. K. ONNES, and J. C. SWALLOW (*Compt. rend.*, 1925, **180**, 1005—1007; cf. A., 1922, ii, 440).—The density of liquid and gaseous helium has been determined at temperatures between −268·38° and −270·79°. Helium obeys the law of rectilinear diameters, the data agreeing well with those calculated from the equation for the diameter: $y=-0{\cdot}40263-0{\cdot}0017616t$. The following constants are recorded: t_c −267·90°, d_c 0·06930, and the critical coefficient RT_cd_c/p_c 3·270 as compared with the value 3·276 for hydrogen. G. M. B.

Secondary Spectrum of Hydrogen. J. W. NICHOLSON (*Month. Not. Roy. Astr. Soc.*, 1925, **85**, 449—464).—The Fulcher hydrogen bands are to be regarded as two parts of a single band system, of great complexity, which is probably due to un-ionised hydrogen molecules. The lines of these bands do not show the Zeeman effect. The most characteristic components in the first Fulcher band are in each case arranged in triplets about 100 Å. apart. In addition to the strong lines noted by Fulcher, it is shown that practically all the weak lines in the region 6000—6400, not showing the Zeeman effect, are to be regarded as components of a single scattered band. Similarly, groups of lines in the region 5300—5700 are related to the second Fulcher band, the chief components of which are triplets of mutual separation 120 Å. The wave-numbers of the strongest components in these two bands may be expressed by formulæ of the type $n=\alpha+\beta(m+\mu)^2$, in which the values of α for the two series are approximately equal. The two bands thus possess a common limit. Examination of the lines in the blue region which do not show the Zeeman effect indicates the existence of other widely separated bands analogous to those of Fulcher, and the probability that the number of distinct bands in the secondary spectrum of hydrogen is small. F. G. T.

Secondary Spectrum of Hydrogen at Very Low Temperatures. J. C. MCLENNAN and G. M. SHRUM (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 177—182).—The secondary spectrum of hydrogen was photographed with the discharge tube at (*a*) the ordinary temperature, (*b*) −180°, and (*c*) −252°. The lines of Fulcher's S_3 group (*Physical Rev.*, 1923, [ii], **21**, 375) were greatly

enhanced at the low temperatures, those of the S_2 unchanged and those of the S_1, S_0, and $\bar{X}$ groups all weakened. Tables are given for a large number of lines which are enhanced, weakened, or entirely suppressed at −252°. J. S. C.

Regularities in the Secondary Spectrum of Hydrogen. O. W. RICHARDSON and T. TANAKA (*Proc. Roy. Soc.*, 1925, **A**, **107**, 602—623; cf. *ibid.*, 1924, **A**, **106**, 640, 663).—It has been found possible to arrange 123 additional lines provisionally in 22 series. Three of these form a P, Q, R combination. The present indications are that the moments of inertia of the emitters are spread fairly well over a range extending from the high value deduced from the P, Q, R combination found provisionally to a value somewhat below the lowest value which has been deduced from Fulcher's second band. This involves an extreme variation by a factor of almost 6 in the moment of inertia. L. L. B.

Third Negative Group of Carbon. Spectrum of the Tails of Comets. Extension on the Red Side and Structure of the Bands. F. BALDET (*Compt. rend.*, 1925, **180**, 820—822).—Previous work (this vol., ii, 180) has been extended by making use of panchromatic plates and a high-dispersion spectroheliograph, and seven new bands are now recorded in addition to the three measured previously. The fine structure can be interpreted in terms of rotational quantum numbers and the combination rules of Heurlinger. Alternative combination rules are given which show better agreement. A more detailed treatment of structure will appear elsewhere.

The measurements of Baldet and Baume-Pluvinel on the Morehouse comet (1908) have now been reproduced in every detail with pure carbon monoxide. Helium need not be present for the production of the first or third negative groups of carbon. R. A. M.

Influence of Pressure on Carbon Band Spectra in Discharge Tubes. Consequences for the Theory of Comets. F. BALDET (*Compt. rend.*, 1925, **180**, 1201—1203; cf. preceding abstract).—Pressure plays an essential part in the appearance of the different groups in the carbon monoxide spectrum. The light arises either from impacts of electrons (the speed of which exceeds that corresponding with the ionisation potential) on neutral or ionised molecules, or from collisions of neutral and ionised molecules. Thus, different groups appear. At low pressures, when electron impacts predominate, only the first and third groups occur. At higher pressures, the molecular collisions influence the spectra by exciting new groups. The effect of pressure is also seen on the structure of the bands of the third negative group. At very low pressures, the heads are intense as in the cometary spectra. It is concluded that the carbon monoxide in the tails of comets must be bombarded by electrons from the sun. R. A. M.

Band of Unusual Structure probably due to a Highly Unstable Calcium Hydride Molecule. R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **25**, 509—522).—An isolated band with head at 3533·6 Å. observed in the spectrum of the calcium arc in hydrogen

at 3—20 mm. has been measured and analysed. The emitting molecule is probably a compound of a hydrogen atom with an excited, but not ionised, calcium atom. A. A. E.

The CuH Molecule and its Band Spectrum. H. Bell (*Phil., Mag.*, 1925, [vi], **49**, 23—32).—The figures of Frerichs and Bengtsson (*Z. Physik*, 1923, **20**, 170, 229) for the bands shown by copper in the region 4700 to 4000 are used in the application of a formula for band spectra in the visible region, developed by the author. The presence of the CuH molecule is verified, and the half quantum for its rotation established. The distances between the hydrogen and copper nuclei for the initial and final configurations are calculated, and a diagram is given showing variation of radial force function with distance. C. W. B.

Budde Effect in Bromine. E. B. Ludlam (*Proc. Roy. Soc. Edin.*, 1924, **44**, 197—201).—Ordinary pure bromine vapour when illuminated showed an immediate rise in temperature with corresponding volume change. Purified bromine containing no water vapour showed no Budde effect under various conditions of illumination. It is suggested that, as proposed by Perrin (A., 1919, ii, 177), pure bromine radiates in all directions the energy which it absorbs, but that traces of water vapour have a catalytic effect on the dissociation into atoms, which on re-combining effect an increase in temperature with an appropriate volume change. A. E. M.

Electrical Excitation of the Band and Line Spectra of Iodine. G. Cario and O. Oldenberg (*Z. Physik*, 1925, **31**, 914—919).—The primary object of the work was to find a spectrum of the positively charged iodine molecule, I_2^+. Only a weak, narrow group of bands was found at about 2700 Å., indicating that the stability of this form is slight. The bands in the blue and near ultra-violet, observed in a narrow capillary, were resolved into a series of single bands. The diffuse band at 3460 Å. was also resolved into a series of single bands. By using a silica tube heated at above 1000°, the line spectrum for atomic iodine was obtained and the wave-lengths were measured as far into the ultra-violet as the strong line at 2062·2 Å. E. B. L.

Band Spectrum of Mercury. E. Hulthén (*Z. Physik*, 1925, **32**, 32—55).—These bands are obtained when an uncondensed discharge is passed through mercury vapour, but a trace of moisture or hydrogen is necessary. Mercury hydride is considered to be the source of the bands. The bands are classified and tables of wave-lengths given. E. B. L.

Emission Band Spectra of Aromatic Compounds. I. Their Connexion with Infra-red Absorption Bands and a Classification. J. K. Marsh (*Phil. Mag.*, [vi], 1925, **49**, 971—980).—Baly's relationship that the frequencies of the heads of absorption bands in the ultra-violet and visible regions are integral multiples of that of a fundamental infra-red band, is made the basis

of a classification of the emission band spectra of a number of aromatic compounds. Of these, one class is characterised by groups of bands at frequency intervals of 102 waves/mm. These are considered to be multiples of the benzene infra-red band at 9·8 μ. An aromatic–aliphatic derivative type, exemplified by *p*-xylene, has band intervals of 40 or 80 in the ultra-violet. With the Tesla discharge, these substances give a green glow, consisting of two bands at an interval of 160. A third class, of which benzaldehyde is typical, gives a blue Tesla luminescence characterised by three very strong bands with frequency differences of 172. A fourth, less defined, class of substances containing condensed nuclei shows three or four bands near 4000 Å., with frequency intervals of 142 for anthracene and its derivatives, and of 47 for naphthalene. Many substances do not give any emission, or only one of a continuous character, and cannot be classified. In the infra-red, bands of absolute frequency equal to the above ultra-violet frequency differences are in each case well-marked and characteristic of the groups. F. G. T.

Relation between the Constants of the Infra-red Bands of Triatomic Molecules. E. Fermi (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 386—387).—The theory of infra-red bands leads to the formula $\Delta\nu=h/4\pi^2I$, where h represents Planck's constant, I the moment of inertia of the molecule, and $\Delta\nu$ the constant frequency difference between the lines of the infra-red band. For triatomic molecules, the three atoms must lie in a plane, and the three principal moments of inertia are connected by the expression $I_1=I_2+I_3$; hence $1/\Delta\nu_1=1/\Delta\nu_2+1/\Delta\nu_3$. This equation is obeyed closely for water vapour, the molecule of this being the only one for which the necessary experimental data are available. T. H. P.

Electrodeless Discharge in the Vapours of Phosphorus and Sulphur. W. W. Shaver (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 145—149).—The spectrum of the electrodeless discharge in phosphorus vapour has been investigated in the fluorite region, the frequencies and wave-lengths of 12 lines between 1859·4 and 1671·5 Å., some of which have been previously reported (Saltmarsh, A., 1924, ii, 436), being given. The frequencies and wave-lengths of 9 lines in the corresponding spectrum for sulphur are recorded in the region 1903·6—1666·5 Å. J. S. C.

Spectrographic Study of the Iodo-cadmium Complex. P. Job (*Compt. rend.*, 1925, **180**, 1108—1110).—The existence of K_2CdI_4 complex has been shown in several ways, but the author's method of detecting double salts in aqueous solution by absorption spectra measurements gave negative results. Examination of the spectrograms suggested that this was due to complexity of cadmium iodide itself. This view was tested by photographing absorption spectra of cadmium sulphate–potassium iodide mixtures. The ultra-violet absorption was considerable and passed through a sharp maximum at 80% potassium iodide corresponding with the ion CdI_4''. A rough idea of the stability of the complex can be obtained

by determining the equilibrium constant of the reaction $Cd^{\cdot\cdot}+4I'\rightleftharpoons CdI_4''$, by using the composition-maxima of solutions of the two iodides at various concentrations. R. A. M.

Absorption of Ultra-violet Light in Dilute Solutions. C. J. W. Grieveson (*Phil. Mag.*, 1925, [vi], **49**, 1006—1020).—A method is described of comparing the transparency to ultra-violet light of aqueous solutions by measuring the photo-electric effect of the transmitted light. The transmission coefficients at a series of concentrations are given for the chloride, hydrogen carbonate, carbonate, sulphate, and nitrate of sodium, disodium hydrogen phosphate, manganese chloride, copper sulphate, potassium permanganate, and calcium nitrate. Of the sodium salts, the sulphate is very transparent. The presence of the nitrate ion renders a solution highly opaque. The addition of tap water containing 0·3 g. of impurity per litre greatly reduced the transparency of the solutions. The relation between the absorption and the thickness of the solution layer was examined for calcium nitrate.

F. G. T.

Ultra-violet Absorption as a Function of p_H of some Organic Acids, considered as Ultra-violet Indicators. F. Vlès and (Mlle.) M. Gex (*Compt. rend.*, 1925, **180**, 1342—1345; cf. this vol., ii, 292).—The ultra-violet absorption spectrum of certain organic acids is different from that of the corresponding salt; p_H measurements should therefore be taken into account. If ϕ is the ratio of the extinction coefficients at wave-lengths λ_1 and λ_2 at a definite p_H value, the curve ϕ against p_H will then bear a relation to the changing constituents of the solution. Oxalic acid has a wide absorption band from 350 $\mu\mu$ to the extreme ultra-violet with a succession of breaks near 230, 255, 260, 272, 284, 298, 320, and 345. Taking ϕ=ratio of e at 260 to e at 273, and graphing against p_H, a curve is obtained with a maximum between p_H 0 and p_H 1, a minimum between p_H 1 and p_H 4, an inflexion between p_H 4 and p_H 10, and a steep portion between p_H 10 and p_H 13. There are five possible successive constituents: undissociated acid, two anions, the monosodium ion, and undissociated disodium salt at very strong p_H. The middle portion of the curve can be calculated from equilibrium data if p_K is taken as 3·6 (Scudder's conductivity data gives 4·31) and p_{K_1} as 1·05.

Benzoic acid shows seven bands, λ max. equals 245, 250, 261, 266, 273, 278, and 285 $\mu\mu$, which vary with p_H. The bands 272 and 250 increase and the bands 261, 266 decrease with lowered p_H. The ratios ϕ_1=273/261, ϕ_2=273/256, ϕ_3=273/250 graphed against p_H give curves for benzoic acid quite as complicated as for oxalic acid, in spite of its univalency. A middle portion similar in appearance to a neutralisation curve is found near p_K (constant) and can be calculated from the dissociation equation. The curves for ϕ_1, ϕ_2, and ϕ_3 against p_H are all similar in type and show maxima and minima. These latter cannot be accounted for on the assumption of three possible constituents, namely, undissociated benzoic acid, benzoate ion, and undissociated sodium benzoate. It seems as if

two other constituents must occur. The idea of supplementary constituents requires recourse to very hypothetical notions, such as modification of the carboxyl group or activation of the benzene ring. It is suggestive that preliminary work indicates that the absorption spectrum of aqueous benzene varies with hydrogen-ion concentration.

R. A. M.

Relationship of Thyroxin to Tryptophan. C. S. Hicks (*J. Chem. Soc.*, 1925, **127**, 771—776; cf. Kendall, A., 1919, i, 496).—Measurements of the ultra-violet absorption spectra of thyroxin in *M*/8000—*M*/40,000 alkaline solution compared with those of tryptophan in *M*/10,000—*M*/50,000 alcoholic solution reveal a definite group resemblance. In thyroxin, the bands are shifted towards the red, owing to the iodine present. Similar relations are shown to hold between the spectra of isatin and iodoisatin. The conclusion is arrived at that the indole skeleton is present in thyroxin.

W. A. C.

Döppler Effect in the Reflexion of Resonance Fluorescence. W. Rump (*Z. Physik*, 1924, **29**, 196—208).—It is shown that a re-emitted line in a resonance fluorescence spectrum shows a greater Döppler effect than that of the incident radiation when the source of secondary radiation is at a higher temperature than that of the primary radiation. The width of a line is unchanged by reflexion from glass, metal, or mercury vapour. R. W. L.

Resonance Fluorescence of the Line 1849 Å. of Mercury Vapour. W. Rump (*Z. Physik*, 1925, **31**, 901—902).—Light from a quartz mercury vapour lamp crossed a space from which oxygen had been driven out by carbon dioxide and fell on mercury vapour in a quartz tube. The resonance radiation emitted in a direction at right angles to the incident light fell on the slit of a fluorite–quartz spectrograph filled with carbon dioxide, and the photograph showed the line 1849, the plate having been rendered fluorescent by a thin layer of paraffin oil. The production of this line had been predicted as the result of the absorption of the line 2536·7 followed by a further absorption of light by the atom in the $2p_2$ state. E. B. L.

Effect of an Alternating Magnetic Field on the Polarisation of the Resonance Radiation of Mercury Vapour. E. Fermi and F. Rasetti (*Nature*, 1925, **115**, 764).

Fluorescence and Channelled Absorption of Bismuth at High Temperatures. K. R. Rao (*Proc. Roy. Soc.*, 1925, **A**, **107**, 760—762; cf. A., 1924, ii, 804).—The absorption and fluorescence spectra of bismuth vapour at 1500° to 1600° have been photographed and compared. The fluorescence spectrum is practically the exact complement of the absorption spectrum in this region. In contrast to the bands in the ultra-violet, some of the absorption bands show a distinctly fine structure. It is considered that the existence of a fluorescent banded spectrum in the

above region is a criterion for molecular radiation processes, and that in elements which are polyatomic, the radiating systems are molecules instead of atoms. L. L. B.

Extinction of Fluorescence of Dyes at High Concentration. S. J. Wawilow (*Z. Physik*, 1925, **31**, 750—764).—As the concentration of the solution of the dye is increased a point is reached at which the extinction begins and it increases thereafter in simple exponential relation to the concentration. It is suggested that the critical concentration is related to the life-period of the activated molecule and the Brownian movement to which the molecule is subjected. There appears to be no relation between the extinction and the conductivity of the solutions. The presence of other dyes was found to reduce the fluorescence, but experiments to detect an analogous effect to the Cario and Franck transference of energy have not yet led to a decisive result. E. B. L.

Decay and Regeneration of Radio-luminescence. C. H. Viol, G. D. Kammer, and A. L. Miller (*Nature*, 1925, **115**, 801—802).—It is believed that the decrease with time of the luminescence of phosphorescent zinc sulphide etc. is due to the masking of the radiation luminosity by the colour which the material acquires, due to the action of the radiation. A. A. E.

Luminescence of Grignard Compounds. Spectra and Brightness. R. T. Dufford, D. Nightingale, and S. Culvert (*J. Amer. Chem. Soc.*, 1925, **47**, 95—102).—In continuation of previous work (A., 1923, ii, 714) the following organometallic halides are reported as chemiluminescent: calcium phenyl iodide, magnesium *p*-fluorophenyl bromide, magnesium *o*-chlorotolyl bromide, magnesium 2-cymyl bromide, magnesium α- and β-naphthyl iodides. Direct spectrum photographs have been obtained and quantitative measurements of brightness made. Previous conclusions have been quantitatively verified. L. J. H.

Emission of Light by Solidified Gases at the Temperature of Liquid Helium and the Origin of the Spectrum of the Aurora. L. Vegard, H. K. Onnes, and W. H. Keesom (*Compt. rend.*, 1925, **180**, 1084—1087; cf. A., 1924, ii, 436, 509, 584, 713, 805).—The study of the light emitted by bombarding solid nitrogen or mixtures of nitrogen and neon with high-velocity cathode rays has been continued at the temperature of liquid helium. The N_1 band of nitrogen has its maximum at 5555 with two secondary maxima; cooling does not result in a diminution in the width of the band. The N_2 band is strong and is divided into two components (5236, 5222). The spectrum shows a regular series of seven bands extending from 3986 to 5770. At higher temperatures, these are broad and diffuse, but on cooling they are each resolved into two fine lines shading off on the red side. In argon containing a trace of nitrogen (at the temperature of liquid hydrogen) the bands are also concentrated into pairs of lines, but their position is different. The

two strongest bands are at 4523, 4473 and 4236, 4211, and they correspond with the bands observed by Rayleigh in diffuse night light. In the region of longer waves, nitrogen, at the temperature of liquid helium, emits 3 or 4 feeble lines 5914, 5952, 6399, and perhaps 6417. These lines probably correspond with feeble ones in the auroral spectrum. Solid neon–nitrogen mixtures show the N_1 band shifted in a similar way as in argon–nitrogen mixtures. Diminishing proportions of nitrogen cause disappearance of the secondary maxima with displacement of the principal maximum towards the red. Qualitatively, the argon–nitrogen and neon–nitrogen mixtures are similar, but the magnitude of the displacement and the law followed are quite different. For both mixtures the wave-length of the principal maximum is a function of the concentration of nitrogen. The shift is due partly to a specific action of the inert gas and partly to a diminution in nitrogen. For argon–nitrogen mixtures, the factors are of the same order, so that a little argon can produce a considerable displacement. The specific effect of neon is very small, so that the shift does not occur until the neon content rises to 70%. As the nitrogen proportion approaches zero, the N_1 band takes the form of a line 5578·6, which nearly coincides with the green line of aurora borealis. The small difference 1·2 Å. is explained by a small specific effect of neon. In neon with traces of hydrogen, the N_2 band is divided into three components (5229, 5220, 5203), of which the first is the strongest. As the proportion of nitrogen increases, the N_2 band has a double line structure, and the spectra show several neon lines. R. A. M.

Radiation from Non-luminous Flames. R. T. Haslam, W. G. Lovell, and R. D. Hunneman (*Ind. Eng. Chem.*, 1925, **17**, 272—277).—Experiments in which the primary air was varied over a range of 80—150% of the theoretical amount, show that the maximum heat radiated from a flame (when no secondary air is present) is at a maximum when the primary air is at its theoretical amount. Helmholtz's theory that the amount of heat radiated from a flame is equal to the sum of the amounts which would have been radiated if the final products of combustion had been produced by burning hydrogen and carbon monoxide ("Licht u. Warmestrahlung verbrannter Gase," Berlin, 1890), is not justified.

The maximum energy radiated from methane, illuminating gas, and carbon monoxide with the theoretical amount of air was 14·9, 13·8, and 10·4%, respectively, of the total latent heat. The relative radiation from flames of different depths follows an exponential law indicating that at about 100 cm. the flame becomes opaque to its own radiation.

Increasing the burner tip area by 50% had no appreciable effect. Preheating the primary air decreases the amount of radiation and this may be due either to a shift of the chemical equilibrium or to pre-combustion. The amount of heat radiated has no simple connexion with the flame temperature, and hence the authors suggest that it is intimately connected with the actual chemical reaction taking place in the flame. M. B. D.

Phosphors of Boric Acid. A. Mickwitz (*Ber.*, 1925, **58**, [*B*], 678—679; cf. Tiede and co-workers, A., 1921, ii, 75; 1922, ii, 8, 245).—The phosphorescence of compounds of boric acid was known at the end of the 18th and beginning of the 19th century. H. W.

Ionisation of Iodine Vapour by Ultra-violet Light. W. West and E. B. Ludlam (*Proc. Roy. Soc. Edin.*, 1924—5, **45**, 34—41).—Instead of the quartz windows used in the hitherto unsuccessful attempts to demonstrate the ionisation of iodine by ultra-violet light, an exposure chamber provided with a fluorite window, thus permitting the passage of light of wave-lengths down to about 120 $\mu\mu$, has been employed. The aluminium spark gap was placed close to the window to prevent absorption by the oxygen of the air. A stream of nitrogen, which is not ionised by light of the wave-length employed, carried iodine vapour of partial pressure 0·13 mm. at 15°. It has thus been found that, provided the aluminium sparking terminals are kept free from oxide, ionisation takes place, both positive and negative charges being given to the electrometer in approximately equal amounts. The effect ceases when the source of light is removed 1 cm. in air away from the fluorite. The results show that iodine vapour is ionised by light of wave-length between 185 and 120 $\mu\mu$. The work of Smyth and Compton (A., 1921, ii, 364) and of Mohler and Foote (A., 1921, ii, 368) on the ionisation potential of iodine indicates a corresponding wave-length of 123 or 131 $\mu\mu$, whilst the spectrum of the aluminium spark in air shows strong lines between 170 and 180, weaker ones at 150 and 160, and a group of stronger lines at 130. Many of the molecules of iodine were probably in a state of fluorescence, and the ionisation potential of fluorescing iodine corresponds with a wave-length of 181 $\mu\mu$ (Smyth and Compton, *loc. cit.*). M. S. B.

Quantum Equivalent for Photo-electric Conductivity in Sodium Chloride Crystals. Z. Gyulai (*Z. Physik*, 1925, **32**, 103—110).—Rock-salt crystals were coloured yellow by exposure to *X*-rays, and the ratio of photo-electric conductivity to the light energy absorbed was determined in the visible and near ultra-violet region. This ratio increases with increasing wave-length throughout the absorption band. About 10,000 quanta were absorbed for each electron detected, from which it was calculated that the mean path of the electron is 1/3000 mm. E. B. L.

Incident and Emergent Velocities of Photo Electrons Emitted from Thin Platinum Films. C. Cha (*Phil. Mag.*, 1925, [vi], **49**, 262—272).—Asymmetry in the velocities of photo electrons emitted from the two sides of thin platinum films is investigated for evaporated and sputtered films. For the former no asymmetry was found over the experimental range of film thickness and wave-length of incident light. The maximum emission energy of a photo electron is given as a linear function of the frequency of light, the slope of the line giving Planck's constant h, 2% lower than the value given by Millikan (*Physical Rev.*, 1916, [ii],

7, 355). With sputtered films, asymmetry occurs, and the ratio of the potentials measuring maximum emission velocities decrease with increasing thickness of film, but are independent of wave-length, confirming the results of Robinson (*Phil. Mag.*, 1913, [vi], **25**, 115) and of Stuhlmann (*Physical Rev.*, 1914, [ii], **4**, 195). The results point to the asymmetry being due to fundamental differences between the types of film. C. W. B.

Motion of a Free Electron in the Field of Plane Electromagnetic Waves. J. Frenkel (*Z. Physik*, 1925, **32**, 27—31).—There can be no photo-electric effect for a free electron: it must be a resonance effect on a bound electron. E. B. L.

Relation between Energy of Escape of Electrons and Electrochemical Normal Potential. A. Günther-Schulze (*Z. Physik*, 1925, **32**, 186—189).—Examination of existing experimental results shows that there is an empirical relation $1{\cdot}3\phi-\epsilon=\text{constant}=\text{approx. } 5$, where ϕ is the energy needed to enable an electron to escape from a metal and ϵ the normal potential of the metal. E. B. L.

Dielectric Constants of some Liquids and their Variation with Temperature. I. G. E. Bell and F. Y. Poynton (*Phil. Mag.*, 1925, [vi], **49**, 1065—1072).—Details are given of a method of measuring the dielectric constants of liquids by means of two valve-maintained oscillating circuits, tuned so that the heterodyne note beats slowly with a third valve-maintained circuit oscillating at audible frequency. Measurements were made of the dielectric constants of castor oil, olive oil, and linseed oil between 18° and 185°. The linear relationship between dielectric constant and temperature is expressed by the formula $K_\theta=K_{20}\,[1-(\theta-20)\alpha]$, where $\alpha=0{\cdot}0015$, $0{\cdot}0008$, $0{\cdot}0009$ for the oils in the above order. The following values, nearest to 20°, were obtained. Castor oil, $K_{17{\cdot}5}=4{\cdot}86$, olive oil $K_{18{\cdot}5}=3{\cdot}21$, linseed oil $K_{19}=3{\cdot}24$.

F. G. T.

Proposed Test of the Space Quantisation of Atoms in a Magnetic Field. A. E. Ruark and G. Breit (*Phil. Mag.*, 1925, [vi], **49**, 504—508).—If properties of matter in bulk may be used as a criterion, the dielectric constant would be the most feasible property for exhibiting an anisotropic nature with respect to the field. The essential condition is that space quantisation shall predominate over a random orientation during an appreciable portion of the time between two collisions. It is shown that this condition is fulfilled with fields of reasonable strength. The feasibility of obtaining anisotropic electric effects by the action of the magnetic field is discussed from the point of view of the reciprocity of action between the two fields. The method of heterogeneous beats is suggested for revealing variations in the dielectric constant.

C. W. B.

Molecular Volumes of Crystals. F. A. Henglein (*Z. Elektrochem.*, 1924, **30**, 5—12).—The molecular volumes in the solid crystalline state can be expressed by an empirical linear equation of

the type, mol. vol.$=x'y'+c'$, provided that the salts have a similar crystalline structure, *e.g.*, halides of the alkali metals. Numerous examples are given to show the validity of the law. H. T.

Quantum Theory of Optical Phenomena. J. C. SLATER (*Physical Rev.*, 1925, [ii], **25**, 395—428).

Molecular Refraction of Natural and of Methyl-rubber. A. D. MACALLUM and G. S. WHITBY (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 191—193).—The average of several determinations of n_D^{20}, d_4^{20}, and $[R_L]_D^{20}$ for purified rubber are 1·5219, 0·9237, and 22·46, respectively. Corresponding values for smoked sheet are 1·5208, 0·9217, and 22·44. The results are in accord with the view that, in the polymerisation of isoprene to caoutchouc only one double bond is lost per C_5H_8, the absence of exaltation indicating that there is no conjugation between double bonds in the polymeride. The following quantities were determined for synthetic "methyl-rubber" from dimethylbutadiene; n_D^{20} 1·525, d_4^{20} 0·9292, $[R_L]_D^{20}$ 27·03.

J. S. C.

Classical Dispersion Formula for Monatomic Gases and Vapours. K. F. HERZFELD and K. L. WOLF (*Ann. Physik*, 1925, [iv], **76**, 567—570).—Corrected tables and data for the paper of the above title (see this vol., ii, 182). F. G. T.

Dispersion of Carbon Disulphide in the Ultra-violet. G. BRUHAT and M. PAUTHENIER (*Compt. rend.*, 1925, **180**, 1018—1020; cf. A., 1924, ii, 713).—Determinations of the refractive index of carbon disulphide have been made throughout the visible spectrum and as far as 2537 Å. in the ultra-violet, with special attention to the neighbourhood of the absorption band at 3220 Å. The results are compared with the values of absorption previously recorded.

G. M. B.

Magnetic Rotatory Dispersion of Certain Paramagnetic Solutions. R. W. ROBERTS (*Phil. Mag.*, 1925, [vi], **49**, 397—422).—Aqueous solutions of certain cobalt and nickel salts show anomalous rotatory dispersion at their principal absorption bands. This is much stronger for cobalt than for nickel solutions. The high-frequency electrons in cobalt solutions, as well as in potassium ferricyanide, give rise to the negative rotation displayed by these salts. The rotatory dispersion in the solutions investigated may be calculated from the formula: $\delta\lambda^2/n(n^2+2)=x\delta_\omega\lambda^2/n_\omega(n_\omega^2+2)+\Sigma a_s/(1-\lambda^{-2}\lambda_s^2)$, derived from Drude's molecular current hypothesis, by taking into account the electric polarisation of the liquids.

C. W. B.

Structure of Molecules in Relation to their Optical Anisotropy. I. K. R. RAMANATHAN (*Proc. Roy. Soc.*, 1925, **A**, **107**, 684—693).—The view is maintained that the optical anisotropy of molecules is due to the mutual influence of the electric doublets induced by the incident light in the constituent atoms (cf. Raman, A., 1924, ii, 512). It is assumed that each atom by itself is isotropic. Diatomic and triatomic molecules are considered mathematically,

and the expressions $(1+\frac{1}{2}R_0k)/(1-R_0k)$ and $(2R_1+R_2+31R_1R_2k/8)/(1-R_1k/8-2R_1R_2k^2).(1+R_1k/16-\frac{1}{2}R_1R_2k^2)/(2R_1+R_2-31R_1R_2k/16)$ (where R_0, R_1, and R_2 are atomic refractivities) are deduced for the optical anisotropy in the two cases. From the known refractivity and polarisation of the scattered light in hydrogen, nitrogen, and oxygen, the atomic refractivities and distances between the "optical centres" in the molecules are calculated. These distances are 1·37 Å., 1·90 Å., and 1·46 Å. for hydrogen, nitrogen, and oxygen, respectively, and are consistent with the values of the molecular radius calculated from the kinetic theory. For the triatomic gases, nitrous oxide, carbon dioxide, and carbon disulphide, the imperfection of polarisation of the transversely scattered light is found by calculation to be 14·1%, 10·8%, and 12·5% respectively, these values being in satisfactory agreement with experiment. L. L. B.

Specific Rotation of Invert-sugar and the Clerget Divisor. F. W. Zerban (*J. Amer. Chem. Soc.*, 1925, **47**, 1104—1111).—From a critical survey of recorded data on the specific rotation of invert-sugar, the following equation is derived, using Vosburgh's data for lævulose (A., 1920, ii, 575), Tollens' for dextrose (A., 1885, 40), and Vosburgh's rule for the rotation of sugar mixtures: $[\alpha]_D^{20}$ of invert-sugar $=-(19{\cdot}415+0{\cdot}07065c-0{\cdot}00054c^2)$. The temperature correction formula is $[\alpha]_D^t=[\alpha]_D^{20}+(0{\cdot}283+0{\cdot}0014c)(t-20)$. A value of 32·95 is obtained from the first equation for the negative constituent of the Clerget divisor, using the general factor 0·34657. A redetermination of the latter gave 0·34615, from which the Clerget constant becomes 32·09. F. G. W.

Configuration of Polyatomic Polar Molecules. II. Molecules consisting of a Negative Ion and Hydrogen Nuclei. F. Hund (*Z. Physik*, 1925, **32**, 1—18; cf. *ibid.*, 1925, **31**, 81).—The variation of potential with distance is calculated from the position of the bands in the spectra of the halogen hydrides and the course of the potential for the ions O″, S″, Se″, and N‴ deduced. The following values are obtained for the shape, size, and energy of the molecules and ions: distance apart of unlike ions $\times 10^8$ cm., HO' 1·0, H_2O 1·03, $H_3O^{\cdot}$ 1·05, HS' 1·5, H_2S 1·5, HCl 1·27, $H_2Cl^{\cdot}$ 1·3, $H_3Cl^{\cdot\cdot}$ 1·3; distance apart of like ions $\times 10^8$ cm., H_2O 1·09, $H_3O^{\cdot}$ 1·11, H_2S 1·6, $H_2Cl^{\cdot}$ 1·4, $H_3Cl^{\cdot\cdot}$ 1·4; energy in kg.-cal. for the complete separation of one hydrogen nucleus from HO' 550, H_2O 370, $H_3O^{\cdot}$ 180, HS' 430, H_2S 310, HCl 316, $H_2Cl^{\cdot}$ 180. E. B. L.

Theory of Metals. J. Frenkel (*Z. Physik*, 1924, **29**, 214—240).—By treating the "wandering" of valency electrons which takes place during the condensation of metal vapours as a self-diffusion process, and by evaluating approximately the corresponding diffusion constant, an analysis is advanced leading to an expression for the mobility of the valency electrons and to the electrical conductivity of a metal. The values for the latter quantity and for its temperature variation agree in order of magnitude with those obtained experimentally. In a similar way, an expression is

obtained for the thermal conductivity which is in agreement with Wiedemann and Franz's analysis; it fails, however, to elucidate the mechanism of the process. The analysis also lends itself to a determination of the tensile strength, compressibility, and grating energy. R. W. L.

Valency of Ruthenium. Ruthenium Tetroxide and Ruthenium Halides. O. Ruff and E. Vidic (*Z. anorg. Chem.*, 1924, **136**, 49—61).—Ruthenium tetroxide may be prepared in a very pure form by distilling at 40—50° in a current of air an acidified solution of the mass obtained by fusing in a silver crucible a mixture of 1 part of ruthenium powder, 2 parts of potassium permanganate, and 20 parts of potassium hydroxide. The tetroxide condenses in a receiver, cooled with ice, in the form of long, golden-yellow needles which are readily soluble in water. The solution is unaffected by addition of hydrofluoric acid, but is reduced with the evolution of the halogen when warmed with the other halogen acids; with dilute hydrochloric acid, the tetroxide is reduced rapidly on warming to the tetrachloride, which slowly decomposes into trichloride and chloride, especially when boiled to expel the chlorine as it forms. A similar reaction occurs with hydrobromic acid, but the second stage of the reduction (to tribromide) is much more rapid. With hydriodic acid, black, insoluble ruthenium tri-iodide is immediately formed. All derivatives of ter- and quadri-valent ruthenium are converted into the sexavalent form by potassium permanganate in alkaline solution; in sulphuric acid solutions, permanganate oxidises ruthenium compounds to the tetroxide. A. R. P.

Ruthenium Tetroxide. III. Valency of Ruthenium in the Tetroxide. F. Krauss and H. Kükenthal (*Z. anorg. Chem.*, 1924, **136**, 62—74; cf. A., 1922, ii, 75).—When ruthenium tetroxide is treated with hydrochloric acid and potassium iodide the iodine set free corresponds with a diminution of 5 in the valency of the tetroxide. From the reduced solution, many salts of the type M'_2RuCl_5 were prepared, as well as ruthenium trihydroxide and ruthenium trichloride, thus showing that the metal is tervalent in these compounds and therefore octavalent in the tetroxide. Solutions of potassium ruthenate obtained by fusion liberate three equivalents of iodine from acid iodide solutions, and hence ruthenium is sexavalent in this compound. Pure ruthenium trihydroxide is prepared by heating at 120° in a nitrogen atmosphere the black precipitate obtained by addition of alkalis to solutions containing the trichloride. The latter has been prepared in a pure state for the first time by the interaction of dry ruthenium tetroxide vapour and dry hydrogen chloride at 105—115°, as well as by exposing the pure trihydroxide to dry hydrogen chloride at 105°. Thus formed, the trichloride is a dark violet-brown, deliquescent mass having a metallic lustre. A. R. P.

Higher Valencies of Onium Compounds. W. Tschelinzev (*Bull. Soc. chim.*, 1925, [iv], **37**, 176—181).—The heats of formation of ammonium, oxonium, and thionium complexes (with EtO·MgI)

were determined. They are in the order given. Successive additions (up to a maximum of three) have lower heats of formation. Substituted derivatives were also studied. The order is probably determined by the basicity of the central atom. L. J. H.

Strengths of the Higher Valencies and their Significance for Assimilation, Catalysis, and other Chemical Processes. W. TSCHELINZEV (*Bull. Soc. chim.*, 1925, [iv], **37**, 181—187).—The ease with which a group may be replaced parallels the heat of formation; this may be applied to the higher valencies of onium compounds. The tendency to form onium compounds progressively diminishes in the order: aldehydes, ketones, esters, acids, alcohols, ethers. These higher valencies may play an important part in assimilation, catalysis, and other chemical processes. A scheme representing the formation of hexoic acid from carbon dioxide and water by the successive formation of oxonium compounds, rearrangement, loss of water, and oxidation is put forward. L. J. H.

Chemical Affinity and Electronic Structure. I. The Non-polar Band. B. H. WILSDON (*Phil. Mag.*, 1925, [vi], **49**, 354—369).—A quantitative theory to explain the facts of chemical affinity built up on the basis of the constitution of the atom. In order that the free valency orbits of uncombined atoms shall be capable of forming a chemical bond, they must have identical or harmonically related frequencies. An expression is developed by which heats of formation of non-polar compounds can be calculated, using only theoretical values for the frequencies of the atoms in their ground orbits, and without using arbitrary quantum numbers. An insight into the geometrical structure of the molecule is afforded by the theory, and its application to the structural relations of carbon compounds is considered. C. W. B.

Chemical Affinity and Electronic Structure. II. The Polar Link. B. H. WILSDON (*Phil. Mag.*, 1925, [vi], **49**, 900—911; cf. preceding abstract).—The necessary condition for a stable molecular combination is that the frequencies of the valency orbits concerned shall be synchronised. If ν_1 and ν_2 represent the frequencies of the valency electrons of the combining atoms in their ground orbits, $h(\nu_1—\nu_2)$ represents a quantum of energy which is termed the available energy of accommodation. This energy is supposed to be responsible for the changes involved in the transfer of a valency electron or electrons from the positive to the negative atom, and for the potential energy of valency electrons and " trunk " in the field of the stripped positive ion. The change in frequency of the valency orbits produced under these conditions, multiplied by the unit of action, must represent the change in kinetic energy. The heat of reaction, which must equal the total energy change, may be calculated if the ratio of the kinetic to the total energy in the field of the molecule is known. This latter ratio has been calculated by Bohr. An analysis of the potential energy change resulting from molecular combination shows that two types of quantum jump should be possible in that process. In the first, the equatorial quantum

number remains unaltered; in the second, it increases by one unit. On this basis, two distinct types of polar compound may be expected. Experimental results support this, the distinction arranging elements into classes which correspond with the A and B sub-groups of the periodic table. A comparison of the experimental heats of formation of the alkali halides, and those of copper, silver, and mercury, with the values calculated by the above theory gives good agreement except for hydrogen fluoride and silver fluoride. F. G. T.

Electrical Meaning of Chemical Affinity. M. BORN (*Z. Elektrochem.*, 1924, **30**, 383—386).—A review of recent work and theories. A. R. P.

Relative Internal Friction. W. HERZ and A. WEGNER (*Z. anorg. Chem.*, 1925, **144**, 85—86).—Whilst absolute internal friction always diminishes with rising temperature, the coefficient relative to that of water may rise or fall. With formic acid and ethyl and allyl alcohols, the relative value first rises to a maximum and then falls. S. I. L.

Simple *X*-Ray Apparatus for the Examination of Powdered Crystals by the Seemann–Bohlin Method, giving Higher Resolution with Shorter Exposure. H. LANGE (*Ann. Physik*, 1925, [iv], **76**, 455—476).—Full details are given of the construction of a steel *X*-ray tube embodying low cost, high resolution, low power consumption, and simplicity of manipulation. Water-cooled electrodes are insulated by molybdenum glass from a water-cooled steel tube which carries an aluminium foil window, the junctions being secured by mercury seals. In conjunction with a camera chamber described, an accuracy of 0·05% is attained in lattice measurements, whilst the exposure for a 45-kilovolt tube potential is reduced to 90—100 milliamp.-minutes. In test measurements with this apparatus, the value 4·036±0·002 Å. was obtained for the aluminium lattice constant, and for the difference in the K_α doublet of copper, 0·00385±0·00005 Å. F. G. T.

***X*-Ray Spectroscopic Examination of some Alloys by the Seemann–Bohlin Method.** H. LANGE (*Ann. Physik*, 1925, [iv], **76**, 476—492).—Errors in measurements by the apparatus previously described (cf. preceding abstract) are discussed. These arise from errors in plate reading, the influence of the breadth of the slit on that of the lines, and from the existence of inhomogeneity, or predominance of crystals of a particular composition, in a mixed crystal specimen. Diffuse lines arising from such inhomogeneity may be improved by heat treatment of the specimen. The lattice constants were determined for various alloys in the systems copper–nickel and copper–gold. Kirchner's results (*ibid.*, 1922, **69**, 59) for the latter system are confirmed. Except for slight deviations attributable to the inhomogeneity of the alloy specimens, the lattice constants in each case are linear functions of the molar percentage composition of the alloys, in agreement with Vegard's rule.

Measurements were made of the lattice constants of duralumin during the process of hardening. This phenomenon is shown to

be accompanied by the development of a second lattice in the crystal, with a constant slightly greater than the first. This behaviour is in agreement with the theory of Konno (*Sci. Rep. Tôhoku Imp. Univ.*, 1922, **11**, 269) that the hardening is due to the reciprocal action of the compounds Mg_2Si and Al_2Cu with the aluminium. According to this theory, the hardening accompanies the partial separation of Mg_2Si from a solution of Al_2Cu in aluminium. On the other hand, the theory of Fraenkel and Scheuer (*Naturwiss.*, 1924, **13**, 145) does not account for the appearance of this second lattice. F. G. T.

Application of *X*-Ray Diffraction to the Determination of the Transformation Temperature of Thallium. G. ASAHARA (*Sci. Papers, Inst. Phys. Chem. Res.*, 1924, **2**, 125—137).—Earlier work (Nishikawa and Asahara, *Physical Rev.*, 1920, [ii], **15**, 38) showed that the transformation of α- into β-thallium was accompanied by an abrupt change in the *X*-ray pattern. The transformation temperature measured in this way had the mean value 227°. Various investigators have reported values between 225° and 238°, based on thermal analysis. A new method has been devised whereby a series of photographs is obtained as the metal is heated through the transformation temperature and cooled. The value 231·9° was obtained on heating and 230·7° on cooling. The metal used contained 99·74% Tl (0·11% Al, 0·14% Ca, 0·13% Mg), and 231·3° is given as the transformation temperature. R. A. M.

Focussing Method in Crystal Powder Analysis by *X*-Rays. J. BRENTANO (*Proc. Physical Soc.*, 1925, **37**, 184—193).—The locus of all powder particles from which *X*-rays from a point source are reflected to a definite point is a toroid surface. Since in practice a plane surface coated with powder is used, sharply-defined spectral lines can only be obtained within a small angular region, such that $\sin\alpha/\sin\beta=a/b$, where a is the distance source to powder, b the distance powder to film, and α and β are the glancing angles of incidence and emergence with respect to the powdered surface. The extreme angular broadening ω_2 of any spectral line due to the substitution of a flat plane for a toroid is expressed by $\omega_2=0{\cdot}25\epsilon^2\cot\beta$, where ϵ is the angular width of the incident beam. At the same time, since for a given position of the powdered surface only one point on the film corresponds with correct definition, the lines will broaden unless the film is screened off save for this one point. The angular broadening thus effected is given by $\omega_1=[a/2(a+b)]\epsilon\eta\cot\beta$, where η is the angular stretch of film exposed. A spectrometer designed to minimise these errors and a hot-cathode *X*-ray tube giving only the $K\alpha$ and $K\alpha'$ copper rays are described. The (100) spacing of nickel oxide is thus found to be 4·172 Å. W. A. C.

Theory of the Width of the Modified Spectrum Lines in the Compton Effect. G. E. M. JAUNCEY (*Phil. Mag.*, 1925, [vi], **49**, 427—433).—The increase in width of modified spectrum lines, in excess of that accounted for by the change in direction of the rays, is given by the formula $\delta\lambda^\phi=4\lambda_0\sin\phi/2\sqrt{2h/mc\lambda_s}$. Calculated and observed values agree for the scattering of molybdenum $K\alpha$ rays

by the L electrons of carbon. For aluminium the calculated values are too great. The formula only seems applicable for small values of the binding energy of the electron. C. W. B.

Structure of Solid Nitrous Oxide and Carbon Dioxide. J. DE SMEDT and W. M. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 839—846).—A method has been worked out for obtaining the X-ray spectra of solidified gases at low temperatures, by means of which the structures of nitrous oxide and carbon dioxide are compared. Nitrous oxide crystallises cubically (a= 5·72 Å.), the distance between the neighbouring nitrogen and oxygen atoms being 1·15 Å. Assuming 4 mols. in the unit cube, the calculated density is 1·55, whereas at the m. p. the liquid has d 1·299. Carbon dioxide also crystallises in the cubic system, with (a=5·63 Å.), and the distance between a carbon and an oxygen atom is 1·05 Å.; the calculated d is 1·63, which agrees with the value found by Dewar at the temperature of liquid air. L. L. B.

Crystal Structure of Magnesium Fluoride. H. E. BUCKLEY and W. S. VERNON (*Phil. Mag.*, 1925, [vi], **49**, 945—951).—The substance was examined in powdered form by the copper K_α radiation. It crystallises on a structure possessing the symmetry D_{4h}^{14}. The unit cell is a tetragonal prism with a=4·660 Å., c= 3·078 Å., and $a:c$=1 : 0·660. The distance of closest approach of magnesium to fluorine is 2·07 Å., which agrees with the value 2·08 Å. calculated from Bragg's radii. F. G. T.

Crystal Structure of Mercuric Sulphide. II. N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 847—850).—The striking agreement between the Debye–Scherrer photograms of the cubical (black) and trigonal (red) mercuric sulphide is caused by the complete equality of their dimensions in the octahedral or basis plane. The difference between the two modifications consists only in the manner in which these planes are piled up, at least as regards the arrangement of the centres of the particles. None of the different modifications, including β′-HgS, mentioned by Allen and Crenshaw, were found by X-ray analysis to contain crystals different from those of the ordinary black and red forms. L. L. B.

Two Crystal Forms of Zinc Hydroxide. R. FRICKE (*Z. anorg. Chem.*, 1924, **136**, 48).—The thin needles of zinc hydroxide prepared by Goudriaan's method (A., 1920, ii, 113) from zinc sulphate are metastable; when kept in contact with the mother-liquor for some time, they slowly change into the short, thick, apparently rhombic crystals described by Fricke and Ahrndts (A., 1924, ii, 681). A. R. P.

Orthorhombic Space Group Criteria and their Application to Aragonite. R. W. G. WYCKOFF (*Amer. J. Sci.*, 1925, [v], **9**, 145—175).—Spectrum and Laue photographic data for aragonite are recorded. It is shown that the space group must be $2Di$–16 if

aragonite possesses holohedral symmetry. The nature of this group is briefly discussed. S. K. T.

Crystal Structure of Barite. L. PAULING and P. H. EMMETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1026—1030).—The crystal unit of orthorhombic barite contains 4 mols. and has $d_{100}=8{\cdot}846$ Å., $d_{010}=5{\cdot}430$ Å., and $d_{001}=7{\cdot}10$ Å. The crystal belongs to the space group V_h^{16}; its structure is based on the simple orthorhombic lattice Γ_o. The two parameters determining the exact positions of the barium atoms were not evaluated. S. K. T.

Space Group of Barite ($BaSO_4$). R. W. G. WYCKOFF and H. E. MERWIN (*Amer. J. Sci.*, 1925, [v], **9**, 286—295).—Laue and spectrum photographs were taken with plates of barytes cut parallel to (010) and (001). For the spectrum photographs the plate was rotated to and fro through 25° about a crystallographic axis. The results agree with a unit cell containing 4 mols. of $BaSO_4$ and of dimensions $a=8{\cdot}89$, $b=5{\cdot}45$, $c=7{\cdot}17$ Å., corresponding with the axial ratio $a:b:c=1{\cdot}633:1:1{\cdot}316$. The symmetry is orthorhombic holohedral, the lattice Γ_o, and the space-group $2Di$–16. L. J. S.

Space Group of Diopside. R. W. G. WYCKOFF and H. E. MERWIN (*Amer. J. Sci.*, 1925, [v], **9**, 379—394).—From the X-ray spectra given by the rotating crystal and the Laue photographs, the dimensions of the unit cell of diopside containing 4 mols. $CaMg(SiO_3)_2$ are deduced as $X=5{\cdot}24$, $Y=9{\cdot}71$, $Z=8{\cdot}89$ Å. (Here the usual orientation is changed; $X=-c$, $Y=a$, $Z=b$; $\beta=74°\ 10'$.) The lattice is Γ'_m and the space-group $2Ci$–6. L. J. S.

Influence of X-Rays on the Crystallisation of Bismuth. E. ADINOLFI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 382—386).—X-Rays exert on the arrangement of bismuth during solidification an effect similar to, but distinct from, a debasing effect, and varying in nature with the hardness of the rays used. T. H. P.

Calculation with Pole-systems: Crystal Groups and Crystal Dynamics. E. WAELSCH (*Ann. Physik*, 1925, [iv], **76**, 534—560).—Mathematical. F. G. T.

Connexion between Thermo-electric Power and Space Lattice for Pure Iron. A. GOETZ (*Physikal. Z.*, 1925, **26**, 260—264; cf. this vol., ii, 187).—The change from β- to γ-iron at the A3 point is accompanied by a change from the space-centred cubic lattice to the surface-centred cube, together with a great decrease in dE/dT (Richardson equation). This ratio increases in the γ to δ transformation. The space-centred lattice is thermo-electrically positive with respect to the other form. E is proportional to the capacity of the negative component for absorbing electrons, which itself depends on the crystal structure. In spite of its greater density, γ-iron has a smaller capacity for holding electrons than the β-modification. The author considers the thermo-electric processes to be governed by the atomic force-fields. Each atom has its own sphere of force, and between atoms there is a free space

where these are small. The free space determines the power of retaining electrons and the thermo-electric properties.

It is assumed that the radius of the force-field is half the smallest distance between atoms in the lattice. This leads to the conclusion that this distance does not change at the transformation point. The assumption is justified within the limits of error by experiment on the thermo-electric power near the transformation point. Moreover, the behaviour of iron under dilatation and compression, together with the trifling change in the temperature–resistance curve at this point, can all be harmonised with the conception. The iron crystal lattice which is capable (in the thermo-electric sense) of retaining most electrons, possesses (in the sense of the Richardson equation) the largest number of free electrons. R. A. M.

Physical Properties of Nacreous Sulphur. H. WHITAKER (*J. Physical Chem.*, 1925, **29**, 399—405).—When sulphur condenses on a glass plate in droplets it is found that these droplets gradually assume various crystalline structures. Nacreous sulphur forms six-sided plates having the three pairs of opposite sides parallel. The colours shown by these plates are due to interference. The plates gradually disintegrate on ageing, probably into the more stable octahedral variety. M. B. D.

Structure of Quenched Carbon Steels. B. D. ENLUND (*J. Iron and Steel Inst.*, May, 1925 [Advance proof]; 10 pages).—The structure of quenched carbon steels as ascertained from measurement of changes in electrical resistivity and specific volume with annealing temperature is described. The results confirm the view that martensite is transformed into troostite at 100—200° and also that austenite, retained after quenching, is decomposed at about 260°. In this way, it may be shown that even low-carbon steels contain some untransformed γ-iron after quenching. [Cf. *B.*, 1925, 404.] M. E. N.

Artificial Magnetic Anisotropy of Nickel. Phenomena of Large Discontinuities. R. FORRER (*Compt. rend.*, 1925, **180**, 1253—1255).—Nickel can be obtained in a state showing new magnetic properties. Barkhausen amplified the currents induced by progressive magnetisation of a substance and found discontinuities. Van der Pol found 6500 discontinuities using a sample of iron, and 5000 with ferro-nickel. He further found that discontinuities could be observed with nickel even without amplification. This is confirmed for ordinary nickel wire, but if the same wire is drawn out the magnetisation discontinuities disappear. If this drawn specimen is wound round a cylinder, the phenomenon reappears in an intensified form. The cycles have been studied by means of a magnetometer under different field limits. With nickel stretched almost to breaking point, the cycle is wide and regular. When the same wire is wound round a cylinder, the results indicate sudden irregularities comparable in magnitude with the total magnetisation. This sudden increase in magnetisation occurs in spite of the gradual

decrease in the field under the experimental conditions. The property persists over long periods of time. Heating for a few seconds above 1000° causes the cycles observed to revert to those ordinarily found. Heating at 500° does not effect the reversion, whilst heating at temperatures between 500° and 700° causes progressive diminution in the discontinuities. About 720° the crystalline lattice probably undergoes rearrangement. R. A. M.

Temper-brittleness of Steels: Susceptibility to Temper-brittleness in Relation of Chemical Composition. R. H. Greaves and J. A. Jones (*J. Iron and Steel Inst.*, May, 1925 [Advance proof]; 25 pages).—Phosphorus and manganese increase the susceptibility to a marked extent, silicon and vanadium have only a slight effect, and tungsten has practically none. Molybdenum has a very pronounced reducing effect. Temper-brittleness in certain steels may be overcome by cooling in water, or preferably in oil, or by cooling in water to 400° and then air-cooling. [Cf. *B.*, 1925, 405.] M. E. N.

Anhysteretic Magnetostrictive Effects in Iron, Nickel, and Cobalt. P. McCorkle (*Physical Rev.*, 1925, [ii], **25**, 541—549).

Effect of a Superposed Alternating Field on Apparent Magnetic Permeability and Hysteresis Loss. T. Spooner (*Physical Rev.*, 1925, [ii], **25**, 527—540).

Modified Reflexion in Metallography. J. Czochralski (*Z. anorg. Chem.*, 1925, **144**, 131—141).—The reflexion of light from the etched surface of a metal is governed by the degree of attack of the etching agent, which varies with the inclination of the exposed crystal faces to the crystal axes. The directions of maximum reflexion, which may be determined experimentally, suffice to fix the orientation of the crystal, and hence are of assistance in the examination of the structure of a metal or alloy. Methods of arriving at these directions are described. S. I. L.

Thermal Expansion of Binary Mixed Crystal Systems. C. H. Johansson (*Ann. Physik*, 1925, [iv], **76**, 445—454).—Measurements have been made by the double-mirror dilatometer (this vol., ii, 27) of the expansion coefficients at a series of temperatures between 35° and −180° of the systems silver–gold, copper–nickel, gold–palladium, silver–palladium, copper–palladium, and copper–gold. The coefficients for all mixtures are less than those calculated by the simple mixture rule. The deviations are attributed to distortion of the atomic lattices owing to differences of atomic volume and of atomic force-field between the pairs of components. The magnitude of the maximum deviation runs parallel with the difference of atomic volume of the components. Since the well-developed peaks which characterise the diagrams of the electrical properties of the systems copper–palladium and copper–silver do not occur in the above curves, these properties are not related.

F. G. T.

Plastic Extension and Fracture of Aluminium Crystals. G. I. TAYLOR and C. F. ELAM (*Proc. Roy. Soc.*, 1925, **A**, **108**, 28—51).—A physical and mathematical paper in which the distortion and fracture of crystals are considered and a theory of fracture is outlined. J. S. C.

Martensite and Troostite. J. H. WHEATLEY (*J. Iron and Steel Inst.*, May, 1925 [Advance proof]; 24 pages).—A consideration of the origin of the different forms of martensite and troostite and their behaviour on tempering as ascertained from a microscopical examination of the quenched specimens. The different types of martensite and troostite are described in detail and the formation of martensite is discussed. [Cf. *B.*, 1925, 404.] M. E. N.

Increase in Strength of Single Crystals by Alloying and Cold-drawing. P. ROSBAUD and E. SCHMID (*Z. Physik*, 1925, **32**, 197—225).—The rigidity of metallic crystals is expressed quantitatively by the shearing force in the plane of slip which is necessary to produce plastic change of shape. The critical value is independent of such force as may be perpendicular to the plane; for zinc containing 0·03% of cadmium at the ordinary temperature it is 94 g./mm.^{2} Single crystals of zinc containing 0·53% of cadmium show 9 times the strength, with 1·03% of cadmium 12·2 times; extrapolating for pure zinc the value 40 g./mm.^{2} is obtained. Zinc containing more than 0·1% of tin solidifies with inclusions of zinc–tin eutectic; with 0·5% of this eutectic the strength is 3 times that of the crystal free from tin. The increase of strength produced by cold-drawing the zinc–cadmium crystals rises with increase of the cadmium content. Photomicrographs are reproduced. E. B. L.

Metal Crystals. III. Thermal Expansion of Zinc and Cadmium. E. GRÜNEISEN and E. GOENS (*Z. Physik*, 1924, **29**, 141—156).—Henning's expansion apparatus has been modified for determinations at temperatures in the neighbourhood of that of liquid hydrogen. The mean coefficients of expansion parallel to and perpendicular to the hexagonal axis have been determined over the range +100° to −253° for single crystals of cadmium and zinc having axes approximately perpendicular to the hexagonal axis. The values observed for the two directions are not identical; their temperature variation is extraordinary and has considerable bearing on the theory of the solid state. An analysis is developed on the basis of the theories of Born and Debye which leads to values of the expansion coefficients agreeing well with the values obtained experimentally. R. W. L.

Heat of Formation of Calcium Hypochlorite. B. NEUMANN and G. MÜLLER (*Z. angew. Chem.*, 1925, **38**, 193—195).—The heat evolved in the chlorination of calcium hydroxide moistened with 4% excess water is 100·1 cal. per g. of lime, or 247·5 cal. per g. of chlorine. More or less water yields an inferior product. Perfectly dry chlorine and lime will not react. S. K. T.

X-Ray Study of Fatty Acids and Dibasic Acids. J. J. TRILLAT (*Compt. rend.*, 1925, **180**, 1329—1332; cf. this vol., ii, 195).—The orientation of fatty acid molecules on glass is very regular if a small quantity of alcoholic solution is allowed to evaporate. The invisible films give clear *X*-ray spectra corresponding with the length of the side-chain, and diffuse effects due to thicker, uneven layers of crystals are eliminated. The maximum distances for the fatty acids are: stearic 39·1 Å., palmitic 35·13, myristic, 31·14, lauric 27·24, decoic 23·30, hexoic 19·30. Thus $\Delta\lambda$ for $C_{n+2}-C_n$ is 3·94 (mean). A supposed C_{17} acid gave two series corresponding with a mixture of stearic (C_{18}) and palmitic (C_{16}) acids, an interesting analytical application. Thin layers of fused dibasic acids were prepared on glass. The spectra, although feeble, are similar. Succinic acid, maximum distance 4·5 Å.; adipic, 7·0; suberic, 9·3; sebacic, 11·4; $\Delta\lambda$ for $C_{n+2}-C_n=2·3$ Å. Two acids with odd numbers of carbon atoms were examined, pimelic (C_7) and azelaic (C_9), with distances of 7·6 and 9·6 Å., respectively, $\Delta\lambda=2·0$. The length of side-chain for an acid with an odd number of carbon atoms is not midway between the two acids with even numbers on either side. Neither are the melting points midway. Thus the CH_2 groups in a chain are not evenly spaced. The distance between C_{2n+1} and C_{2n} is smaller than that between C_{2n} and C_{2n-1}. R. A. M.

Tensimetric Determination of Molecular Weight with Liquid Ammonia as Solvent. A. STOCK and E. POHLAND (*Ber.*, 1925, **58**, [*B*], 657—661).—The apparatus consists of two tubes one of which contains liquid ammonia, whereas the other is provided with an electro-magnetically operated stirrer and contains the solution of the substance under investigation in liquid ammonia. The tubes are connected with the two arms of a differential mercury gauge and, by means of mercury valves, to the vacuum apparatus. The molecular weight (M) is calculated from the formula $M=17Sp/L\Delta p$, in which S and L are the weights of solute and solvent, p and Δp the vapour tension of the solvent and the difference between the vapour tensions of solvent and solution, respectively.

The additive compound of diborane and ammonia (cf. A., 1923, ii, 408) contains the simple molecule B_2H_6 in the solution. H. W.

Variation of the Molecular Condensation of Tin with Temperature. A. JOUNIAUX (*Bull. Soc. chim.*, 1925, [iv], **37**, 67—84).—The molecular weight of tin is calculated for various temperatures, from its boiling point, heat of vaporisation, and Trouton's rule; from cryoscopic measurements in various metals and in iodine; from vapour-pressure measurements of its amalgams; and from surface tension measurements of the liquid. The molecule is approximately triatomic at 100°, the mean molecular weight decreases linearly with temperature until the molecules are monatomic at about 620° and then remains constant until the b. p., 2270°. Some anomalous cryoscopic results are considered. L. J. H.

Explosion Potential in Carbon Dioxide at High Pressures. C. E. GUYE, P. MERCIER, and J.-J. WEIGLÉ (*Compt. rend.*, 1925, **180**, 1251—1253).—Summary of data. R. A. M.

Thomson Effect in Copper, Iron, and Carbon Steels. J. YOUNG (*Proc. Physical Soc.*, 1925, **27**, 145—157).—Measurements over a range of 40—300° in annealed wires show that $(\sigma_{Fe}-\sigma_{Cu})/T$, where σ is the Thomson effect coefficient, and d^2E/dT, where E is the thermo-electric difference of potential, when respectively plotted against temperature give parallel curves (theory requiring congruence) both of which have a minimum at 180°. The Thomson effect in steel wires increases with their carbon content and passes through a minimum value near 250°. Different quantitative results are obtained according as the current is sent along or against the temperature gradient; this is ascribed to structural asymmetry due to the direction in which the wire was drawn through the die. W. A. C.

Allotropy of Mecuric Iodide. S. C. BOKHORST and H. VAN DER ZEE (*Bull. Soc. chim.*, 1925, [iv], **37**, 153—157).—Polemical against Damiens (*ibid.*, 1924, [iv], **35**, 87). L. J. H.

Allotropy of Mecuric Iodide. A. DAMIENS (*Bull. Soc. chim.*, 1925, [iv], **37**, 157—162).—Polemical against Bokhorst and van der Zee (cf. preceding abstract). L. J. H.

Calorimetric Researches. VIII. The Paraffin Oil Method: an Aid in the Determination of the Heats of Combustion of Difficultly Combustible and Hygroscopic Substances. P. E. VERKADE, J. COOPS, and H. HARTMAN (*Rec. trav. chim.*, 1925, **44**, 206—216).—The technique of the combustion of organic substances in the calorimetric bomb is described in detail and discussed. Methods of ignition with or without such auxiliary substances as naphthalene are sometimes unsatisfactory, but success is always attained when a porous pellet of the substance is drenched with paraffin oil, and the results are accurate in spite of the use of a relatively large proportion of auxiliary substance of high heat of combustion. Comparative determinations are recorded by this and other methods for a number of compounds. The difficult cases which have been successfully dealt with include substances of low heat of combustion, substances of high melting point, substances which form voluminous masses of crystals, and hygroscopic substances. The following heats of combustion are recorded: *i*-tartaric acid 1845·8, *d*-*N*-benzyltartrimide 5602, tetraethylsuccinic anhydride 7639, *s*.-*N*-diethyl-*i*-tartramide 5219·5, *trans*-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dibenzoate 7521·5, acetone compound of hydrobenzoin 8434, anhydrous oxalic acid 678·0, ammonium hydrogen *d*-tartrate 2050·6, *iso*phthalic acid 4629·5, *d*-*N*-phenyltartrimide 5245·7, *s*.-diphenylsuccinic acid 6691·8, *r*-diethylsuccinic anhydride 6375·8 cal./g. G. M. B.

Physical Properties of Nitro Derivatives. L. DESVERGNES (*Mon. Sci.*, 1925, **15**, 73—78).—*p*-Chloronitrobenzene obtained by

purification of the technical product has m. p. 83·19° (literature, 83°); its solubility in water at 17° is 0·0028; at 50°, 0·0125; at 100°, 0·0153. 1-Chloro-2 : 4-dinitrobenzene has m. p. 50·08° to 50·12° (Post and Naumann give 50°; Ullmann, 51°; Würtz, 53°). It is stated in the literature to be insoluble in water, but at 15° the solubility was found to be 0·008, at 50° 0·041, at 100° 0·159. The solution of chloro-2 : 4-dinitrobenzene is brown and after some time a violet-black substance, m. p. 170°, separates (cf. Vongerichten, A., 1900, i, 51). Alkalis convert the substance into pyridine dinitrophenate (deep red) (cf. Spiegel, A., 1900, i, 51) from the alcoholic solution of which 2 : 4-dinitrophenol is precipitated by hydrochloric acid. 1-Chloro-2 : 4 : 6-trinitrobenzene, pale straw-coloured crystals when pure, has m. p. 81·64—81·67° (literature gives 83°). Its solubility in water (g. substance per 100 g. water) is 0·0178 at 15°, 0·053 at 50°, 0·346 at 100° (literature states insoluble in water). Some hydrolysis takes place with water, yielding picric acid, particularly at 100°. 1-Chloro-2 : 4 : 6-trinitrobenzene gives an intense black coloration with pyridine in the cold. Evaporation of the solution leaves an amorphous substance from which hot benzene extracts picric acid; the residue on treatment with cold chloroform yields a yellowish-orange, crystalline substance, the alcoholic solution of which gives ruby-red crystals, m. p. 129—130°, the composition of which appears to correspond with the formula $2C_6H_2(OH)(NO_2)_3,5C_5H_5N$. The undissolved reddish, amorphous residue softens at 100°. The solubilities of the substances in several organic solvents have been determined. A. C.

Thermal Data on Organic Compounds. I. Heat Capacities and Free Energies of Methyl, Ethyl, and *n*-Butyl Alcohols. G. S. Parks (*J. Amer. Chem. Soc.*, 1925, **47**, 338—345).—From thermal measurements extending to very low temperatures the specific heats of the crystalline and liquid forms of methyl, ethyl, and *n*-butyl alcohols were measured and also their heats of fusion. Methyl alcohol has two crystalline forms with a transition point at 161·1° Abs., the second form melting at 175·3° Abs., the heat of fusion being 23·7 cal./g. The heats of fusion of ethyl and *n*-butyl alcohols are respectively 25·76 and 29·93 cal./g. Using the third law of thermodynamics and the formula of Lewis and Gibson (A., 1920, ii, 585), up to 90° Abs. the entropies per mol. at 298° are 32·6, 42·3, and 60·2 and the free energies of formation are −44500, −44000, and −44100 cal. The entropy of supercooled ethyl alcohol exceeds that of the crystalline form by 3·7 units per mol. at 87° Abs. L. J. H.

Ratio of Specific Heats for Liquids. F. A. Schulze (*Physikal. Z.*, 1925, **26**, 153—155).—The values of C_p-C_v and C_p/C_v for 37 unassociated and for 16 associated liquids are tabulated. The difference between the molar heat capacities at constant pressure and constant volume lies between 10 and 11 for all unassociated liquids. For associated liquids the value is considerably lower.

F. G. T.

Specific Heats and Latent Heats of Fusion of Ice and of Several Organic Compounds. O. MAASS and L. J. WALDBAUER (*J. Amer. Chem. Soc.*, 1925, **47**, 1—9).—An apparatus is described for measuring the heat capacity of substances between 16·5° and various temperatures ranging from −180° to 0°. From this the specific heat is calculated and the latent heat of fusion if the solid melts below 16·5°. The specific heat of ice may be represented by $c=0{\cdot}485+0{\cdot}000914t-0{\cdot}00000546t^2$. The latent heats of fusion of water, benzene, acetone, and methyl alcohol are 79·42, 30·56, 19·60, and 16·40, respectively. Where the specific heat of a compound varies greatly with the temperature the atomic heat is a highly constitutive property. L. J. H.

Trouton's Ratio at the Absolute Zero. N. PERRAKIS (*Compt. rend.*, 1925, **180**, 579—580; cf. *ibid.*, 1924, **179**, 562).—As the temperature falls, Trouton's ratio varies according to an exponential function of the temperature and tends to a limiting value, at the absolute zero, equal to $1{\cdot}5R$, the specific heat at constant volume of a monatomic gas. G. M. B.

Heats of Formation of Phenol–Water Solutions at 75°. J. B. FERGUSON and W. B. HOPE (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 121).—The maximum heat effect occurs at approximately 61% phenol by weight and is 5·0 cal./g. of solution (heat absorbed). J. S. C.

Cooling of Hot Bodies in Gases and Liquids. R. SEELIGER (*Physikal. Z.*, 1925, **26**, 282—295).—A review and bibliography of the hydrodynamic and gas film theories of cooling. F. G. T.

Temperature–Entropy Diagrams for Nitrogen and Oxygen. W. H. RODEBUSH, J. W. ANDREWS, and J. B. TAYLOR (*J. Amer. Chem. Soc.*, 1925, **47**, 313—319).—A method of determining the heat content of superheated liquids depending on the proportion vaporised on adiabatic expansion is described and applied to nitrogen and oxygen. The temperature–entropy diagrams are given for these elements, as liquids under their own vapour pressure, from the boiling to the critical points. L. J. H.

Entropies of the Vapours of Zinc and Lead. W. H. RODEBUSH and A. L. DIXON (*J. Amer. Chem. Soc.*, 1925, **47**, 1036—1043).—The vapour pressure of zinc, measured by the method described previously (A., 1923, ii, 738), is expressed by the relation: $\log p(\text{mm.}) = -6967/T - 2{\cdot}162 \log T + 2{\cdot}298\times10^{-4}T + 15{\cdot}1817$, which also includes Braune's figures (A., 1920, ii, 491). The measurements for lead, which entailed some experimental difficulty, are given by the following equations, which include Egerton's results (*Phil. Mag.*, 1917, [vi], **33**, 33): $\log p(\text{mm.}) = -9854/T + 7{\cdot}822$ between 900° and 1600° Abs., and $\log p(\text{mm.}) = -10100/T - 0{\cdot}65 \log T + 10{\cdot}05$ between 600° and 900° Abs. The entropies of the vapours calculated by means of these equations agree with the values predicted by Tetrode (*Ann. Physik*, 1912, [iv], **38**, 434). S. K. T.

Specific Gravity of Solid Binary Compounds. U. PANICHI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 572—579).—With minerals (cf. this vol., ii, 64) and a number of solid binary compounds examined, as the ratio of the atomic volume to the valency of the element combined with the non-metal decreases, the excess of the calculated density (*loc. cit.*) over the actual density tends first to assume maximum positive values and then to diminish gradually. T. H. P.

Vapour-pressure Curves of Salts. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **143**, 336—342).—Lorenz (A., 1924, ii, 654) has shown that the constant q in Dühring's vapour-pressure formula $(T_2-T_1)/(\theta_2-\theta_1)=q$ is in many cases equal to T_1/θ_1. Values of q and of T_1/θ_1 have now been evaluated for a considerable number of halides for which vapour-pressure data are available, water and hexane being used as reference substances. The value of q is reasonably constant over a range of temperatures; the agreement between q and T_1/θ_1 is less good, but is considered as close as could be expected for substances so different in character as halides and water or hexane. Tantalum fluoride is an exception, q not being constant, whereas cuprous chloride, bromide, and iodide and thallium fluoride give constant values for q, but much lower or higher values for T_1/θ_1. A. G.

Partial Pressure of Water Out of Aqueous Solutions of Sulphuric Acid. C. H. GREENEWALT (*Ind. Eng. Chem.*, 1925, **17**, 522—523).—A series of curves showing vapour pressures plotted against concentrations for even temperatures was prepared, and from these curves others correlating $\log p$ with $1/T$ were plotted. The parameters for the equations of these curves are given in a table. [Cf. *B.*, July 3rd.] D. G. H.

Germanium. VIII. Physical Properties of Monogermane. R. B. COREY and A. W. LAUBENGAYER [with L. M. DENNIS] (*J. Amer. Chem. Soc.*, 1925, **47**, 112—117).—One litre of monogermane, GeH_4, under standard conditions weighs 3·420 g. (theoretical 3·416), the composition being confirmed by analysis; m. p. −165°, b. p. −90°, d at −142° 1·523. It decomposes into its elements at 280—285°. The vapour pressures from −145° to −90° are given. The results differ from those of Schenck (A., 1922, ii, 855), but are probably more trustworthy since the log P–$1/T$ curve is linear. L. J. H.

Saturation Pressure of Mercury up to 2000 kg./cm.² F. BERNHARDT (*Physikal. Z.*, 1925, **26**, 265—275).—The saturation pressure of mercury was measured up to a temperature of 1435° and a pressure of 2020 kg./cm.² For low pressures, an electrically heated glass capillary tube was used. For higher pressures and temperatures, a Des Coudres bomb with a quartz window was employed. For the highest pressures, the window was omitted. In the latter case, the mercury was contained in a quartz vessel, and the boiling point determined by changes of resistance of a mercury thread in a capillary tube forming part of the quartz vessel. An

investigation of the strengths of glass capillary tubes showed that at equal temperatures the strength of ordinary Jena glass is greater than that of hard glass. The saturation pressures at temperatures up to 850° are slightly less than those found by Cailletet. The following pressures, in kg./cm.^{2}, are typical of higher temperatures: 1000°, 260; 1100°, 425; 1200°, 665; 1300°, 1025; 1400°, 1600; 1435°, 2020. The Hertz–Knudsen formula holds satisfactorily up to 1000°. The author's values are consistently higher than those calculated from the density measurements of Bender (A., 1915, ii, 673). Taking Bender's value of 1650° as the critical temperature of mercury, extrapolation gives a critical pressure of 3000—3500 kg./cm.^{2} F. G. T.

Vapour Pressures of Solid and Liquid Benzophenone between 0° and 48°. M. Volmer and P. Kirchoff (*Z. physikal. Chem.*, 1925, **115**, 233—238).—The vapour pressures of the equilibrium forms were determined by a modification of Knudsen's method (*Ann. Physik*, 1909, [iv], **29**, 179); the apparatus employed is described. The vapour pressures of super-cooled liquid benzophenone were obtained by the method of Volmer and Estermann (A., 1922, ii, 193). The measured value of the vapour pressure of solid benzophenone at 40° is about 11% too low; this error, however, probably decreases at lower temperatures. L. F. G.

Vapour Pressures and Boiling Points of Mono- and Di-methylanilines and Mono- and Di-ethylanilines. O. A. Nelson and H. Wales (*J. Amer. Chem. Soc.*, 1925, **47**, 867—872).—The vapour pressures of mono- and di-methylanilines and mono- and di-ethylanilines were measured at 5° intervals from 40° to 220°. The latent heats L and vapour pressures P at various temperatures T are given by the following equations: monomethylaniline, b. p. 195·70°/760 mm., $L=17369{\cdot}0-12{\cdot}933T$; $\log P=28{\cdot}1580-(3706{\cdot}4/T)-6{\cdot}504\log T$; dimethylaniline, b. p. 193·50°/760 mm., $L=12953{\cdot}0-4{\cdot}62T$; $\log P=15{\cdot}14437-(2828{\cdot}5/T)-2{\cdot}3234\log T$; monoethylaniline, b. p. 204·72°/760 mm., $L=13248{\cdot}0-3{\cdot}9T$; $\log P=14{\cdot}1910-(2892{\cdot}9/T)-1{\cdot}9613\log T$; diethylaniline, b. p. 216·27°/760 mm., $L=1412{\cdot}6-5{\cdot}3081T$; $\log P=16{\cdot}40076-(3102{\cdot}3/T)-2{\cdot}6693\log T$. F. G. W.

Temperatures of Corresponding Densities. W. Herz (*Z. anorg. Chem.*, 1925, **144**, 40—44).—The ratios of the temperatures at which the density of a fluid is a definite fraction of the critical density, to the critical temperatures, have been calculated for a great number of fluids, both temperatures being absolute. The ratio T/T_k, T being the temperature at which the density is one-half of the critical density, is very close to 0·978, the maximum divergence in 39 cases being only about 1%; for lower ratios of the density, the divergence increases, the ratio being 0·830 with a maximum divergence of 6% for one-tenth of the critical density, and 0·697 with a maximum divergence of 11·5% for one-fiftieth of the critical density. Ratios of temperatures at which the densities are 2 and 2·75 times the critical density are also compared; the agreement is not so good. S. I. L.

Equation of State of Liquids and Solids at High and Low Temperatures. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 897—913).—The quantity b in the van der Waals' equation is assumed to be a function of v, equal to $b_g/[1+(b_g-b_0)/v]$. Certain consequences of this assumption are discussed and the equation of state is derived from thermodynamic relations. L. L. B.

Definition of a Perfect Gas. A. L. CLARK (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 293—311).—Four criteria are usually applied to define a perfect gas. These may be expressed mathematically: as I $Pv=f(T)$; II $v=kT$; III $\lambda=T\left(\frac{\delta P}{\delta T}\right)_T-P=0$, and IV $\mu=[T\left(\frac{\delta v}{\delta T}\right)_P-v]/Cp=0$. ($P$=pressure, v=volume, T=Abs. temperature, λ=internal pressure, μ=the change in temperature on expansion without doing external work.) The above are not independent, and it is shown mathematically that if any two are satisfied the others are also. The best method of defining a perfect gas depends on the purpose at hand. A definition free from all uncertainty and applicable to all experimental work is that "a perfect gas is one which obeys the laws of Boyle and Joule." J. S. C.

Entropy and Probable State of Ideal Gases. F. VON HAUER (*Physikal. Z.*, 1925, **26**, 281—282).—Consideration of the heat exchange between a mass of gas and a gas reservoir at a very much higher temperature shows that the probable state of the gas at a given temperature and volume, calculated by the application of Maxwell's distribution law alone (*Ann. Physik*, 1915, [iv], **47**, 365), is related to the entropy by an equation identical in form with the Boltzmann equation $S=k\log W+\text{constant}$. F. G. T.

Quantising of Monatomic Gases. M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 49—57).—Mathematical. An investigation as to whether, in view of the conclusions of Stern and Gerlach (*Z. Physik*, 1922, **9**, 349), quantum statistical methods may be applied to the theory of gases. Previous conclusions (A., 1920, ii, 414) are modified by regarding each state of a gas system of N molecules as characterised by $N!$ different phase points, since two phase points in which two or more atoms have exchanged coordinates or velocity components are to be regarded as in identical states. Each quantum cell is thus defined by $N!$-congruent cells in generalised space. To each "nuclear cell" the space h^{3N} is ascribed. On this basis, expressions are developed for the free energy, entropy, and energy content of a monatomic gas. Gas degradation at low temperatures and high densities is predicted by these expressions, which are compared with those deduced by Einstein (cf. following abstract). F. G. T.

Quantum Theory of the Monatomic Perfect Gas. A. EINSTEIN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 3—14).—Mathematical. Continuation of previous work (*ibid.*, 1924, 261—

267). In the earlier paper the conditions necessary for a perfect gas to have its entropy, statistical, and thermodynamic character in accordance with Boltzmann's hypothesis were investigated and the classical gas equation was discussed. In the present paper, the theory of the deviation of the gas equation is extended. At any temperature a saturation density of perfect gas is postulated such that the molecules in excess of this density do not take part in thermal agitation. The statistical properties (density and vibration frequencies) are considered mathematically. The following approximation for the equation of state is given: $p=RT\eta[1-0{\cdot}186h^3N^4\eta/(2\pi MRT)^{3/2}]$, where η=molecular concentration, N=number of molecules per mole, M=molecular weight. R. A. M.

Entropy of Perfect Gases at Absolute Zero. N. DE KOLOSSOWSKY (*J. Chim. phys.*, 1925, **22**, 77—78).—Theoretical. Planck's equation $\log p=-U_0/ART+\alpha/AR+C_p/AR\,.\log T$ (1) combined with the equation for the entropy of a perfect gas, S_g, gives the relation (2) $S_g=U_0/T+C_p$, from which Planck ("Vorlesungen über Thermodynamik") concluded that the entropy of a gas at absolute zero is $+\infty$. Equation (1) is identical with empirical formulæ of the type $\log p=A+B/T+C\log T$, in which C is found experimentally to be negative. The proof adopted by Planck thus involves the assumption that C_p is negative, which is contrary to experimental fact. The proof is therefore unjustifiable, although the conclusion that $S_g=+\infty$ at the absolute zero is possibly correct.
W. H.-R.

Validity of Gas Equations. I. W. HERZ (*Z. Elektrochem.*, 1924, **30**, 604—607).—Nernst's gas equation $p(v-v_1)=RT(1-p/p_C)$, where p, p_C are the pressures and critical pressures, v, v_1 the volumes of gases and liquids respectively at absolute temperature T, and R is the molecular gas constant, is tested for various organic and inorganic substances from $T=273°$ upwards, using values given in the Landolt–Börnstein tables. Apart from inaccuracies due to interpolation, the value of R is found, in general, to be correctly given up to temperatures of 0·8 to 0·9 of the critical temperatures. It is suggested that deviations may be attributed to molecular association.
C. H. D. C.

Surface Tension: Interpretation of the Eötvös Expression. L. BRILLOUIN (*Compt. rend.*, 1925, **180**, 1248—1251).—Theoretical interpretations of the Eötvös expression $-\delta A/\delta T\,.\,V_m^{2/3}$=constant are inadequate. (A=capillary constant of a liquid, V_m=molecular volume; the constant for very different liquids is 2·1—2·25 *C.G.S.*) Two factors are considered: waves of capillarity setting in motion the molecules of the surface layer and penetrating little into the interior of the liquid, and compression waves agitating the interior. The velocity W of capillarity waves is given by $W=[2\pi A\nu/(\rho_1-\rho_2)]^{1/3}$, where ν is frequency and ρ_1, ρ_2 are the densities of liquid and vapour, respectively. If S_m is the area of a unimolecular film of 1 g.-mol. of liquid there are N/S_m mols. per unit area; since each has three degrees of freedom the number per unit area is $3N/S_m$. The energy of agitation (Debye) will then be $\epsilon=3N\,.\,KT/S_m=3RT/S_m$.

This energy is partitioned among frequencies extending from 0 to an upper limit ν_ϵ with an accumulation near the limit. These waves exert on unit length a force $\omega = W_{g\epsilon}/2W = 3\epsilon/4$, where W_g represents the velocity of the group $\delta\nu/d(\nu/W)$ and is equal to $3W/2$. This force will diminish the static surface tension A_0 (that obtained in the absence of thermal agitation) so that the surface tension coefficient at temperature T will be $A_T = A_0 - 3\epsilon/4 = A_0 - 9RT/4S_m$, an expression closely resembling that of Eötvös when differentiated: $-\delta A/\delta T \,.\, S_m = 9R/4$=constant.

If d is the mean distance separating molecules in the liquid (*i.e.*, $Nd^3 = V_m$), and δ is the mean distance in the surface layer $N\delta^2 = S_m$, and if d and δ are equal, $S_m = N^{1/3}V_m^{2/3}$. Hence $-\delta A/\delta T \,.\, V_m^{2/3} = 9/4 \,.\, RN^{-1/3} = 2{\cdot}2$, since $R = 8{\cdot}31 \times 10^7$ and $N = 61 \times 10^{22}$. The agreement justifies the assumptions made, and in particular that $d = \delta$, *i.e.*, that the distance separating molecules in the surface layer is little different from that in the bulk of liquid, although the distances between the first and second layers may be very different.

R. A. M.

Determination of Surface Tension from the Rise in Capillary Tubes. S. Sugden (*J. Amer. Chem. Soc.*, 1925, **47**, 60—64).—Mathematical. L. J. H.

Compressibilities of Gases at 0° and below one Atmosphere, and the Divergence from Avogadro's Law. III. Ethylene, Nitrous Oxide, Nitric Oxide, and Methyl Ether. T. Batuecas (*J. Chim. phys.*, 1925, **22**, 101—115).—A continuation of previous work (cf. Guye and Batuecas, A., 1922, ii, 617). The following values are found for the divergence from Avogadro's law $(1 + \lambda)$ and the compressibility at 0°. Ethylene, 1·00780 and 102×10^{-6}; nitrous oxide, 1·00739 and $97{\cdot}8 \times 10^{-6}$; nitric oxide, 1·00112 and $14{\cdot}7 \times 10^{-6}$; methyl ether, 1·02540 and 326×10^{-6}. The results for ethylene give 12·000 as the atomic weight of carbon, and those for nitrous and nitric oxides give, respectively, 14·003 and 14·006 as the atomic weight of nitrogen. The results for methyl ether are not in such good agreement, and in this case the compressibility diminishes as the pressure is lowered. W. H.-R.

Compressibilities of Gases at 0° and below one Atmosphere, and the Divergence from Avogadro's Law. IV. T. Batuecas, G. Maverick, and C. Schlatter (*J. Chim. phys.*, 1925, **22**, 131—141; cf. Guye and Batuecas, A., 1922, ii, 617, and preceding abstract).—A new apparatus has been constructed generally resembling that used by Guye and Batuecas (*loc. cit.*), but differing in dimensions and minor details. For oxygen, the divergence from Avogadro's law is determined as $1 + \lambda = 1{\cdot}00087$, in good agreement with the value 1·00085 found with the old apparatus, and indicating that for oxygen the errors due to adsorption on the glass surfaces are negligible. W. H.-R.

Compressibility of some Organic Liquids. K. Schmidt (*Ann. Physik*, 1925, [iv], **76**, 571—589).—The compressibilities of *n*-hexane, nitrobenzene, bromobenzene, chlorobenzene, chloroform, toluene, *o*-nitrotoluene, *o*-toluidine, and *m*-toluidine were

measured at 18° and 8° by Röntgen's method. The measurements were comparative, with Röntgen's value for water as a standard. A full discussion is given of the corrections applied to the results, which are estimated as correct to within 0·6%. F. G. T.

Relation between the Viscosities of Liquids and their Molecular Weights. D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, **27** [Advance proof]).—The viscosities of liquids are best compared at temperatures at which the free space is a definite fraction of the total volume. Since the expression $\eta_t x_t^4 = c$, where η_t and x_t are the viscosity and free space at temperature t, does not contain the temperature, it is more simple to calculate the free space at 0° for all liquids, and then to adjust the viscosity by calculation to a fixed value of the free space. The free space at 0° (x_0) can be calculated from the viscosities at 0° and 10° by the relation $\eta_0/\eta_{10} = (x_0+V_{10}+1)/x_0V_{10}$, where V_{10} is the volume at 10° of 1 c.c. at 0°. When the molecular weights are plotted against the viscosities of each liquid with the free space adjusted to a fixed ratio 1/10th of the total volume, normal substances lie approximately on a straight line, whilst associated substances are removed from this line. The factors by which the molecular weights must be multiplied in order to make associated substances lie on the normal line (see above), are in general agreement with the association factors found by other means. The viscosity of a liquid may therefore be expressed in the form $\eta = KMa/x$, where $K = 0{\cdot}5492$, M is the molecular weight in the gaseous phase, a the degree of association in the liquid, and x the relative amount of free space. W. H.-R.

Physical Properties of Water. D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, **27** [Advance proof]; cf. preceding abstract).—In most liquids, association causes a loss both of volume and of free space, but viscosity and density data indicate that in water association results in a loss of free space but a gain in volume, owing to the bulky nature of the associated molecule. As the temperature is raised from 0°, the bulky molecules dissociate, causing a decrease in volume which is counteracted by the ordinary thermal expansion, and this causes a minimum volume to occur at 4°. The viscosity, however, decreases continuously with rise of temperature because the dissociation causes a decrease in molecular weight and an increase in free space, both of which diminish the viscosity (*loc. cit.*). When water is compressed, the bulky molecules dissociate and hence water has an added compressibility, but whilst the dissociation increases the free space, further compression reduces the volume and also the free space, and hence the viscosity shows an initial sag with application of pressure followed by a continual rise with further pressure. W. H.-R.

Variation of Viscosity of Fluids as a Function of Volume. J. DUBIEF (*Compt. rend.*, 1925, **180**, 1164—1166).—According to the kinetic theory, the coefficient of internal friction, η_0, is proportional to the mean path, L, and to the mass, M^1, of gas traversing unit surface in unit time, *i.e.*, $\eta_0 = 2M^1L$ (1). But $M^1 = N_1mu/6$ (2), and $L = \lambda^3/\pi\sqrt{2\rho^2}$ (3) (where N_1 is the number of molecules in unit

volume, m the mass of a molecule, u its mean velocity, λ the mean distance, and ρ the diameter of collision). In their application to actual fluids, these relations require correction. For a spherical molecule of a real gas $M'_1=M'v/(v-b_0)$, where M'_1 is the mass of real gas traversing unit volume in unit time, v the volume, and b_0 the co-volume of van der Waals. Since L requires no correction, $n=2M'_1L=2M'Lv/(v-b_0)=n_0v/(v-b_0)$ (4). For carbon dioxide (cf. A., 1912, ii, 832), $b_0=0{\cdot}002363$ and the relations are well verified. Beyond $v=12b_0/\pi$, b_0 should diminish. This conclusion is verified. The van der Waals equation can be written: $v/(v-b_0)=(p+a/v_2)v/RT$ and from (4) $n/n_0=v/(v-b_0)$, thus $n/n_0=(p+a/v_2)v/RT$. The degree of agreement is as good for this expression as for the van der Waals equation itself. Similarly, the Dieterici equation leads to $n/n_0=v/(v-b_0)=(pv/RT)e^{c/vRT}$. The agreement is improved, but discrepancies persist, due, it is suggested, to the lack of an exact equation of state. R. A. M.

Measurements of Viscosity by the Ostwald Viscosimeter. F. Martin (*Bull. Soc. chim. Belg.*, 1925, **34**, 81—116).—An investigation of conditions necessary to obtain accurate viscosities with a simple type of viscosimeter. The values of Thorpe and Rodger for water, ethyl ether, carbon tetrachloride, benzene, and ethylene bromide were taken as standards and a comparison was made of the values found for the viscosities of these liquids in seven viscosimeters of various dimensions at 15° and 30°. Variations of from 3 to 10% were found, the magnitude of the error being roughly proportional to the speed of outflow. By modifying the Ostwald viscosimeter so that the end of the capillary tube projected into a subsidiary bulb lying slightly above and to the side of a larger bulb, a constant level was obtained below the capillary tube. This reduced considerably the variations in viscosities measured in apparatus of different dimensions. An investigation of the effect of hydrostatic pressure showed that there is a critical velocity of outflow beyond which Poiseuille's law does not hold. Data are given for the construction of viscosimeters by the use of which viscosities may be determined to 1% by the application of a formula containing a simple correction term. F. G. T.

Viscosity of Ethyl Ether near the Critical Point. A. L. Clark (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 329—338).—Previous experiments (A., 1916, ii, 16), the results of which were interpreted as supporting the view that the liquid state persisted above the critical temperature, have been repeated and are shown to confirm the classical theory of Andrews. The results of the earlier paper are to be interpreted as due to the inability of the density to distribute itself within the experimental tube except after a long period of time. J. S. C.

Viscosity of Cotton Cellulose. J. O. Small (*Ind. Eng. Chem.*, 1925, **17**, 515—517).—Factors influencing viscosity are origin of the plant and conditions of growth, and the subsequent purification treatment of the cellulose. Viscosity may be determined and

consistent results obtained by a modification of Joyner's "cuprammonium" solution method (T., 1922, **121**, 1511), and the viscosity of the nitrated products may thus be controlled. It is necessary in the case of low-viscosity types of cotton lint to use a solvent containing approximately 3% of copper. [Cf. *B.*, July 3rd.] D. G. H.

Diffusibility of Helium through Crystalline Septa. A. Piutti and E. Boggio-Lera (*Atti R. Accad. Lincei*, 1924, [v], **33**, 532—537; cf. A., 1924, ii, 42, 105).—At 480°, helium cannot traverse thin sheets of mica or thin sections of quartz cut either parallel or perpendicular to the optic axis, although it is able to pass through both ordinary and silica glasses. According to recent views, such glasses are considered to be composed of liquids of high viscosity. T. H. P.

Diffusion of Carbon through Tungsten and Tungsten Carbide. M. R. Andrews and S. Dushman (*J. Physical Chem.*, 1925, **29**, 462—472; cf. A., 1923, ii, 327).—The rate of decarbonisation of tungsten wire at temperatures of about 2000° Abs. is fast until all the tungsten carbide, W_2C, has been decomposed, when a slower rate sets in which depends on the carbon dissolved in the tungsten. In carbonisation, a shell of the second carbide, WC, is formed before the core is completely converted into W_2C, so that the minimum conductivity of the wire is not reached. M. B. D.

Self-diffusion in Solid Metals. G. Hevesy and A. Obrutsheva (*Nature*, 1925, **115**, 674—675).—Lead foil was pressed in a vacuum against lead containing thorium-*B* in homogeneous mixture; on heating, diffusion of the active into the inactive lead took place, the α-particles due to the diffused atoms or their successive products of disintegration producing scintillations on a screen. The rate of self-diffusion increased from 6×10^{-7} cm.^{2} day^{-1} at 260° to $1{\cdot}4\times10^{-4}$ at 324°. Further experiments just below the m. p. indicated that the coefficient of diffusion in a single crystal of lead is less than 10^{-8} cm.^{2} day^{-1}. A slowly-cooled lead bar gave a low, and a suddenly-cooled bar a high, coefficient of diffusion. Comparable results were obtained for the diffusion of similar metals, *e.g.*, thallium and lead, into one another, but in the case of the diffusion of polonium into lead, the coefficient is approximately the same for the foil and the crystal, the atoms of polonium thus loosening the lattice of the individual lead crystals, and diffusing as if through amorphous lead. A. A. E.

Effect of Molecular Attractions on the Total Pressure of a Gas. O. Maass and D. M. Morrison (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 49—55).—The changes in pressure consequent on the mixing of a number of gases, ranging from gases which for experimental purposes may be regarded as ideal (hydrogen, helium, etc.) to gases of the type of ammonia and methyl ether, have been measured, using the apparatus already described (A., 1923, i, 892). The experimental numbers are interpreted in favour of the view that in a two-component gas mixture three distinct forces of attraction come into play, two between the same species and one

between the different species of molecules. The total pressure depends on the magnitude of these attractions and on the extent to which the forces can come into play. At high pressures the influence of the volumes of the molecules becomes very marked. The results of the investigations of Masson and Dolley (A., 1923, ii, 462) on mixtures of argon, ethylene, and oxygen over the pressure range 5—125 atm. may be interpreted by means of the above hypothesis. J. S. C.

Concentration of Ammonia in a Compressed Mixture of Hydrogen and Nitrogen over Liquid Ammonia. A. T. LARSON and C. A. BLACK (*J. Amer. Chem. Soc.*, 1925, **47**, 1015—1020).—The volume percentages of ammonia in a compressed mixture of hydrogen and nitrogen over liquid ammonia increase with increasing temperature (−22·5° to 18°) and decreasing pressure (1000 to 50 atm.). A definite equilibrium exists. The values are much higher than those calculated from the vapour pressure of liquid ammonia; possible explanations are given. S. K. T.

Separation of Gas Mixtures by Diffusion. R. LORENZ and A. MAGNUS (*Z. anorg. Chem.*, 1924, **136**, 97—113).—The separation under ideal conditions of a mixture of two gases by diffusion through a porous cell has been calculated from considerations based on the kinetic theory. If y is the percentage by volume of a gas of molecular weight M_1 in admixture with a gas of molecular weight M_2 after diffusion and x the volume percentage of the first gas in the mixture before diffusion, then $y=(100x\sqrt{M_2/M_1})/[100-x(1-\sqrt{M_2/M_1})]$. The degree to which it is possible to separate the gases by diffusion varies with the composition of the mixture and is at a maximum when $x=100/(1+\sqrt[4]{M_2/M_1})$. For mixtures of hydrogen and carbon monoxide, maximum separation is obtained when the mixture contains 34·08% of hydrogen; the gas after diffusion then contains 65·9% of hydrogen. An apparatus is described for testing the efficiency of porous earthenware cells in separating gases by diffusion, the efficiency of a cell being defined as the ratio of the actual enrichment of the lighter gas after passing through the cell to the theoretical enrichment calculated from the above equation. The results obtained showed that the efficiency of a cell depends on the size of its pores, the rate of passage of the gas mixture over the cell, and the rate of removal of the diffused gas from the interior of the cell. The greatest efficiency observed in the tests was 97%, but only a very small amount of enriched gas was obtained in this case. A. R. P.

Vapour Pressures of Solutions of Phenol and Water at 75°. J. B. FERGUSON and W. S. FUNNELL (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 122—123).—The vapour pressure of mixtures of phenol and water (7—60% phenol) at 75° is found to be almost independent of the composition of the mixture. J. S. C.

Composition of Liquid and Vapour Phases of Glycerol–Water Mixtures. M. IYER and F. L. USHER (*J. Chem. Soc.*, 1925, **127**, 841—844).—Mixtures of glycerol and water of known

composition were distilled in a vacuum and the distillates analysed refractometrically. For liquid phases, which contain 75, 98, and 99% of glycerol, the vapour phases contain 0·2, 1·7, and 17·0%, respectively. W. A. C.

Solid Solutions of the Alkali and Ammonium Halides. R. J. HAVIGHURST, E. MACK, jun., and F. C. BLAKE (*J. Amer. Chem. Soc.*, 1925, **47**, 29—43).—Solid solution may be due to substitution in the space lattice of the solvent by the solute atoms, but this is possible only if the atoms are chemically similar and do not differ greatly in molar volume. The effect on the space lattice is additive. Another type of solid solution is interstitial, the solute atoms being packed between the solvent atoms enlarging the unit cell whatever the atomic volumes. *X*-Ray measurements are given for solid solutions of a number of binary systems of the alkali and ammonium halides. They are of the first type, are completely miscible at the ordinary temperature, and obey the law of additivity until the difference in the cube sides of the pure components exceeds 5% of the mean of the two, after which the law does not hold strictly. For completely miscible systems, each solid solution behaves towards *X*-rays as though it were a pure substance, the reflecting power and volume of the compound atom being determined additively by the atomic numbers and volumes of the constituent atoms. L. J. H.

Structure of Alloys. A. WESTGREN and G. PHRAGMÉN (*Koll.-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 86—91).—An ideal solid chemical compound is defined by the chemical identity of the structurally equivalent atoms. In an ideal solid solution all the atoms are structurally equivalent. These two types of structure are to be regarded as limiting cases; most metallic phases represent intermediate stages. Many alloys can be regarded as solid solutions in intermetallic compounds, the formulæ of which may be obtained by means of the *X*-ray-spectrograph. Certain structural types are found in several different alloys. Thus the *X*-ray spectrograms (by the powder method) for certain phases of the copper–zinc, silver–zinc, gold–zinc, silver–cadmium, silver–aluminium, copper–tin and silver–tin systems correspond with the interference forms of the lattice with the closest possible hexagonal packing of spheres. Agreements of this type bring out important relationships between different systems of alloys. E. M. C.

Silver–Tin Amalgams. G. TAMMANN and O. DAHL (*Z. anorg. Chem.*, 1925, **144**, 16—39; cf. Joyner and Knight, T., 1911, **99**, 195; 1913, **103**, 2247; 1914, **105**, 639).—Amalgams prepared by grinding powdered silver–tin alloys with excess of mercury in a mortar and expressing the excess of mercury under constant pressure vary in composition and properties with the age and previous history of the powdered silver–tin alloys; freshly prepared alloys retain more mercury than old or previously heated powder, the difference being greatest for an alloy containing 73% of silver corresponding with the composition Ag_3Sn, and disappearing for

pure silver and tin, respectively. At the same composition, the amount of mercury retained is a maximum. The limits within which the components of the ternary system are the compound Ag_3Sn, mixed crystals of tin and mercury, and mixed crystals of Ag_3Hg_4 and tin are plotted, and tables for hardness, breaking strain, and volume change given. The amalgams obtained from an alloy of the composition Ag_3Sn are the hardest, most easily broken, and show the greatest volume increase; those prepared from old silver–tin powder show contractions in all cases. The ageing effect of the silver–tin alloys is accompanied by increase in density and reluctance to take up mercury. S. I. L.

Thermal and Electric Conductivities of some Aluminium Alloys. H. MASUMOTO (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 229—242).—The thermal and electrical conductivities of several aluminium alloys were determined by the method previously described (*ibid.*, 1917, **6**, 111). The alloys were examined in the chill-cast and annealed states, after quenching, and after cold-drawing and annealing. Both conductivities decreased with increase in the amount of other constituents in the alloy, the effect being greatest for manganese and chromium, and least for tin. The conductivities were increased by annealing the cast specimens, but reduced by quenching. The cold-drawn and annealed specimens had the highest conductivities. The product of the electrical resistance and thermal conductivity was practically constant ($6{\cdot}91\times10^{10}$ *C.G.S.* units) for all the alloys, the lower values corresponding with the lower conductivities. C. S.

Constitution of Technical Iron. F. WEVER (*Z. Elektrochem.*, 1924, **30**, 376—382).—The parameter of the iron lattice in austenitic steels containing manganese is a function of the carbon and manganese content and may be expressed by the formula (3·578+ 0·0005Mn+0·00645C) Å.; the specific volume is given by the expression $v=0{\cdot}1246+0{\cdot}0004\text{Mn}+0{\cdot}0041\text{C}$, the proportion of manganese and carbon in each case being expressed in atomic percentage. The lattice parameter of α-iron is 2·861 Å. and is increased to 2·87—2·88 Å. in hardened steel, but is practically unchanged in annealed steel. Carbon therefore appears to fill spaces in the lattice of α-iron and not to replace iron in the lattice structure. [Cf. *B.*, 1925, 403.] A. R. P.

Viscosity Measurements with Glass. V. H. STOTT, E. IRVINE, and D. TURNER (*Proc. Roy. Soc.*, 1925, **A**, **108**, 154—171).—The viscosities of thirteen glasses have been determined at various temperatures. Very high viscosities (10^9—10^{17} *C.G.S.* units) are measured by applying torsional forces to the two ends of a circular rod of the glass to be examined. For viscosities lower than these values, the glass is held in a cylindrical container and a cylindrical co-axial rod, made from a nickel–iron–chromium alloy, is plunged into the glass and rotated. In each case the time required for the moving portion of the apparatus to rotate through a given angle under the influence of a known torque is a measure of the viscosity.

The shape of the temperature–viscosity curves can be determined accurately, but the absolute values depend largely on the circularity and uniformity of diameter of the rods. Viscosity determinations at high temperatures have been made by measuring the rate of fall of a partly counterpoised platinum–iridium ball through the glass. J. S. C.

Mutual Solubilities of Cetene (Hexadecene) and Liquid Sulphur Dioxide. W. F. SEYER and J. L. HUGGET (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 213—216).—The critical solution temperature is in the region of 42·7°. The freezing point of cetene (3·5°) is lowered to −2·2° in presence of sulphur dioxide. It is shown that under ordinary working conditions diolefines are soluble and mono-olefines insoluble in liquid sulphur dioxide. This difference may be utilised with advantage in the refining of mineral lubricating oils. [Cf. *B.*, 1925, 388.] J. S. C.

Mutual Solubility of Sulphur Dioxide and *n*-Hexane. W. F. SEYER and A. F. GILL (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 209—211).—Above 10·1°, the two liquids are completely miscible. *n*-Hexane freezes at −93·7°, this temperature being lowered to −96° in presence of sulphur dioxide. The f. p. of sulphur dioxide, −72·8°, is lowered to −73·5° in presence of hexane. The solubility curve is very similar to that found for sulphur dioxide–*cyclo*hexane (A., 1923, i, 313). At temperatures in the region of −10°, the solubilities of the two hydrocarbons differ but slightly, and assuming the two substances to be typical of the class of compounds to which they belong it does not appear possible to separate naphthenes from paraffins by means of liquid sulphur dioxide (cf. Moore, Morrell, and Egloff, A., 1918, i, 285). J. S. C.

Supersaturation of Gases in Liquids. K. S. WYATT (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 127).—An aqueous solution of nitrogen saturated at a pressure of above 100 atm. at the ordinary temperature was brought to atmospheric pressure without the immediate formation of bubbles in the body of the liquid. The phenomenon has not yet been reproduced. J. S. C.

Solubilities of Rare Earth Salts. I. M. D. WILLIAMS, H. C. FOGG, and C. JAMES (*J. Amer. Chem. Soc.*, 1925, 47, 297—301). —The solubilities of the hexahydrated trichlorides of yttrium, samarium, and neodymium in water are, respectively, 217·0, 218·4, and 243·0 parts of the hydrate in 100 parts of water at 20°. Values at other temperatures from 10° to 50°, and similar values for the solubility in hydrochloric acid (*d* 1·1051) are also given, together with the solubility of ytterbium trichloride hexahydrate in the latter solvent. The melting points are 124°, 142·5°, 161—163°, and 153—155° for the hydrates in the order named. L. J. H.

Supersaturated Solutions of Uric Acid. R. STERN (*Klin. Woch.*, 1924, 3, 1583; from *Chem. Zentr.*, 1924, ii, 1925).—Colloidal solutions of monosodium urate may be obtained by simple dispersion in water. The solubility of uric acid in a 1% solution of sodium

salicylate is twice as great, and in 0·1% solution of the sodium compound of " atophane " three times as great as in water.

G. W. R.

Solubility of the Double Fluorides of Zirconium and Hafnium. G. VON HEVESY, J. A. CHRISTIANSEN, and V. BERGLUND (*Z. anorg. Chem.*, 1925, **144**, 69—74).—The solubilities of the ammonium and potassium double fluorides, $(NH_4)_2RF_6$, $(NH_4)_3RF_7$, and K_2RF_6 (R=Zr,Hf) in water, and in solutions of ammonium fluoride and hydrofluoric acid have been determined. The first are more soluble than the second, and the hafnium compounds more soluble than those of zirconium, the difference being most marked with the salts $(NH_4)_2RF_6$ and K_2RF_6. The solubilities are higher in presence of ammonium fluoride and hydrofluoric acid. S. I. L.

Solubility of Ferrous Hydroxide and its Effect on Corrosion. W. G. WHITMAN, R. P. RUSSELL, and G. H. B. DAVIES (*J. Amer. Chem. Soc.*, 1925, **47**, 70—79).—The solubility of ferrous hydroxide in pure water is $6·7\times10^{-5}$ mol./litre and its dissociation constant is $6·8\times10^{-10}$, the ionisation in saturated solution at 25° being 30%. The solubility in various salt solutions is also given, affording data from which the solubility in any non-oxidising salt solution in which the ionic strength does not exceed unity may be calculated. The free energy of formation of ferrous hydroxide is −57,200 cal. The precipitation of colloidal ferric hydroxide in salt solution has no direct connexion with the rate of corrosion. The rate of corrosion in salt solutions parallels the solubility of ferrous hydroxide in these solutions. It is suggested that this is due to changes in film protectivity with the solubility of the ferrous rust. L. J. H.

Solutions in 100% Sulphuric Acid. Solvolysis and Double Decomposition Reactions. A. W. DAVIDSON (*J. Amer. Chem. Soc.*, 1925, **47**, 968—981).—The solubilities of aluminium, zinc, and lead sulphates in 100% sulphuric acid are not increased by the presence of sodium sulphate, showing that soluble additive compounds are not formed. Salts are readily " solvolysed " in sulphuric acid solution; salts of metals of which the sulphates are insoluble in the acid, or of insoluble acids, are either themselves insoluble or are largely solvolysed to form insoluble products and *vice versa*. Additive products of salt and solvent could not be isolated. With potassium ferrocyanide pale yellow plates of $H_4Fe(CN)_6,H_2SO_4$ were obtained, and with calcium phosphate, $CaSO_4,H_2SO_4$. Qualitative solubility data for a number of salts are recorded. Double decomposition occurs readily between ionised salts in sulphuric acid solution, though not always instantaneously, probably because of the high viscosity of the solvent. S. K. T.

Equilibrium in the System: Carbamide, Methyl Alcohol. J. H. WALTON and R. V. WILSON (*J. Amer. Chem. Soc.*, 1925, **47**, 320—323).—From saturated solutions of carbamide in methyl alcohol at 0°, solvated crystals, of composition $CO(NH_2)_2,MeOH$, separate. Solubility data for this and for unsolvated carbamide are given, and the transition point is 19·25°. L. J. H.

Theory of Extraction. M. FRENC (*Z. angew. Chem.*, 1925, **38**, 323—324).—A short account of the methods for separating quantitatively two substances by shaking out with immiscible liquids, with a mathematical treatment of the different methods. [Cf. *B.*, 1925, 429.] P. M.

Partition of Silver between Lead and Zinc. W. A. NAISH (*Trans. Faraday Soc.*, 1925, **27** [Advance proof]).—The partition of silver between lead and zinc has been determined at temperatures from 550° to 850°. For mixtures containing more than 5% of silver, no consistent values can be found for the partition coefficient, but for dilute solutions the results may be expressed by the relation $C_{Zn}=KC_{Pb}$, where C_{Zn} and C_{Pb} are the weight concentrations of silver in the zinc and lead layers, respectively, and the partition coefficient $K=301{\cdot}9$ at 550°, rising to (approximately) 342, 388, and 415 at 650°, 750°, and 850°, respectively. The values of K are independent of the proportion of lead to zinc and when expressed in volume concentrations, substitution in the van't Hoff equation $d\log K/dT=-Q/RT^2$, leads to the value $Q=2048$ cal. approximately. W. H.-R.

Partition Phenomena. N. DE KOLOSSOWSKY (*Bull. Soc. chim.*, 1925, [iv], **37**, 372—381).—The partition data for hydrogen peroxide and propionic acid between water and ethyl ether at 18° are represented satisfactorily over a large range of concentration by empirical equations of the type, $C^{a+bS}/C'=$constant, in which C and C' are respectively the concentrations of the dissolved substance in the aqueous and ethereal layers, a and b constants and $S=C+C'$. The purely empirical supplementary term bS compensates for the deviations from the simple Nernst formula consequent on changes in the total concentration of the solute. The data for acetic acid require a more complex expression involving S^2. No simple algebraic equation can be applied to the partition numbers for ferric chloride, the value of the ratio C/C' varying from 470 to 1·85 when the concentration of ferric chloride in the aqueous phase is increased from N to $3{\cdot}6N$. J. S. C.

Absorption of Water by Dried Films of Boiled Starch. F. D. FARROW and E. SWAN (*J. Text. Inst.*, 1923, **14**, T, 465—474).—Two methods are described for determining the moisture relations of thin films of boiled starch. In one, the material was allowed to come to constant weight at 20°, in an atmosphere controlled by sulphuric acid solutions, and in the other a vacuum vessel was used in which the film could be periodically treated with measured quantities of water . With the latter method, temperature was controlled to $20\pm0{\cdot}05°$ and pressures reproduced to about 0·05 mm. The absorption curve is sigmoid and not considerably affected by the type of starch used or the mode of cooking the paste. Prolonged heating of the film reduces its capacity for water. Starch persistently retains more moisture in a given atmosphere if introduced from a wetter atmosphere than from a dryer. The dehydration curve of starch, however requires further study. J. C. W.

Sorption by Cotton. H. F. COWARD, L. SPENCER, and F. C. WOOD (*J. Text. Inst.*, 1925, **14**, T, 529—533).—Using the centrifuge to remove interfibrillar liquid (A., 1923, i, 305), the amounts of water and various reagents absorbed by bleached cotton at the ordinary temperature have been determined. 100 g. of cotton absorb about 50 c.c. of water, saturated sodium chloride, dilute sodium hydroxide (below $N/20$), or dilute sulphuric acid (below $N/25$). A solution is taken up as a whole, except that a small but easily measurable preferential absorption of solute takes place with alkali or acid. With more concentrated solutions of sodium hydroxide, the volume taken up is very much greater and the preferential absorption of alkali is considerable. A similar example of high preferential absorption is observed with dilute solutions of copper oxide in ammonia solution; cotton becomes much bluer in these solutions than the corresponding baths. It appears that preferential absorption is a necessary antecedent to both swelling and solation of cotton. J. C. W.

Adsorption. VIII. Adsorptive Capacity of Air-dried Manganese Dioxide Hydrate. P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 375—377; cf. A., 1924, ii, 594, 732, 733, 833).—The adsorption of silver by freshly precipitated air-dried hydrated manganese dioxide from silver nitrate solution has been studied. The solution, when neutral before adsorption, becomes afterwards strongly acid. The adsorption of silver ions is a chemical process and can be explained by the amphoteric character of the manganese dioxide, which in this case acts as an acid. D. C. J.

Experimental Investigation of the Dynamical Equation of the Process of Gas Sorption. D. H. BANGHAM and W. SEVER (*Phil. Mag.*, 1925, [vi], **49**, 935—944).—The sorption of carbon dioxide by glass-wool has been determined over long periods. Over a considerable range the equation previously obtained (A., 1924, ii, 392) $\log s = \log t/m + c$ is obeyed. Time–sorption data beyond this range are satisfactorily represented by the formula $\log [\sigma/(\sigma - s)] = kt^{1/m}$, where σ is the limiting value of the sorption s, as t approaches infinity. It is shown that the form of the time–sorption curve in the latter stages of sorption cannot be reconciled with the normal laws of diffusion. F. G. T.

Influence of Rate of Flow on the Adsorption of Gases. R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1924, **136**, 147—148).—When a mixture of hydrogen and carbon monoxide is passed over charcoal the rate of flow has little effect on the adsorption at the beginning, but as the charcoal becomes nearly saturated with the gas, the adsorption decreases with increase in the rate of flow, complete saturation being effected in a shorter time with a slow stream of gas. The ratio by volume of the gases adsorbed is the same as that in the original gas mixture. A. R. P.

Adsorption Experiments with Solutions. E. BERL and E. WACHENDORFF (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 36—40).—The adsorption of crystal-violet from water and "tetralin"

solutions, of brucine from water and toluene solutions, and of iodine from aqueous potassium iodide and toluene solutions by a number of charcoals shows a general agreement with the integral heats of wetting with water and benzene. A silica gel adsorbed much greater amounts of crystal-violet from "tetralin," and of brucine from toluene than did the charcoals, but it did not adsorb iodine from a solution in toluene. E. M. C.

Adsorption Phenomena in the Vicinity of the Critical Temperature. W. A. PATRICK, W. C. PRESTON, and A. E. OWENS (*J. Physical Chem.*, 1925, **29**, 421—434).—The adsorption isotherms for carbon dioxide and nitrous oxide on silica gel at 0°, 20°, 30°, and 40° at pressures below 1 atm. do not show any discontinuity at the critical temperature. The adsorption equation deduced from the capillary theory (cf. A., 1920, ii, 417; 1922, ii, 262) does not apply if the experimental values of the surface tension are used. By assuming that the surface tension is correct at the lower temperatures it is possible to calculate what it should be near the critical temperatures. The results show that capillarity lowers the vapour pressure of the liquid, increases its surface tension, and raises the critical temperature. M. B. D.

Adsorption from the Gas Phase at a Liquid–Gas Interface. III. T. IREDALE (*Phil. Mag.*, 1925, [vi], **49**, 603—627).—It is shown by two independent methods of measuring the surface tension of mercury, when the mercury surface is exposed to vapours of different pressures, that these vapours adsorb on the surface to give films which are probably only 1 mol. thick. In the saturated state, under special conditions, it is possible to form films which are of much greater thickness; but it is argued on thermodynamical grounds that such condensation is impossible under strictly isothermal conditions, if the tension of these films is not less than the tension of the unimolecular films. The mercury surface is easily contaminated by traces of impurities. Such contamination is irreversible, and the adsorbed impurities cannot be removed at the ordinary temperature under the highest vacua. The adsorption of organic vapours is largely reversible, except for such compounds as methyl iodide which are known to form a definite compound with mercury. It is suggested that a distinction must be drawn between a "surface compound" and a "surface solution." C. W. B.

Solution of Solids in Liquid Surfaces, and the Properties of the Resulting Films. M. VOLMER and P. MAHNERT (*Z. physikal. Chem.*, 1925, **115**, 239—252).—Experiments in which solid benzophenone was brought into contact with a mercury surface show that the adsorption of the former is direct, and not determined by vaporisation and subsequent adsorption of the vapour, nor by preliminary true solution followed by concentration at the surface. On decreasing the mercury surface, benzophenone separates out. The thickness of the adsorbed film has been determined between −9° and 25°, and in all cases is less than unimolecular. Langmuir's equation of state $(\sigma_0-\sigma)\Omega=RT$ (A., 1917, ii, 25) is modified

to the form $(\sigma_0-\sigma)(\Omega-\beta)=RT$, in which β is a correction for the close packing of the molecules. L. F. G.

Photographic Action of Methylene-blue as an Adsorption Effect. J. EGGERT and J. REITSTÖTTER (*Koll.-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 298—305).—The addition of methylene-blue at the rate of 10^{-6} g. per c.c. to silver bromide–gelatin emulsion causes fogging on alkaline development and a reduction of light-sensitivity to one-half. The adsorption of methylene-blue by silver bromide is complete under these conditions and corresponds with about 5000 mols. of methylene-blue per silver bromide crystal. The effect of the methylene-blue is regarded as a heterogeneous catalysis and is ascribed to the sulphur atom, since dimethyl-*p*-phenylenediamine is not adsorbed and gives no fogging. There is a general similarity between this catalysis and that of the silver produced by exposure to light, but the two effects are not additive. [Cf. *B.*, June 26th.] E. M. C.

Property of Very Small Bubbles of Gas in Water. H. A. MCTAGGART (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 129—131).—Microscopical observations of the movements of minute globules of oil on the surface of small gas bubbles in water point to the existence of electric repulsive forces between the globules. J. S. C.

Upper Limit for the Thickness of the Adsorption Layer on Silica. D. C. JONES (*J. Physical Chem.*, 1925, **29**, 369—375).—Powdered silica glass passing through a 100—120-mesh sieve was added to a solution of nitrobenzene in kerosene. No change in concentration of the nitrobenzene could be detected with an interferometer. On the assumption that the particles of silica were cubes, the layer of nitrobenzene molecules adsorbed on the surface of the silica must be less than three or four molecules thick. M. B. D.

Capillary Adsorption. W. A. PATRICK (*Koll.-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 272—277).—The author reviews his earlier experimental work on the adsorption of vapours by silica gel. The presence of small quantities of permanent gases plays an important part in the hysteresis phenomena. The application of the usual laws of capillarity to the very narrow capillaries postulated in porous adsorbents is criticised. E. M. C.

Capillary-Chemical Reaction in Spot-tests. F. FEIGL (*Kolloid-Z.*, 1924, **35**, 344—345).—A collected account, with references, of a number of instances of the application of spot-tests on filter-paper to inorganic qualitative separations (cf. A., 1921, ii, 278; 1923, ii, 508). D. C. J.

Flow of Starch Paste through Capillary Tubes. F. D. FARROW and G. M. LOWE (*J. Text. Inst.*, 1923, **14**, T, 414—440).—The work was undertaken in order to define the method and the nature of the measurements which are required to specify the fluid properties of starch pastes. The factors considered were temper-

ature, method of preparation, concentration and age of the paste, type of viscosimeter used, and origin of the starch. To avoid effects due to gelation, the measurements were made and the pastes stored at 90°. The pastes were prepared by blowing steam into a suspension of the starch in water contained in an asbestos-jacketed cylindrical separating funnel, steam being admitted for a definite time (usually 2 hrs.) after reaching 100°. The apparent viscosity of farina paste gradually rose until a concentration of 0·7% was reached and thereafter rapidly, the upper limit studied being 5%. The viscosity rapidly decreased, however, on storage at 90°. With maize pastes, the rapid increase in viscosity set in at 1·5%, and decrease with time was only slight. Maize pastes, therefore, were used in further studies on the effect of the design of the instrument on the apparent viscosity and it was soon found to be necessary to take into account the rate of flow. Experiments were therefore made in an Ubbelohde viscosimeter which could be fitted with capillaries of known dimensions and in which the driving pressures could be varied. The apparent viscosity was found to be less as the driving force was increased, thus accounting for variations from one instrument to another. By altering the usual equation to $[\eta]=P^N\pi r^4t/8l\,.\,V$, however, an expression was obtained which took this effect into account, and also the nature of the paste; P is the pressure in absolute units, r and l are the dimensions of the capillary, and V is the volume flowing in time t. The exponent N was determined by plotting the logarithm of the rate of flow against the logarithm of the pressure and measuring the tangent of the angle between the graph and the log. P axis; N is unity for water and purely viscous liquids, but greater for starch pastes, increasing with increasing concentration. The number $[\eta]$ was then found by calculation; it is designated the "coefficient of flow," and is regarded as a provisional, practical number which summarises the influence of unknown factors on the apparent viscosity. The values of $[\eta]$ and N fully describe the way in which the pastes will flow through capillary tubes; N is probably an expression of the fact that in two-phase systems the viscosity varies instantaneously with the rate of shear, which in a capillary tube rises from zero at the axis to a maximum at the wall. J. C. W.

Surface Tensions of Water–Phenol Mixtures. A. K. Goard and E. K. Rideal (*J. Chem. Soc.*, 1925, **27**, 780—787).—The surface tensions against air of phenol–water mixtures have been redetermined by the drop-weight method. With rising temperature, the surface tensions of the two phases in contact differ by amounts which diminish regularly up to the critical temperature of miscibility, without any inversion at 40—45°. With two-liquid systems in general the difference between the surface tensions of the conjugate solutions is greater the more remote the systems are from the critical solution temperature. W. A. C.

Heat of Wetting of Oils and Metal and its Relationship to Lubricating Power. W. Bachmann and C. Brieger (*Koll. Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 142—154).—Oils of high lubricating

power have much higher heats of wetting against finely-divided copper than oils of low lubricating power. From experiments in which the oil was diluted with half its weight of benzene, which has a low heat of wetting, the heats of wetting in calories per 100 g. of copper, calculated for the pure oil, were castor oil 12·1, linseed oil 13·8, and liquid paraffin 3·85. Petroleum without benzene gave 5·7 and the addition of 1% oleic acid increased the value to 21·3. [Cf. *B.*, 1925, 435.] E. M. C.

Adsorption. X. Coagulation of Diluted Sols by Electrolytes, Acclimatisation, and Behaviour towards Mixed Electrolytes. S. GHOSH and N. R. DHAR (*J. Physical Chem.*, 1925, **29**, 435—461; cf. A., 1924, ii, 394, 733, 737).—The precipitation value for all electrolytes decreases as a sol is diluted. The behaviour of negatively charged mastic sol is abnormal, since the precipitation values for potassium chloride and barium chloride increase as the sol is diluted. The coagulating power of the barium ion is seven times that of the potassium ion with this sol, whereas normally it is about fifty times greater. The coagulation by potassium chloride of Prussian-blue on dilution gives abnormal results, contrary to the experience of Weiser and Nicholas (A., 1922, ii, 266). The precipitation values of a mixture of two electrolytes on antimony sulphide, Prussian-blue, and mastic sols are abnormal in that they are greater than the additive values of the salts alone. The influence of the rate at which the electrolyte is added on the precipitation value (acclimatisation) is more pronounced with mastic sol than with negatively charged ferric hydroxide. The amount of electrolyte required to precipitate arsenic sulphide sol decreases with the age of the sol. The authors consider that the abnormality of sols with respect to dilution, in their behaviour towards mixtures of electrolytes and in respect of acclimatisation, is mainly due to adsorption of ions carrying the same charge as the sol. Negatively charged stannic hydroxide sol has been prepared. M. B. D.

Molecular Association of Furfuraldehyde. F. H. GETMAN (*J. Physical Chem.*, 1925, **29**, 395—398).—Furfuraldehyde gives a normal lowering of the freezing point of benzene and water in dilute solutions. The molecular lowering of the freezing point rises to a maximum at about 0·1 mol. per 1000 g. of solvent and then decreases. The degree of association of freshly-distilled furfuraldehyde is slightly less than that of a sample which had been exposed to light and when calculated from three empirical formulæ is found to be slightly greater than unity. M. B. D.

Nature of the Undissociated Acids. H. VON HALBAN (*Z. Elektrochem.*, 1924, **30**, 601—604).—A reply to criticisms of the author's theory made by Hantzsch (*ibid.*, 194). The question as to whether the process of electrolytic dissociation has an influence on light absorption is discussed, in relation to the alternative views of Hantzsch and Bjerrum. Hantzsch's hypothesis is found to lead to such difficulties that it is regarded as untenable. C. H. D. C.

Nature of Undissociated Acids. A. HANTZSCH (*Z. Elektrochem.*, 1925, **31**, 167—172).—An answer to the criticisms of von Halban (see preceding abstract). The latter's conception of solvate formation is held to be physico-chemical to such a degree that it is incompatible with chemical observations on the alteration of many substances by solvents. N. H. H.

Dissociation of Polyatomic Salts. II. N. SASAKI (*Z. anorg. Chem.*, 1925, **144**, 114—116).—The dilution of a solution of a salt of a multivalent metal, *e.g.*, ferric chloride, increases the concentration of the simplest ions ($Fe^{\cdot\cdot\cdot}$, Cl'); the intermediate ions ($FeCl^{\cdot\cdot}$, $FeCl_2^{\cdot}$) first increase in concentration and then diminish. S. I. L.

Viscosimetric Neutralisation of Monobasic Acids by Alkalis. Comparison of Alkali Chlorates and Bromates with Nitrates. L.-J. SIMON (*Compt. rend.*, 1925, **180**, 1169—1171; cf. A., 1924, ii, 335, 455).—Measurements of the viscosities of aqueous solutions of constant molecular concentration demonstrate sharply when neutralisation of monobasic acids occurs. The present work does not substantiate the connexion between viscosity and isomorphism noted previously for polybasic acids. When viscosity is plotted against the proportion of acid or alkali, the experimental points lie on straight lines intersecting exactly at equimolecular proportions. The viscosities of chloric, bromic, and nitric acids are quite different from one another, whilst those of the salts are quite near. For sodium chlorate and bromate the viscosity is proportional to the concentration, a relation which does not hold for the nitrate. Since the correlation of viscosity with isomorphism fails, it is suggested that an examination of sodium metaphosphate would test whether the formal similarity between sodium nitrate, bromate, and chlorate has any bearing on the matter. R. A. M.

Dielectric Constants of Solutions of Electrolytes. P. WALDEN, H. ULICH, and O. WERNER (*Z. physikal. Chem.*, 1925, **115**, 177—202; cf. *ibid.*, 1924, **110**, 43; A., 1924, ii, 648, 824).—An apparatus is described for determining these constants by a resonance method, somewhat similar to those employed by Theodortschick (*Physikal. Z.*, 1922, **23**, 344) and Lattey (A., 1921, ii, 426). Errors due to damping of waves are eliminated. Theoretical considerations show that with the short wave-length employed (4·5 metres) the conductivity of the dielectric has only a slight effect on the measurements; this was confirmed experimentally and is not in agreement with Lattey (*loc. cit.*). L. F. G.

Light Scattering in Salt Solutions. C. W. SWEITZER (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 125—126).—Solutions of sodium chloride, ammonium chloride, and sodium sulphate have been rendered dust-free by the method of envelopment using aluminium and cadmium hydroxides as precipitates. The observed light scatterings in the solutions are much smaller than those calculated by the Smoluchowski–Einstein–Cabannes formula. J. S. C.

Theory of Concentrated Aqueous Solutions of Strong Electrolytes. E. HÜCKEL (*Physikal. Z.*, 1925, 26, 93—147).—Equations are derived on the basis of the Debye theory for electrode potentials and the electromotive force of simple cells. Activity coefficients of sodium chloride calculated from electromotive force measurements of the cell HgNa|NaCl|HgCl,Hg (T., 1919, **115**, 1020), fall with increasing concentration, pass through a minimum, and then rise. The decrease at lower concentrations is explained by the action of interionic forces in solution. Each positive ion will on the average be surrounded by more negative than positive ions, and *vice versa*. For each ion this inequality of distribution will occur over a characteristic range which will depend largely on the dielectric constant of the solvent. This distribution gradient and therefore its effect on the interionic forces will increase with concentration. A formula for the activity coefficient derived on this basis reproduces the fall in activity at lower concentrations, but the minimum occurs at a much higher concentration than the experimental value.

The effect of the interionic forces on the ions is to cause a deformation of their electron orbits with the development of polarity. This, on the close approach of two ions in water, establishes a repulsive force between them, which may overcome the ordinary attraction and so increase the activity coefficient (*i.e.*, a result comparable with hydration of the ion). Owing to the very steep potential gradient at the surface of an ion the water dipoles at that surface will be strongly oriented, "electrically saturated," and thus the imposition of an external field (due to other ions) will not cause a polarisation proportional to its strength (*i.e.*, to the dielectric constant of the water), but a much smaller one. In effect the dielectric constant of the water will have been lowered by the ions. The magnitude of this decrease depends on the polarising tendency, volume, and the radius of the "saturation sphere" of the ions. Taking the fall in dielectric constant as a linear function of the ion concentration (cf. Blüh, A., 1924, ii, 824) the Debye calculation of the activity coefficient (A., 1924, ii, 386) is modified on this basis. The expression so obtained consists of two parts, one expressing the electrical work due to the ionic force field in the transfer of ions from a weak to a stronger solution, the other the electrical work arising from the change of dielectric constant during this concentration change. An approximate expression for a univalent electrolyte is given as $\log f = -0{\cdot}354\sqrt{2\gamma}/(1+A\sqrt{2\gamma})+C2\gamma$, where $A = a\ 0{\cdot}232\times10^8$ (a=ionic radius), γ=molar concentration, and C= a constant, which for a univalent ion is a determined function of the lowering of dielectric constant of the solvent.

Owing to the lack of data for dielectric constants of solutions, the assumption has been made that the increase of activity coefficients at high concentrations is due entirely to the lowering of dielectric constant. By using electromotive force determinations of the activity coefficients of the chlorides of lithium, sodium, and potassium to evaluate the lowering of dielectric constant in these cases, the values 20, 9, and 6 for normal solutions were obtained.

Values of the same order may be calculated from Blüh's results, and indirectly from the refractive indices of the salt solutions on the assumption that the polarising tendency of water molecules is unaffected by the presence of ions. The activity coefficients for a series of hydrochloric acid solutions were calculated on the assumptions that (1) all the H^+ ions exist free in solution, (2) hydration is practically complete to H_3O^+. The agreement between calculated and observed results is so close in each case that no decision between these views is possible. The activity coefficient in low concentrations is lowered by the addition of a salt with a common ion, but in stronger solutions is considerably raised, the more so the greater the increase of activity coefficient with concentration of the pure salt. F. G. T.

Partial Pressures of Aqueous Solutions of Hydrochloric Acid at 50°. N. C. YANNAKIS (*Bull. Soc. chim.*, 1925, [iv], **37**, 389—404; cf. A., 1923, ii, 611).—Methods for the determination of the partial pressures of aqueous solutions of the halogen acids are reviewed and the effect of errors of experiment on the pressure values obtained is considered. The partial pressures of water and hydrogen chloride over aqueous solutions of hydrochloric acid (6·65—35·9% HCl) have been measured by the distillation method at 50°. A cooled receiver serves to arrest all the water in the distillate, together with a small percentage of acid, the bulk of which is, however, absorbed in U-tubes containing metallic zinc. The partial pressure of hydrogen chloride remains small until the acid concentration reaches 25% and then increases rapidly with increasing concentration, 97% of the total pressure of the 35·9% acid solution being due to hydrogen chloride. A reply is made to the criticisms of Dunn and Rideal (J., 1924, **125**, 676). J. S. C.

Temperature of Vapour above Boiling Salt Solutions. W. H. BAHLKE and R. E. WILSON (*Chem. Met. Eng.*, 1925, **32**, 327—328).—A solution of zinc chloride boiling at 152° was vigorously boiled in a large flask, the vapour passing through screens of wire gauze to a thermometer, and then returning to the bottom of the flask by a reflux condenser. The thermometer readings depend on the outside temperature and varied from 126° to 150°, the latter value being obtained with an outside temperature of 152°. The temperature of the vapours evolved from boiling salt solutions when correctly measured is thus the same as that of the solution, in contradiction to the work of Schreber, whose results are contrary to the second law of thermodynamics. W. H.-R.

Importance of Colloid Chemistry in Mineralogy and Geology. C. DOELTER (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 95—103). E. M. C.

Silver Iodide Hydrosol. Method of Formation of Hydrosols and Gels. IV. A. LOTTERMOSER, W. SEIFERT, and W. FORSTMANN (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 230—244; cf. A., 1907, ii, 851; 1908, ii, 364; 1910, ii, 278).—In the titration of rapidly stirred potassium iodide and silver nitrate solutions the

point of complete flocculation and clearing of the silver iodide sol coincides with the equivalent point only in extremely dilute solutions. In solutions of medium concentration, clearing takes place in both cases before the equivalent point is reached, owing to the flocculating action of the potassium nitrate formed. With less rapid stirring of very dilute solutions of potassium iodide, more than the equivalent amount of silver nitrate is required for complete clearing. The interval between the commencement and the completion of flocculation is greater for the addition of silver nitrate to potassium iodide than for the addition of potassium iodide to silver nitrate. The positive silver iodide hydrosol is thus less stable than the negative one. Pure silver iodide may be prepared by titrating potassium iodide with silver nitrate to the point of clearing and removing potassium iodide from the precipitate by repeated washing and prolonged shaking with water. The positive and negative hydrosols show marked flocculation when equal amounts are mixed and some flocculation when the positive hydrosol is in slight excess. Positive silver thiocyanate hydrosol is much less stable than the negative hydrosol. By analogy with the gold value, a silver iodide value is defined as the amount, in mg., of a protective colloid which serves to prevent complete flocculation during the titration with 0·1*N*-silver nitrate of 25 c.c. 0·1*N*-potassium iodide, diluted to a definite volume. For a series of decreasing potassium iodide concentrations, the silver iodide values of a commercial dextrin were found to decrease exponentially and asymptotically to a constant value. Potassium iodide solution containing dextrin required more than the equivalent amount of silver nitrate for complete clearing; the excess increased regularly with the amount of dextrin up to a maximum value. On the other hand, silver nitrate containing dextrin required less than the equivalent amount of potassium iodide, the numerical relationships being more complicated. E. M. C.

Dispersoid Study of Cellulose. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 103—109).—A lecture, outlining the work in progress in the author's laboratory on the dispersion of cellulose in concentrated salt solutions. E. M. C.

Wool as an Amphoteric Colloid. II. Chemical Theory of Dyeing. J. B. SPEAKMAN (*J. Soc. Dyers and Col.*, 1925, **41**, 172—179; cf. *B.*, 1925, 38).—The dyeing of wool is regarded as a typical case of the combination of an acid or base with an amphoteric colloid, the isoelectric point being about p_H 4·8. De-aminated wool combines with acid dyes in virtue of the -CO·NH- groups. The electric charge on wool is ascribed to membrane equilibrium and this charge may be the immediate cause of dyeing with colloidal dyes. Thus the electrical theory, as also the adsorption theory, is regarded as a particular case of the chemical theory of dyeing. [Cf. *B.*, July 3.] A. G.

Lyophile Colloids and Poiseuille's Law. H. R. KRUYT (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 218—230; cf. de Jong, A., 1923, ii, 132).—When the ratio of the hydrostatic

pressure to the length of the capillary was varied from 0·23 to 1·08, it was found that the viscosity remains constant and Poiseuille's law is obeyed by sols of agar and gelatin, above their gelatinising temperatures, and also by starch, gum arabic, casein, cerium oxide, and silica sols. Agar and gelatin sols below their gelatinising temperature do not obey Poiseuille's law. An "aged" vanadium pentoxide sol showed deviations. Gelatin and cerium sols, which are normal in the Ostwald viscosimeter, are also normal in the Hess viscosimeter. Deviations from Poiseuille's law occur when the particles are not spherical. E. M. C.

Physico-chemical Studies on Gold Hydrosols. A. Galecki (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 154—184).—Gold hydrosols prepared in several ways have been examined with respect to their viscosity and catalytic activity towards hydrogen peroxide. During the ageing and flocculation of gold hydrosols prepared by Zsigmondy's method, the viscosity falls to a minimum value and then increases. During flocculation by the addition of salts the minimum viscosity corresponds with the first change from red to violet. On prolonged ageing, the gold hydrosols give a constant viscosity which is lower than the initial values owing to some precipitation. Exposure of the hydrosols to light increases the viscosity by an amount proportional to the amount of incident light. The catalytic decomposition of hydrogen peroxide by gold hydrosols prepared by Zsigmondy's formaldehyde method decreases with the age of the hydrosol and is increased by the addition of alkali. For gold hydrosols prepared by Zsigmondy's nuclear method, the catalytic activity increases in a linear manner with the dispersion. Gold hydrosols prepared by Doerinckel's method are inactive in neutral solutions and have an optimum concentration of alkali. They inhibit the catalytic activity of the Zsigmondy hydrosols. Gold hydrosols prepared by the Gutbier and Varádi method of reduction with hydroxylamine are more active in neutral solution when prepared at 50° than at other temperatures. There is an optimum alkali concentration for hydrosols prepared below 50°, but no such optimum for those prepared above 50°. It is suggested that the two broad divisions of colloids should be termed the "gold type" and the "protein type." E. M. C.

Water-combination in Colloids. G. F. Hüttig (*Kolloid-Z.*, 1924, **35**, 337—339).—Four general types of water-combination in solid substances can be distinguished. The first type (A) is exemplified by the crystalline hydrates in which the chemically combined water molecules occupy fixed positions in the crystal lattice. For such systems, the vapour pressure–composition curve has the well-known step-like form. In type B, a portion of the water is chemically combined—fixed in the crystal lattice—whilst another portion is free to move in the crystal lattice. A kinetic equilibrium is suggested between these two kinds of attracted water molecules. The vapour pressure–composition curves show strong deviations from the step-like curve of type A. Of the very few cases that have been thoroughly studied, yellow tungstic acid, WO_3,H_2O, and

K_2RuCl_5,H_2O (β salt) are instances in which most of the water is held as in type A, whereas in the zeolites the greater portion of the water is free to move in the crystal lattice. The palladium–hydrogen system is of this type.

In type C most of the water is free and conditions are obtained to which the osmotic laws are applicable. For such systems, the vapour pressure is given by the equation $\log_e p_o/p = k/n$ where p_o is the vapour pressure of pure water at a free surface, k is a constant for the particular system, p is the observed vapour pressure, and n is the adsorbed amount of water. White tungstic acid (α) is an instance of this type, in which case $k = 3{\cdot}0$. This type occupies a position midway between the purely chemical and the purely colloidal systems.

For colloidal systems the vapour pressure is a function of the radius of the capillary as expressed in the relation of Zsigmondy and Anderson (cf. A., 1914, ii, 632). This is type D, of which silica gels afford an example. Type C differs from type D only in that the capillaries in the former are of molecular size. Various combinations of these different types exist. D. C. J.

Colloidal Properties of Soap Solutions. L. GURWITSCH (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 196—199).—Solutions of soaps of the naphthenic acids dissolve considerable amounts of mineral oil. The amount of oil dissolved per unit weight of soap increases with increasing concentration of the soap solution and with increasing molecular weight of the soap. The solubility of the oil decreases with increasing temperature. The interfacial tension of slightly acid mineral oils against water decreases slightly with increase of temperature, but that against sodium hydroxide solutions increases considerably. In dilute alcohol, the soaps are unimolecular and dissolve only traces of oil. These observations are interpreted in terms of the size of the soap micelles; greater amounts of oil are dissolved by soaps with larger micelles.

E. M. C.

Electrical Behaviour of Radioactive Colloidal Particles of the Order of 10^{-5} cm. as Observed Separately in a Gas. F. EHRENHAFT.—(See ii, 465.)

Colloid-chemistry of Linseed Oil. H. VOLLMANN (*Z. angew. Chem.*, 1925, **38**, 337—339).—A survey of the evidence in favour of regarding linseed oil as a colloidal solution, although there is no indication to show which constituents of the oil form the disperse phase. Its colloidal character is shown by its stabilising action on suspensions of finely-divided pigments. Suspensions of Milori-blue, chrome-yellow, ivory-black, and zinc-white were made in equal concentrations in linseed oil and in a paraffin oil of slightly higher viscosity, and in every case the suspension in linseed oil showed a markedly higher stability, this difference being greatest in the case of Milori-blue, and least in the case of chrome-yellow.

P. M.

New Type of Silica Gel. H. N. HOLMES and J. A. ANDERSON (*Ind. Eng. Chem.*, 1925, **17**, 280—282).—It is more satisfactory to wash silica gel free from chlorides after drying and not before in order to prevent collapse of the capillary walls. Silica gel was precipitated together with ferric oxide. After keeping for 2—3 days, the sludge was filtered and allowed to dry very slowly in thick masses. It was then broken up, washed free from chlorides, and activated at about 140° for 12 hrs. This gives a very active gel and the activity can be increased by dissolving out the ferric oxide with hydrochloric acid. Nickel chloride may be substituted for ferric chloride. M. B. D.

Electrolyte-free, Water-soluble Proteins. IV. Acid–Protein Compounds. I. F. MODERN and W. PAULI (*Biochem. Z.*, 1925, **156**, 482—505).—Highly purified solutions of glutin (1·2%), serum-albumin (1·0%), and ovalbumin (1·57%) prepared by a process of dialysis followed by electrodialysis, are shown to give characteristic reproducible values for hydrogen-ion concentration (C_H=7·88×10^{-6}, 3·3×10^{-6}, 1·67×10^{-5}, respectively) and for chlorine ion activity, with mercurous chloride ($C_{Cl'}$=1·27×10^{-4}, 1·82×10^{-4}, 3·17×10^{-4}, respectively). The behaviour of these solutions towards acids is studied and from the $C_{H'}$, $C_{Cl'}$ data an insight is gained into the constitution of acid–protein compounds. Preliminary determinations of the isoelectric points of these solutions have been made using conductivity measurements and the alcohol precipitation method. The C_H for optimum precipitation for ovalbumin is slightly, and for serum-albumin and glutin appreciably higher than the C_H of the corresponding pure protein solutions. The value of C_H for ovalbumin given above is slightly higher than Sørensen's figure (1·574×10^{-5}). P. W. C.

Proteins. VII. Coagulation of Proteins by Heating. M. SØRENSEN and S. P. L. SØRENSEN (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, (9), 1—26).—Mainly the text of a lecture delivered before the American Chemical Society on 3rd October, 1924. C. I. B. V.

Casein. K. KONDO (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, (8), 1—39).—When casein is shaken with aqueous hydrochloric acid, it is found that the amount of protein dissolved decreases as the amount of casein in contact with the solution increases. In explanation, it is suggested that the chlorine ions are bound partly as a complex in the solutions and partly with the hydrogen ions in the solid phase. Calculations show that the casein in solution binds about 2×10^{-4} g.-equiv. of chlorine ions. The observations of Loeb are confirmed by the osmotic pressure and membrane potential measurements of casein solutions with varying quantities of hydrochloric acid. Results in agreement with those of Loeb and of Pauli for the viscosity and conductivity of alkali caseinate solutions are also obtained, except that the casein solutions do not alter their condition in the course of time so long as the quantity of base added is small. The influence of sodium chloride on the

osmotic pressure and membrane potential of sodium caseinate in alkaline solutions is accompanied by a marked increase in the concentration of the hydrogen ions. A theory closely allied to that of Donnan is put forward, and on this basis it would appear that the molecular weight of casein is high. C. I. B. V.

Elasticity of Gelatin Jellies and its Bearing on their Physical Structure and Chemical Equilibria. H. J. Poole (*Trans. Faraday Soc.*, 1925, 27; Advance proof).—The behaviour of cylinders of gelatin jellies under tensile stress has been examined. The strain produced by a steady stress is not a function of the stress alone, but is also governed by a time factor or "creep." If E is the extension of a cylinder of jelly after time T, the graph connecting E and dE/dT consists of two portions, the first being a straight line and the second curved, in agreement with equations deduced from the assumption that jellies are liquid–solid structures, where the solid phase has the form of a mesh of fine fibrils, and in which the "creep" is due chiefly to a reversible flow of the liquid phase in the interstices of the solid, and, to a lesser extent, to an irreversible plastic deformation of the solid. For this type of structure the elasticity at constant temperature should vary approximately with the square of the volume concentration of the solid phase, and this is approximately the case for temperatures from 5·7° to 27°. The elasticity varies greatly with temperature and this is attributed to changes in the equilibrium constant of a reversible reaction, either hydration or hydrolysis, which removes part of the protein substance from the solid to the liquid or *vice versa*. W. H.-R.

Determination of the Elasticity of Gelatin Gels. E. Sauer and E. Kinkel (*Z. angew. Chem.*, 1925, **38**, 413—421).—Methods are described for the determination of the modulus of elasticity of gelatin gels against a shearing force. Such a gel if formed within a glass cylinder adheres firmly to the glass and the deformation of the longitudinal axis under a given air pressure can be measured. For pure gelatin Leik's observation, that it varies as the square of the concentration, is confirmed. [Cf. *B.*, June 26th.] C. I.

Second Isoelectric Point of Gelatin. E. O. Kraemer (*J. Physical Chem.*, 1925, **29**, 410—413).—From the experimental evidence available, the second isoelectric point of gelatin at p_H 7·8 cannot be the isoelectric point of the sol form postulated by Wilson and Kern (A., 1923, i, 68). The author suggests that the behaviour of gelatin is analogous to that of ferric hydroxide sol (cf. Kruyt and Spek, A., 1919, ii, 498). When ferric hydroxide sol is treated with dilute sodium hydroxide it is found to have two regions of stability, corresponding with charges of different signs, and two precipitation zones. The two regions of instability correspond with the two isoelectric points. M. B. D.

Periodic Precipitation in Dilute Gelatin Gels. G. W. Scott-Blair (*Phil. Mag.*, 1925, [vi], **49**, 90—96).—The phenomenon of the formation of Liesegang rings is investigated with silver nitrate and 0·019% potassium dichromate in 0·5 and 1% gelatin.

The age of the gel influences the distance from the surface of the last ring formed. It is suggested that a change in the structure of the gel accounts for this. The effect of exposure to light of different wave-lengths is investigated and there is a fundamental difference in the behaviour with visible and ultra-violet light. As a modification of Ostwald's theory, it is suggested that no sharp metastable region exists, but one of concentration where precipitation becomes probable. Experimental evidence is put forward in support of this view. C. W. B.

Thermolability of Collagen. A. W. THOMAS and M. W. KELLY (*J. Amer. Chem. Soc.*, 1925, **47**, 833—836).—Comparison of the fixation of gallotannin and wattle bark extract by collagen at 40°, in aqueous solution with that at 25° indicates that at 40° collagen is converted into a "sol" form, the isoelectric point of which is approximately p_H 8. [Cf. *B.*, 1925, 370.] F. G. W.

Heat Changes of the Globulins. M. ADOLF (*Kolloid-Z.*, 1924, **35**, 342—344; cf. this vol., ii, 199; see also A., 1924, ii, 831, 728; i, 101; 1923, i, 396). D. C. J.

Theory of Swelling and Reversibility Phenomena of Colloids. W. BILTZ (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 49—52).—In crystalline hydrates and ammoniates the molecular heat of formation and the volume contraction decrease with successive additions. By analogy with such systems, it is suggested that the swelling of colloids is associated with the possession of relatively low lattice-energy. Anhydrous minerals have high lattice energy, as shown in their hardness, and do not swell. Hysteresis effects in the dehydration of hydrated oxides may be due to the formation of some of the anhydride. Protective colloids oppose the action of the lattice forces by preventing sufficiently close contact between the colloidal particles. E. M. C.

Method for Measuring Small Changes of Swelling. P. A. THIESSEN and G. CARIUS (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 245—252).—Changes in the thickness of thin solid discs on treatment with liquids or atmospheres of known humidity are magnified optically. A rod suspended from one pan of an analytical balance rests lightly on the disc and the other pan is connected to the pan of a smaller balance, carrying a mirror on its beam. E. M. C.

Swelling-promoting Effect of Alcohol. F. LOEBENSTEIN (*Kolloid-Z.*, 1924, **35**, 345—353).—The swelling effects of acids such as hydrochloric and sulphuric acids and a series of organic acids, *e.g.*, acetic, propionic, lactic, etc., in the presence and absence of alcohol, on hide-powder have been determined. Measurements were also made using various protein hydrolysis products such as carbamide, alanine, and glycine and also putrefactive decomposition products. The swelling velocity was also approximately determined. It is shown that in many cases alcohol increases enormously the swelling of the protein. Especially is this the case with carbamide, *n*-butyric, phenylacetic, and phenylpropionic acids.

In these cases, a large increase in swelling velocity was also noticed. The effect of the sugars on this phenomenon is of considerable physiological interest. Sucrose and maltose produce a slight volume diminution, which was largely increased on increasing alcohol concentrations. Lactose produced a slight swelling increase both with and without alcohol, whilst dextrose produced scarcely any change in aqueous solution and a slight decrease in alcohol.

D. C. J.

Cell Permeability. I. Swelling of Gelatin under the Influence of Carbamide. F. CHODAT (*Bull. Soc. Chim. biol.*, 1925, **7**, 113—123).—When cylinders or discs of 90% gelatin (neutral, or faintly alkaline to litmus) are immersed in solutions of carbamide at various concentrations, swelling of the gelatin, as measured by the quantity of liquid absorbed, increases with increasing concentration of carbamide up to the point of complete dispersion. At all p_H values there is greater swelling in the presence of carbamide than with water alone, the effect being at a minimum with gelatin at the isoelectric point (p_H 4·7) and increasing on both sides of this point. Glycine, biuret, and hydroxylamine do not show the same phenomena. It is considered that the specific action of carbamide is entirely a physical one and is due to the reduction of surface tension of the liquid caused by its presence.

A theory explaining the course of the swelling of gelatin in weak acids, based on Donnan's theory of membrane equilibrium, is put forward.

C. T. G.

Physico-chemical Analysis of Oxide Sols. A. LOTTERMOSER [with F. FRIEDRICH, H. M. HÜBNER, and A. SZABÓ] (*Z. Elektrochem.*, 1924, **30**, 391—393).—The ultrafiltration of sols of chromic, ferric, or aluminium hydroxide peptised with the corresponding chloride gives an ultrafiltrate that contains only hydrochloric acid and the hydrogen ion concentration of which is the same as that of the sol; the micelles therefore retain chloride ion, the negative charge on which compensates the positive charge on the colloid particles and the original sol may be formulated as $[(x\mathrm{Fe_2O_3},y\mathrm{HCl},z\mathrm{H_2O})\mathrm{H^+}]_n+n\mathrm{Cl^-}$. The specific conductance of the sol is higher than that of the ultrafiltrate, the difference being the true conductivity of the micelles which may thus be considered as complex electrolytes, the equivalent conductivity of which at infinite dilution may be calculated from the equation, $\Lambda_{m\infty}=1000K_m/c_K$, where K_m is the conductivity of the micelles and c_K that of the free chloride ion. The mobility of the micelle cation, $1000K_m/c_K-l_a$, rises abnormally with increasing dilution in sols containing little chlorine owing to displacement of the adsorption equilibrium, but in sols containing much chlorine Λ_∞ approaches a constant as the sol more nearly approximates to a true electrolyte.

A. R. P.

Constitution of Silicic Acid Sols. I. W. PAULI and E. VALKÓ (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 334—340).—Graham's silicic acid sol gives a well-defined specific conductance which remains constant after dialysis. Its constitution may be

represented as $[x(SiO_2+nH_2O).ySiO_3H^-]+y[H^+ \text{or } Na^+]$. In the sol obtained by simple dialysis hydrogen and sodium ions are present in varying proportions. The sodium ions may be replaced by hydrogen ions by electrodialysis. In such purely acidoid sols, there is a close agreement between the values for the hydrogen-ion activity obtained potentiometrically, by conductimetric titration, and from the conductivity. Electrodialysis provides a suitable method for preparing highly concentrated from dilute sols. Although such sols set to fairly hard jellies, they may be redispersed in water and show the same composition as the more dilute sols. In a series of sols the ratio $x : y$, or the number of neutral molecules associated with one ion, varied from 320 to 1200. E. M. C.

Organic Sols of Arsenic Trisulphide. J. J. Bikerman (*Z. physikal. Chem.*, 1925, **115**, 261—272).—The cataphoresis of colloidal solutions of arsenic trisulphide in nitrobenzene and ethyl acetoacetate, in the presence of dissolved salts, has been investigated. Precipitation takes place at a definite potential which is practically independent of the solvent and of the concentration of the sol. The rule connecting the precipitating power of ions with their valency holds in these non-aqueous solutions. L. F. G.

Electrosynthesis of Sulphide Hydrosols. F. V. von Hahn (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 277—286).—The synthesis of hydrosols of sulphide minerals by means of electrical disintegration was studied. Galena and molybdenite gave stable sols on cathodic disintegration and antimonite gave a very slight turbidity. The disintegration of molybdenite took place only when the temperature exceeded 53°; the value of this critical temperature varied by a few degrees according to the source of the mineral. This is the first case of a critical temperature in the electrical synthesis of colloidal solutions. The molybdenite sol showed a striking increase in the amplitude of its Brownian movement when a current was passed through it. The oscillatory discharge gave colloidal solutions with antimonite, sphalerite, chalcocite, and molybdenite; galena and iron pyrites gave only coarsely dispersed systems. Disintegration in the electric arc gave stable sols with galena, chalcocite, iron pyrites, and molybdenite. E. M. C.

Influence of Agitation on the Coagulation of Hydrophobic Sols. H. Freundlich and S. K. Basu (*Z. physikal. Chem.*, 1925, **115**, 203—223).—The effect of agitation on the coagulation of arsenic trisulphide, ferric oxide, vanadium pentoxide, cupric oxide, and gold sols has been investigated. Acceleration is observed especially with comparatively large electrolyte concentrations and strongly coagulating ions; with the last three sols, retardation is observed and this is attributed to peptisation which becomes more effective the lower the concentration of electrolyte and the weaker the coagulating power of the ions. Coagulation velocity curves, without agitation, of cupric oxide sols show an initial induction period which is reduced on increasing the electrolyte concentration or on agitating. These effects, and the temperature effect, are in agree-

ment with Smoluchowski's theory. The formula of Schalek and Szegvari (A., 1924, ii, 115) expresses the influence of electrolyte concentration on slow coagulation. L. F. G.

Ultramicroscopy and Coagulation. A. DE G. ROCASOLANO (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 80—82).—It is suggested that ultramicroscopic observation of the cessation of Brownian motion affords a satisfactory criterion of the occurrence of flocculation in all types of systems. E. M. C.

Stability of Suspensions. I. Rate of Sedimentation of Kaolin Suspensions. W. O. KERMACK and W. T. H. WILLIAMSON (*Proc. Roy. Soc. Edinburgh*, 1924—25, **45**, 59—70).—A comparison has been made of the rates of sedimentation of a kaolin suspension in presence of varying concentrations of electrolyte at different p_H values. Contrary to the general behaviour observed, sodium chloride, and, to a less extent, sodium sulphate, inhibit precipitation in acid solution, possibly due to chemical reaction with the kaolin. Monocalcium phosphate, and still more "superphosphate," have an abnormally large precipitating action above a certain concentration in alkaline solution. This is ascribed to precipitation of basic phosphate on the kaolin particles. In acid solutions, the tervalent aluminium, ferric, and lanthanum ions have very little effect, but a zone of very marked flocculation occurs at p_H 7—8, separating an alkaline region within which the unsedimented particles are negatively charged, from an acid region in which they are positively charged. Similar behaviour has been observed with ordinary colloidal sols such as gold or gum benzoin (Kermack and Voge, following abstract), and also with soil clays (Comber, A., 1922, i, 212). [Cf. *B.*, June 26th.] M. S. B.

Action of Salts with Multivalent Cations on Colloidal Solutions of Gold and Gum Benzoin. W. O. KERMACK and C. I. B. VOGE (*Proc. Roy. Soc. Edinburgh*, 1924—25, **45**, 90—101).—The precipitating action of beryllium sulphate and calcium, ferric, aluminium, and lanthanum chlorides on gold and gum benzoin sols has been examined at different p_H values. There is a marked difference between the behaviour of bivalent and tervalent cations, for, not only do the latter precipitate at very much lower concentrations than the former, but with increasing concentration of the tervalent ions the charge on the colloid changes from negative to positive, and between these regions lies a precipitating zone of concentration. The salts hydrolysed in a greater degree, for example ferric chloride, confer a positive charge in more acid solution than those hydrolysed to a less degree, *e.g.*, lanthanum chloride. The phenomenon appears, therefore, to be related to the presence of hydroxide. Too large an increase in the amount of hydroxide, however, decreases stability, so that probably a certain concentration of metallic ions is necessary. Possibly, therefore, a complex between colloid and hydroxide is formed, associated with a positively charged tervalent ion. The tervalent ions may have a more powerful atomic field of force than the bivalent ions, and thus be

able to form such associated complexes more easily. By testing the non-precipitated, positively-charged, colloidal solutions, protected regions were observed in the case of gold sol with aluminium chloride and of gum benzoin sol with ferric chloride. This should be the region where the highest number of positively charged metallic ions exist simultaneously with sufficient hydroxide to form a surface layer. M. S. B.

Influence of Neutral Salts on some Properties of Gelatin. E. STIASNY (*Kolloid-Z.*, 1924, **35**, 353—358).—It has been shown (cf. A., 1923, ii, 301) that sodium thiocyanate not only causes swelling in collagen but peptises it to a considerable extent; the thiocyanate has no hydrolysing action. Similar effects are found with gelatin. The hydrolytic effect was determined by the formol titration method and by a determination of the Van Slyke value. The peptising effect was determined by ultrafiltration experiments, mutarotation measurements, and viscosity measurements on the dialysed solutions. Sodium thiocyanate produces the same effect in decreasing the specific rotatory power of gelatin at 15° as does a rise of temperature to 35°. Further heating produces no change in the value of the constant. The effectiveness of other salts in decreasing the specific rotatory power follows the Hofmeister series for anions. The effects of sodium thiocyanate on the viscosity of gelatin solutions are traced to a swelling effect which increases the viscosity and a peptising effect which decreases it. It is possible to follow these two effects by observing the viscosity before and after dialysis, because the swelling effect is completely reversible while the peptising effect is not. The peptising effect is not attributable to the rupture of principal valencies but rather to a breaking down of the protein molecule, composed of aggregates of peptone molecules into simpler groups and finally into the peptone molecules themselves. D. C. J.

Action of Colloidal and Semi-colloidal Ferric Hydroxide on Aqueous Gelatin Solutions. I. R. WINTGEN and E. MEYER (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 369—379).—When constant amounts of ferric hydroxide sol are mixed with increasing amounts of gelatin solution and water to give constant final volumes, two types of flocculation are obtained according as the necessary amount of water is added to the ferric hydroxide or the gelatin solution. When the water is added to the gelatin solution, flocculation commences at a well-defined point and the amount of precipitate increases to a maximum. Irregularities are shown when the water is added to the ferric hydroxide. For increasing amounts of gelatin, there is a well-marked commencement of flocculation, followed by an increase to a rather indefinite point of maximum flocculation, a sudden fall to a point of no flocculation and a renewal of increasing flocculation. The amount of gelatin required for the first flocculation decreases with increase in the concentration and the age of the initial gelatin solution. For a series of dilutions of ferric hydroxide sols of different origin, the amount of gelatin required for flocculation decreases in a linear manner with the dilution for typical colloidal

sols, but decreases in a linear manner with the concentration of semi-colloidal sols, containing much hydrochloric acid. The first case is regarded as a simple mutual flocculation and the second as involving, in addition, an increasing dispersion of the gelatin with increasing amounts of hydrochloric acid. E. M. C.

Influence of Gelatin on the Stability of a Colloidal Solution of Cholesterol and on the Charge on the Particles. W. O. KERMACK and P. MACCALLUM (*Proc. Roy. Soc. Edinburgh*, 1924—25, **45**, 71—89).—The stability of a cholesterol sol, prepared by the addition of an alcoholic solution of commercial cholesterol to distilled water, and subsequent filtration, has been examined in solutions of varying p_H value. The minimum amount of sodium chloride required to produce precipitation increases at first with increasing p_H value, reaches a maximum at p_H 7—8, remains constant up to p_H 12, and then returns to zero, indicating that the cholesterol is precipitated by the alkalinity of the solution alone. An examination of the effect of gelatin on the sol, combined with a study of the cataphoretic potential difference (*P.D.*) between the cholesterol particles and the medium, in the presence of gelatin of varying concentration and p_H, shows that gelatin brings about precipitation through a range of p_H values which varies in position for varying concentrations of gelatin and exactly separates the region of positively charged from that of negatively charged colloid. When sufficient gelatin is present the cholesterol particles show a zero potential at p_H 4·7, the isoelectric point of gelatin. On decreasing the p_H the particles acquire a positive charge which increases until a *P.D.* of about 14 mv. is reached, when it remains approximately constant or decreases. Similarly, above p_H 4·7 the *P.D.* becomes negative up to values of about 25 mv. The effect of sodium chloride in the presence of gelatin is to widen the zone of precipitation. The gelatin, however, exerts a protective action against precipitation by sodium chloride, which probably reaches a minimum at the isoelectric point. The amount of gelatin required to protect against precipitation by sodium chloride is approximately that necessary to cover the particles of the sol with a unimolecular layer of gelatin from one to two atoms in thickness. This is also sufficient to keep the particles in suspension even when the *P.D.* is zero. The protective action of gelatin against precipitation by acid and alkali has also been studied. M. S. B.

Effect of Dielectrics on the Stability of Colloids. D. DEUTSCH (*Magyar orvosi Archivum*, 1924, **25**, 511—514).—The concentrations of dielectrics which are able to annul the colloid coagulating action of ammonium sulphate are in the order of their (low) dielectric constants. Organic acids with low dielectric constants are in the same order. By suitable combination of electrolytes and dielectrics, blood-serum, casein, and albumose could be brought into a globulin-like phase. CHEMICAL ABSTRACTS.

Peptisation of Bismuth Hydroxide. A. KUHN and H. PIESCH (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 310—318).—By repeated washing or dialysis of bismuth hydroxide precipitates a

point is reached at which the precipitate forms a sol, stable for a day or two. Sucrose and mannitol act as peptising agents and have maximum effects in 0·05*N*-solutions. With glycerol and lactose the amount of bismuth hydroxide in solution increases regularly with the concentration until the whole of the precipitate is peptised; the peptisation appears to be followed by the formation of chemical complexes. E. M. C.

Protective Action of Soaps for Zsigmondy Gold Hydrosols. B. PAPACONSTANTINOU (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 329—333).—The protective action of soaps towards gold hydrosols, as measured by the reciprocals of their gold values, decreases in the order oleate, palmitate, stearate, myristate, and laurate at the ordinary temperature. Increase of temperature increases the protective action of these soaps, presumably by decreasing the micelle size. Linoleates have about the same protective action as oleates at the ordinary temperature, but the protective action decreases with increase of temperature. The potassium and sodium soaps of lauric, myristic, and palmitic acids have approximately equal actions. At high temperatures, potassium stearate and linoleate are more active than the sodium salts, but sodium oleate is much more active than potassium oleate. E. M. C.

Protection in a Colloidal Solution by Addition of an Electrolyte in Quantities too Small to Effect Flocculation. A. BOUTARIC and (MLLE.) G. PERREAU (*Compt. rend.*, 1925, **180**, 1337—1340; cf. A., 1924, ii, 595).—Addition of small amounts of an electrolyte to a colloidal solution can prevent its flocculation by a much larger quantity of the same electrolyte than is normally necessary. If the time which elapses before flocculation occurs is graphed against the quantity of electrolyte added the curve shows an asymptote parallel to the time axis, of which the abscissa α measures the maximum amount of electrolyte which can be added without causing flocculation. A small amount of sulphuric acid was added to a gamboge suspension which was then left to stand. Redetermination of the graph time/amount of coagulating electrolyte (sulphuric acid), indicated a uniform increase in stability of the suspension. The higher value (β) of the abscissa for the asymptote is a measure of the maximum amount of electrolyte which cannot effect coagulation, and $\beta-\alpha$ indicates the degree of protection.

Using an arsenic sulphide sol treated with lithium chloride and kept for 11 days, the value of $\beta-\alpha$ has been found for various quantities of lithium chloride. The protective effect at first increases with increasing lithium chloride, passes through an optimum and then diminishes. Using the optimum concentration, the variation of $\beta-\alpha$ with the time which elapses between addition of protecting agent and testing its efficiency has been plotted. At first the protection increases with time, then passes through a maximum and diminishes.

In other cases, *e.g.*, gamboge and sulphuric acid, the protective effect increases steadily with the amount of electrolyte added. This

can be reconciled with the preceding case by supposing the maximum protection to be effected by an amount of electrolyte greater than the maximum quantity which may be added to the untreated suspension without causing flocculation. In all cases, the curve showing variation of protective effect with time (that elapses after introduction of the electrolyte) passes through a maximum.

R. A. M.

Sensitisation and Protection by Lipoids. W. Beck (*Biochem. Z.*, 1925, **156**, 471—481).—Both the positive ferric oxide sol and the negative molybdic oxide sol can be rendered much more sensitive to precipitation by electrolytes by the addition of pure lecithin-sol or cholesterol-sol, the action of the latter being somewhat less than that of the former. Lecithin retains its sensitising property on admixture with serum albumin. Congo-red sols containing lecithin are more sensitive than lecithin sols, whereas Congo-red sols containing cholesterol are less sensitive than cholesterol sols. Congo-red sols containing a mixture of 0·5% lecithin and 0·5% cholesterol sols are less sensitive than the original lipoid mixture.

P. W. C.

Dispersion and Base Exchange (Ion Exchange). G. Wiegner (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 341—369; cf. this vol., ii, 36).—The general significance of base exchange in dispersoid chemistry is illustrated by reference to clay. The charge on clay particles is ascribed to the presence of a complex silicate anion, holding by weak residual electrostatic forces a sheath of cations in dynamic equilibrium. The attractive force on these cations increases with increased valency and decreases with increased hydration. Ultramicrons with heavily hydrated cations, *e.g.*, lithium and sodium, are bulky and viscous and resemble hydrophilic colloids; those with less hydrated cations, *e.g.*, cæsium and calcium, are less viscous and resemble hydrophobic colloids. Simple effects of added electrolytes are obtained only if the added cation is the same as that in the outer sheath of the colloid particle; in other cases flocculation effects always include the effects of a base exchange. An extensive series of experiments with clays containing a single alkali or alkaline-earth metal led to the following conclusions. Ultramicroscopic and viscosimetric measurements show that clays are more stable, more hydrated, more viscous, and less sensitive to electrolytes the greater the hydration of their cations. The less hydrated the cation of an added salt, the more rapidly does it flocculate a clay. Increased concentrations of added salt, for dilute solutions and slow coagulation, increases the size of the aggregates formed, as shown in increased viscosities. For equal concentrations of the added electrolyte, the least hydrated flocculating cation forms the largest aggregates and gives the highest viscosity. For more concentrated salt solutions, the viscosity decreases with increasing salt concentration, owing probably to the removal of water from the ultramicrons by the dissolved salts. The viscosity is higher for coagulated clays with heavily hydrated cations than for those with less hydrated cations. Owing to base exchange, a

small amount of potassium chloride, added to a large amount of a calcium clay, has the same flocculating effect as an equivalent amount of calcium chloride, and the Schulze law is thus invalid. The changes in the relative flocculating powers of uni- and bivalent ions with varied concentrations of colloid probably depend on changes in the amounts and relative importance of the exchanged bases. E. M. C.

Application of the Diffusion Coefficient to the Determination of the Molecular Size of Heavy, Amphoteric Hydrated Oxides in Alkaline Solution. G. JANDER and H. SCHULZ (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 109—118).—In the alkali tantalates the ratio $M_2O : Ta_2O_5$ is 7 : 5 and the basicity of the tantalic acid is at least six, according to the variation of the conductivity with the dilution. Potassium tantalate may be represented as $K_7[Ta(TaO_4)_4]$ with a molecular weight of about 1440. An estimate of the molecular weight was made by comparing its diffusion coefficient with that of a salt of similar molecular weight. The technique employed resembled that of Öholm (A., 1905, ii, 147). 0·05*N*-Sodium hexamolybdic periodate, $Na_5[I(MoO_4)_6]$, with molecular weight of 1202, had a diffusion coefficient of 0·29 at 10° in 0·1*N*- and 0·5*N*-sodium nitrate solutions, but gave much higher values in water and in *N*-sodium nitrate solution. 0·05*N*-Potassium tantalate had a diffusion coefficient of 0·24 in 0·1*N*-potassium hydroxide and 0·1*N*-potassium nitrate solutions, but a higher value in water. The molecular weight of the potassium tantalate was thus 1750. E. M. C.

Centrifuging, Diffusion, and Sedimentation Equilibria of Colloids and Substances of High Molecular Weight. T. SVEDBERG (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 53—64).—A mathematical treatment of the determination of the size-distribution of colloidal particles by means of the ultra-centrifuge and measurements of diffusion. E. M. C.

Theory of Membrane Equilibria. E. HÜCKEL (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 204—217).—An exact thermodynamic theory of membrane equilibria is given for ideal and actual solutions of completely ionised electrolytes. Allowance is made in the case of ideal solutions for the diffusion of the solvent through the membrane. Debye's theory of electrolytes is used for the treatment of the equilibria and leads to equations which are in harmony with the experiments of Donnan and Allmand (T., 1914, **155**, 1941) on the potassium ferrocyanide–potassium chloride equilibria. E. M. C.

Use of Tap Water as the Outer Liquid in Dialysis. E. WILKE-DÖRFURT and M. DEKER (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 305—310; cf. Gutbier, Huber, and Schieber, A., 1923, ii, 131).—Silicic acid sol takes up calcium when dialysed against tap water. The calcium is readily removed by dialysis against distilled water provided that some of the original salts

still remain in the sol. After complete removal of the original salts by tap water, the subsequent removal of calcium is very difficult. Tap water containing iron should not be used, since ferric hydroxide is formed in the silicic acid sol and cannot be removed. E. M. C.

Physical-chemical Studies of Synthetic Colouring Matters. W. KOPACZEWSKI (*Rev. gén. Mat. Col.*, 1925, **39**, 34—35, 105—106).—The rates of diffusion of 53 dyes in 1% aqueous solution at 25° through a collodion membrane prepared under carefully defined conditions were measured, and the results, which differ from those obtained by other workers, are tabulated. Resorcin-yellow, eosin, malachite-green, acridine-yellow, and methyl-violet diffuse rapidly; tropæolin, helianthine, gentian-violet, sudan-*G*, and direct-brown diffuse easily; but direct-grey, hæmoglobin, direct-violet-*J*, and direct-green do not diffuse. It is suggested that the osmotic pressure of dyes in solution is due to the anions and non-dissociated molecules rather than to the cations (*e.g.*, sodium). The results of investigations by other workers on the behaviour of dyes in solution are summarised. [Cf. *B.*, 1925, 348.] A. J. H.

Ultrafiltration of Non-aqueous Solutions. H. BECHHOLD and V. SZIDON (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 259—271).—Membranes for the ultrafiltration of non-aqueous solutions may be prepared in Bechhold and König ultrafiltration vessels by coagulating the impregnating material by means of an organic liquid. The best results are obtained with solutions of collodion in ether, coagulated by benzene or toluene. Light petroleum, carbon tetrachloride, and "tetralin" may also be used for the coagulation and cellulose triacetate in acetone for the impregnation. The relative porosities of the membranes may be compared either by replacing the benzene or toluene by alcohol and water and filtering hydrosols of known degrees of dispersion, or by means of the air-bubble method (A., 1908, ii, 823). Oil sols of a number of dyestuffs were found by ultrafiltration and by diffusion in jellies of aluminium oleate and caoutchouc in benzene to be very finely divided and probably in the molecular state. Oil sols of copper and iron oleates were also very finely divided. Successful fractionations were made with sols of cadmium sulphide, zinc sulphide, iron oxide, and graphite in oil and of asphalt in petroleum. E. M. C.

Ultrafiltration under Pressure. B. BRUCKNER and W. OVERBECK (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 192—196).—The rate of ultrafiltration under high pressures is considerably increased by providing constant stirring immediately above the filtering membrane. Two forms of electromagnetic stirrers are described. In one, an iron stirrer is driven by a rotating electromagnet above the ultrafilter. In the other, a hollow iron cylinder is lifted and dropped by means of an annular water-cooled electromagnet actuated by an intermittent current. This is obtained by passing the current through a heating coil in a hydrogen vessel and arranging that the alternate expansion and contraction of the gas

moves a mercury column which breaks and makes the electrical circuit. E. M. C.

Mechanism of Ultrafiltration. J. Duclaux and J. Errera (*Rev. gén. Colloïd.*, 1925, 3, 97—103).—The rate of passage of different liquids through membranes of cellulose nitrate is approximately proportional to their viscosity (*B.*, 1924, 815). This relation has been confirmed under conditions which minimise changes in the membrane during use, and it is shown that membranes of the cellulose type behave as rigid assemblages of fine capillary tubes towards all liquids which exert no solvent action on them. The bearing of these results on the structure of irreversible gels is briefly considered. F. G. T.

Methylene-blue Test. Evaluation of Active Charcoals. W. Mecklenburg (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 132—142).—Considerable errors may be introduced by assessing the relative values of decolorising charcoals on the basis of the amounts of methylene-blue which are adsorbed by equal weights of charcoal. The time (t) in seconds required by different weights (m) in mg. of charcoal, dried at 120°, to decolorise 20 c.c. of 0·15% methylene-blue solution were found to be connected by the equation $(m - a)Z=K$, where a and K are constants. A charcoal was separated into six fractions and the outer specific surfaces (O) were determined microscopically. The constant a was found to decrease gradually with increasing specific surface and the product $K \cdot O^{1·5}$ remained constant throughout the series of fractions. E. M. C.

Theory of Liesegang Rings. Wo. Ostwald (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 380—390).—In all reacting systems giving typical periodic precipitates there are three principal diffusion waves. The added electrolyte diffuses into the gel, the electrolyte in the gel diffuses outwards and that produced by the reaction may diffuse in both directions. In many cases, the product of the reaction has a higher rate of diffusion than one or both of the reactants. Many and probably all reactions giving typical periodic precipitates are balanced reactions and the precipitation may be prevented by changes of dissociation or hydrolysis and the formation of complex and double salts. The precipitation depends on certain critical mixture ratios of the concentrations of reactants which vary over wide ranges through the interference of diffusion waves. The following facts are advanced in support of the theory. Many Liesegang rings may be destroyed by the subsequent introduction by diffusion of the electrolyte produced in the reaction. Rings may sometimes be produced from a continuous precipitate in a gel, *e.g.*, a uniform precipitate of lead sulphate in a gelatin gel containing ammonia is converted into rings by the diffusion of concentrated ammonium chloride. Replacing one component by a compound not giving a balanced reaction results in a continuous precipitate. The distribution of chloride ions in a gelatin gel containing magnesium chloride was found after the diffusion of

ammonia to show a periodic variation between values much higher and much lower than those in the original gel. E. M. C.

Iodine as an Emulsifying Agent. H. N. HOLMES and H. A. WILLIAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 323—325).—By shaking ethyl ether, ethyl acetate, amyl acetate, or amyl alcohol with water containing iodine in solution emulsions of the oil-in-water type are produced. Adsorption films of iodine at the liquid–liquid interface are formed, the change in the iodine concentration being very marked. L. J. H.

Theory of Mordanting. II. E. ELÖD (*Z. angew. Chem.*, 1925, **38**, 199—201).—The mordanting of wool by means of an aluminium bath is a chemical and not a physical process. The production of deleterious hydrochloric acid is avoided by using baths of aluminium formate or by adding sodium formate and formic acid to the aluminium chloride bath. In the case of silk, the production of the acid is surmounted by the use of suitable complex *tin* salts of organic acids, *e.g.*, $Na_2[Sn(HCO_2)_6],5H_2O$, which is produced within the fibres by soaking the fabric successively in sodium formate solution containing free formic acid and in stannic chloride. S. K. T.

Mutual Action of Charged Particles in Liquid Media. E. F. BURTON and J. E. CURRIE (*Phil. Mag.*, 1925, [vi], **49**, 194—209).—A theoretical discussion is given of the Helmholtz double layer theory in conjunction with Smoluchowski's assumptions of mutual attraction of particles in close proximity, and Gouy's explanations of the effect of electrolytes on the ions in the outer layer. Smoluchowski's assumptions are replaced by postulating that (1) particles are drawn together by capillary action when very close to one another, (2) failure to combine under normal conditions is due to mutual repulsion by the effective charges when particles approach one another within the limits of the diffuse outer layer, (3) electrolytes by suppressing the diffusiveness of the outer layer reduce the effective distance of the repulsive action, (4) electrolytes by discharging the particles destroy the source of the force which kept them apart. Experimental evidence is given of scattering of particles due to charge, proving the existence of mutual repulsion. Scattering coefficients for lead shot in water, turpentine, alcohol, ether, and benzene are given, and the scattering is shown to be proportional to the viscosity of the medium.

C. W. B.

Applications of the Kinetic Theory of Gases. N. DE KOLOSSOWSKY (*J. Chim. Physique*, 1925, **22**, 79—82).—On the assumption that C_p is a linear function of the number (n) of atoms in the molecule of a gas, the kinetic theory leads to the relations (1) $C_p=2n+3$, and (2) $C_v=2n+1$. These equations give a much closer agreement with experimental data than the equation $C_p=3{\cdot}5+1{\cdot}5n$ given by Nernst (*Gött. Nachr.*, 1906, **1**, 12).

Combination of the equation of Laplace for the velocity (U) of sound in a gas with the kinetic theory equation for the arithmetic

mean velocity (u) of translation of the molecules, leads to the relation $U/u=0{\cdot}627\sqrt{(2n+3)/(2n+1)}$, which is in good agreement with experimental data. W. H.-R.

Equilibrium Pressures of Individual Gases in Mixtures and the Mass-action Law for Gases. L. J. GILLESPIE (*J. Amer. Chem. Soc.*, 1925, **47**, 305—312).—A mathematical discussion of the law of mass action for real gases. No equation of state yet proposed permits a complete solution. The rule of Lewis and Randall for calculating the fugacity of a gas in a mixture is made exact by the addition of a term involving the integral of $(\delta v/\delta n_1 - V/n_1)dp$ between zero and the total pressure. Exactness of the Lewis-Randall rule, additivity of volumes and activity of heat content are interdependent. A method of experiment employing solid phases to fix the fugacities of the gases in the mixture is outlined. L. J. H.

Representation of the Haber Equilibrium Data by an Equation. L. J. GILLESPIE (*J. Math. Phys. Mass. Inst. Tech.*, 1925, **4**, 84—96).—The equation $\log K_p=(2679{\cdot}35+1{\cdot}1184p)/T-(5{\cdot}8833+0{\cdot}001232p)$ is shown to represent within the errors of experiment the values of the equilibrium constant determined by the Fixed Nitrogen Research Laboratory (cf. Larson and Dodge, A., 1924, ii, 104; Larson, *ibid.*, ii, 331) for the temperature range 325—500° and from 100 atm. to the lowest pressure. For higher pressures the equation $\log K_p=(2172{\cdot}26+1{\cdot}99082p)/T-(5{\cdot}2405+0{\cdot}002155p)$ yields better results. J. S. C.

Equilibrium Proportions in the Formation of Methane from Carbon Monoxide and Hydrogen, and from Carbon Dioxide and Hydrogen. B. NEUMANN and K. JACOB (*Z. Elektrochem.*, 1924, **30**, 557—576).—The equilibrium relations and conditions of maximum yield of methane according to the equations (*a*) $CO+3H_2=CH_4+H_2O$ and (*b*) $CO_2+4H_2O=CH_4+2H_2O$ are investigated experimentally and theoretically. Mixtures of the reacting gases in (*a*) and (*b*) were led over reduced nickel with porous porcelain or magnesia as carriers at different temperatures, and the resulting gas mixtures analysed. Above the temperature at which the yield of methane is a maximum there is a rapid diminution as the temperature rises. In the carbon monoxide reaction, the following changes appear to be involved: $C+CO_2=2CO$, $C+2H_2=CH_4$, and $CO+H_2=CO+H_2O$, the equilibrium constant for the reaction (*a*) calculated from the known constants for the partial reactions agreeing satisfactorily with that derived from the experimentally found partial pressures. The equilibrium is also considered from the point of view of the van't Hoff isochore, the integration constant being deduced from the experimental measurements and from the chemical constants of the individual gases. Similar considerations are applied to reaction (*b*). C. H. D. C.

Influence of Intensive Drying on Inner Equilibrium. A. SMITS (*J. Amer. Chem. Soc.*, 1925, **47**, 794—795).—An exactly similar explanation as that suggested by Lewis (A., 1924, ii, 98)

concerning Baker's experiments on intensive drying was previously put forward by the author (A., 1922, ii, 358). A short statement regarding the results obtained in recently published investigations (T., 1924, **125**, 1068) is appended. J. S. C.

Equilibrium between Creatine and Creatinine in Aqueous Solution. Effect of Hydrogen Ion. G. EDGAR and H. E. SHIVER (*J. Amer. Chem. Soc.*, 1925, **47**, 1179—1188).—The conversion of creatine into creatinine proceeds, in aqueous solution, to an equilibrium, the ratio of the molecular concentration of creatinine to that of creatine being 0·54 at 25°, 1·02 at 50°, 1·59 at 70°, and 2·89 at 100°. In buffer solutions, the above ratio at 50° is as follows: p_H 1, 36·72; p_H 3, 4·01; p_H 4, 1·33; p_H 5, 1·05; and p_H 6, 1·03. At 25°, about 10% of the material is lost by hydrolytic decomposition before equilibrium is reached. The results are discussed mathematically from the point of view of the ionisation of the two bases (cf. Hahn and Barkan, A., 1921, i, 515) and equations are derived for the influence of temperature and hydrogen-ion concentration on the equilibrium. F. G. W.

Equilibrium Diagram of the Binary Alloys of Antimony and Bismuth. B. OTANI (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 293—297).—The equilibrium diagram for the binary alloys of antimony and bismuth was determined by the method of Konno and Ishara (*ibid.*, 1921, **10**, 57; 1924, **13**, 75). The form of the curves for both solidus and liquidus indicates a continuous series of solid solutions, confirming the results of Gautier. The horizontal form of the solidus suggested by Cook (*J. Inst. Met.*, 1921, **26**, 421) is not confirmed. C. S.

Equilibrium Diagrams and the Heats of Formation in some Binary Organic Systems. I. B. E. KITRAN (*Farmaceutski vjesnik*, 1924, **14**, 583—590, 617—620, 668—674, 702—704, 748—751, 777—783).—The equilibrium relations in binary systems with trichloroacetic acid as the first component (C_1) have been studied by the cooling curve method. In the following summary, the composition of characteristic mixtures is expressed in moles % ( ) of the second component (C_2). C_2=*p*-Toluidine: two eutectic points at 18·2° (15) and at 32·7° (65), and a maximum at 84·0° (33·3), corresponding with the compound $Me{\cdot}C_6H_4{\cdot}NH_2,2CCl_3{\cdot}CO_2H$. C_2=Diphenylamine: two eutectic points at 19·6° (15) and at 51·3° (95), and a maximum at 114·2° (66·6) corresponding with the compound $2NHPh_2,CCl_3{\cdot}CO_2H$. C_2=β-Naphthylamine: two eutectic points at 15·0° (12) and at 98·6° (65) and a maximum at (50). It was not possible to determine the m. p. of the equimolecular compound owing to the decomposition of the trichloroacetic acid. Results with phenol confirmed those previously obtained by Kendall (A., 1916, i, 599). Quinol: two eutectic points at 49·5° (2) and at 77·5° (35), and a maximum at 84·9° (25) corresponding with the compound $C_6H_4(OH)_2,3CCl_3{\cdot}CO_2H$. Pyrocatechol, resorcinol, pyrogallol, and naphthalene form no compounds. The data for the respective eutectic points are:

pyrocatechol, 34·7° (25); resorcinol, 25·0° (30); pyrogallol, 40·2° (12); naphthalene, 35·2° (23). C_2=Camphor: two eutectic points at 6·7° (30), and at 22·3° (67) and a maximum at 62° (50) corresponding with an equimolecular compound. The formation of this compound is significant as it accounts for the difference in the results for the heat of combustion of trichloroacetic acid as determined by Berthelot and Matignon (*Ann. Chim. Physique*, 1893, [6], 28, 565) and those obtained by the author. In the second part of the paper binary systems with phenacetin (C_1) have been investigated. C_2 = Urethane gives a eutectic at 45·0° (93·5); C_2= acetaniline, a eutectic at 75·0° (78·4); C_2=benzoic acid, a eutectic at 86·7° (65·7). The third part of the memoir deals with various binary systems. Naphthalene (C_1) gives with *m*-dinitrobenzene (C_2) a eutectic at 51·0° and 44 mol. % of *m*-dinitrobenzene. The different results of Kremann (A., 1905, ii, 77) are attributed to supercooling, to which the mixture is strongly inclined. Phenol (C_1) and *p*-toluidine (C_2) form an equimolecular compound, which exist in two forms, the metastable modification crystallising at 28·6° and the stable at 29·4° (cf. Philip, T., 1903, 83, 828); the eutectic points are at 9·1° (25) and at 20·8° (69). *m*-Chloronitrobenzene (C_1) and *m*-bromonitrobenzene (C_2) yield only a continuous series of solid solutions as previously found by Küster (A., 1892, 396) and Hasselblatt (A., 1913, ii, 484). S. S. M.

Transformation Points of Solid Solutions of Alumina or Chromic Oxide in Ferric Oxide. H. Forestier and G. Chaudron (*Compt. rend.*, 1925, **180**, 1264—1266; cf. A., 1924, ii, 617).—It has been shown earlier by a dilatometric method that ferric oxide undergoes a reversible transformation at 675°. The influence of the addition of the corresponding oxides of aluminium and chromium has now been investigated. Mixtures of hydroxides not ignited above 400° show no lowering of the transition point, indicating mere juxtaposition of the oxides. Heating at 700° affords evidence of solid solution formation which is completed on heating for 2 hrs. at 900°. Addition of alumina causes a linear decrease in the transformation point up to 12% Al_2O_3. Further addition has no effect, the point remaining fixed at 575°. Addition of chromic oxide causes a similar linear decrease (40% Cr_2O_3 corresponds with 230°), but no sharp break in the curve of temperature against chromium content is observed. At high percentages, the influence of chromium oxide on the transition point is much smaller. The oxides of iron and chromium are miscible in all proportions. This conclusion is supported by the fact that the ratio of their molecular volumes is practically equal to unity. R. A. H.

Hydrated Ferric Oxide and Iron Oxides. A. Simon and T. Schmidt (*Kolloid-Z.*, 1925, 36 (*Zsigmondy Festschr.*), 65—80).—The water lost by hydrated ferric oxide, prepared in several ways, was determined at a series of temperatures and a constant pressure of 10 mm. The isobars were quite smooth and gave no evidence of the existence of definite hydrates. A sample prepared by the dialysis of ferric nitrate held water more strongly than those pre-

cipitated from ferric nitrate or chloride. The form of the isobars suggests that at low temperatures the water obeys the osmotic law for amorphous systems with capillaries of molecular size (cf. Huttig, *Fortschritte der Chem.*, 18, 1), and that at higher temperatures the water is held within and affects the lattice structure of the ferric oxide. An *X*-ray analysis showed that the lattice structure of the heated residue was slightly different from that of the ignited oxide. The 10 mm. isobar for the decomposition of ferric oxide showed a sharp break at 1300°, corresponding with a complete conversion to ferrosoferric oxide without the formation of any intermediate oxide. On *X*-ray analysis the interference lines of ferric oxide were of an unknown type, those of ferrosoferric oxide of the spinel type, and those of a partly decomposed ferric oxide were a mixture of those of the two separate oxides and included no other lines. Neither mixed crystals nor intermediate oxides are formed by the decomposition of ferric oxide by heat.

E. M. C.

Equilibrium States of the Ternary Alloys. I. K. IWASE (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 311—354).—The author discusses the equilibrium states for more complicated cases of ternary systems. The conditions for equilibrium are stated in terms of Gibbs' function $\Sigma=\epsilon-T\eta+Pv$ which has a minimum value in the equilibrium state. Each case is dealt with graphically on a triangular base, the Σ values being represented by the height of the vertical ordinates. The discussion refers to systems in which (1) solid solutions are not formed, (2) solid solutions are formed. In each group, special types are dealt with. The method can be used to determine the equilibrium in more complex cases. C. S.

Graphic Representation of Ternary Iron–Carbon Alloys. A. VON VEGESACK (*Stahl u. Eisen*, 1925, **45**, 458—461).—The representation of ternary iron–carbon alloys on an equilateral triangular diagram confines the results to a small strip remote from the carbon apex. To overcome this disadvantage, the use of the method of Goerens is recommended, in which an isosceles triangle is employed, the distance of the carbon apex being proportional to the increased carbon scale chosen. This method fulfils the requirement that the coordinates of all points on the diagram should add up to 100. [Cf. *B.*, 1925, 405.] T. H. B.

Lead–Zinc–Antimony Alloys. G. TAMMANN and O. DAHL (*Z. anorg. Chem.*, 1925, **144**, 1—15).—Of the three binary systems involved, zinc–antimony alone forms compounds; the most stable, ZnSb, m. p. 537°, decomposes into Zn_3Sb_2+Sb. The space model for the ternary system is divided by a ridge corresponding with the binary system Pb–Zn_3Sb_2 into two regions, Pb–Zn_3Sb_2–Zn and Pb–Zn_3Sb_2–Sb, respectively. The ridge has a eutectic at 312°, corresponding with 2% Zn_3Sb_2 and 98% Pb, which gives the maximum temperature for the univariant system, Pb+Zn_3Sb_2+liquid, the ternary eutectics for the regions on the zinc and antimony sides of the ridge being lower; that on the zinc side contains

very little zinc, and the structure can scarcely be distinguished from that of the Pb–Zn_3Sb_2 eutectic. The eutectic on the antimony side is at 244·5°, with the composition 87·1% Pb, 12·5% Sb, 0·4% Zn; in this region miscibility in the liquid state is complete, whilst on the zinc side two immiscible layers are obtained. S. I. L.

System Molybdenum–Nickel–Tin. H. PFAUTSCH (*Z. Metallk.*, 1925, **17**, 122—124).—The solid solution region at the nickel corner of the ternary diagram of the molybdenum–nickel–tin alloys is bounded by a slightly curved line joining the point corresponding with 34% Mo on the molybdenum side with that corresponding with 15% Sn on the tin side. There are no ternary compounds or eutectics. The alloys consisting of nickel-rich solid solutions are harder than the corresponding alloys in which silicon replaces the tin (cf. this vol., ii, 298), but can be easily worked; they are all relatively easily attacked by acid and alkaline liquids. [Cf. *B.*, June 26th.] A. R. P.

System Aluminium–Molybdenum–Nickel. H. PFAUTSCH (*Z. Metallk.*, 1925, **17**, 125—127).—The system aluminium–molybdenum–nickel contains no ternary compounds or ternary eutectics, and there is only a small region of homogeneous mixed crystals at the nickel corner of the diagram. This includes all alloys containing 89% Ni or more and extends along the molybdenum side of the diagram to the 30% Mo alloy and along the aluminium side to the 12% Al alloy. The Brinell hardness of alloys consisting of solid solutions of molybdenum and aluminium in nickel varies from 200 to 286; these alloys, although inclined to be porous are fairly resistant to attack by alkali metal hydroxides, but are somewhat readily corroded by ammonia and mineral acids. [Cf. *B.*, June 26th.] A. R. P.

Ternary System : Silver Perchlorate, Pyridine, and Water. R. MACY (*J. Amer. Chem. Soc.*, 1925, **47**, 1031—1036; cf. A., 1924, ii, 679).—Pyridine forms a set of *compounds* with silver perchlorate similar to the corresponding aniline compounds, viz., $AgClO_4,4C_5H_5N$ (−43° to m. p. 68°; unstable); $4AgClO_4,9C_5H_5N$ (68° to m. p. 95·6°; unstable); $AgClO_4,2C_5H_5N$ (m. p. 147°; stable). Above 130°, metallic silver is deposited; most aromatic amines are oxidised by silver perchlorate. The solubility of silver perchlorate varies from 20% in pure pyridine to less than 0·5% when much water is present; pyridine is practically insoluble in aqueous solutions of the silver salt. Above 30° conjugate solutions appear in the ternary system. Pure pyridine melts at −40·3°.
S. K. T.

Equilibria between Metals and Fused Salts. R. LORENZ (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 243—258).—The author has investigated the equilibria for a number of fused electrolytes of the type $Cd+PbCl_2 \rightleftharpoons CdCl_2+Pb$ and $Cd+Tl_2Cl_2 \rightleftharpoons CdCl_2+2Tl$. The equilibrium is only slightly affected by temperature in the range 600—700°. The influence of diluents was examined in respect of both phases. No salt was found which is

without effect on the fused chlorides, sodium and potassium chlorides forming complex salts, although taking no part in the reaction. The addition of potassium chloride with sodium chloride shifts the equilibrium with increasing additions until a maximum is reached, further additions producing no effect. Bismuth is an entirely indifferent diluent in the metal phase and produces no shift in the equilibria. Antimony forms compounds with cadmium, but not with lead, and shifts the equilibria to a maximum position as with potassium chloride. In the second case, the equilibrium may be written $Cd+Tl_2Cl_2 \rightleftharpoons CdCl_2+2Tl$, or $Cd+2TlCl \rightleftharpoons CdCl_2+2Tl$. The addition of potassium chloride with sodium chloride would affect the second, but not the first case, and the first scheme is therefore preferred. Similarly it is deduced that the metal is monatomic if cadmium is monatomic. The law of mass action is not applicable to such condensed systems, and a new equation is developed for these cases. C. S.

Molten Electrolytes. R. Lorenz (*Z. Elektrochem.*, 1924, **30**, 371—375).—The paper summarises the earlier work of the author and his collaborators on the equilibrium between molten metals and salts. Tammann's theory is applied to the study of the equilibrium of the system $Pb+CdCl_2 \rightleftharpoons Cd+PbCl_2$, and is shown to be in good agreement with previous experimental results. A new formula derived from van Laar's work is employed to represent the equilibrium between thallium, cadmium, and their chlorides. A. R. P.

System Sodium Palmitate–Sodium Chloride–Water. J. W. McBain and G. M. Langdon (*J. Chem. Soc.*, 1925, **127**, 852—870; cf. McBain and Burnett, T., 1922, **121**, 1320).—Isotherms derived from solubility determinations have been drawn up for 60°, 90°, 120°, and 150°. Nearly half the triangular diagram is occupied by the field of isotropic solutions of soap and salt, which are partly colloidal and partly crystalloidal. There is a large field of "wet curds" in which salt solutions are in heterogeneous equilibrium with anisotropic soap solutions; also a number of small fields representing equilibria of the above phases with curd fibres and with two distinct forms of anisotropic soap solution. Of these latter the more concentrated form (about 63% of fatty acid) appears to be a liquid crystal, whilst the other, which occurs in concentrations of 2·5 to 3·0 N_w, is considered to be a conic anisotropic liquid. W. A. C.

Heterogeneous Dissociation Equilibria of Water Vapour and of Carbon Dioxide over Iron and its Oxides. K. Hofmann (*Z. Elektrochem.*, 1925, **31**, 172—176).—The dissociation constants for water vapour over the phase pairs Fe_3O_4–FeO (*a*) and FeO–Fe (*b*) have been recalculated from Eastman's values (A., 1922, ii, 506) for the corresponding carbon dioxide constants, Eastman's own results in this operation being considered unsatisfactory. The values obtained are $\log K_a = -3237/T + 3{\cdot}509$ and $\log K_b = -834/T + 0{\cdot}636$. In addition, the constant for the carbon dioxide equi-

librium over the phase pair Fe_3O_4–Fe has been calculated from Wöhler and Günther's equation for the corresponding water-vapour dissociation, the value obtained being $\log K = +261/T - 0{\cdot}325$. The results are compared with those of other workers. Since the degree of gaseous dissociation in the systems Fe–O–C and Fe–O–H is small, equilibrium is practically independent of pressure. The presence of four phases should therefore cause invariance. In the blast furnace, a fourth phase, viz., carbon as coke, is continually added so that application of the equilibrium diagrams to this process is uncertain. N. H. H.

Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. III. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 42—51).—A mathematical discussion of the membrane diffusion pressure and the osmotic attraction in ternary systems, in which one or more solid phases occur and water is the diffusing substance. L. L. B.

Differential Methods and Apparatus for the Determination of Dissociation Isochores. Thermal Dissociation of Cadmium Carbonate. L. ANDRUSSOW (*Z. physikal. Chem.*, 1925, **115**, 273—288; cf. Centnerszwer and Andrussov, A., 1924, ii, 665; Mazzetti, A., 1924, ii, 853).—An apparatus is described which was used to determine velocities of reaction and equilibrium constants for the system cadmium carbonate–cadmium oxide–carbon dioxide. The equation for the reaction isochore is in agreement with the Nernst equation. L. F. G.

Activity Coefficients of Hydrochloric Acid in Solutions of Ethyl Alcohol. H. S. HARNED and M. H. FLEYSHER (*J. Amer. Chem. Soc.*, 1925, **47**, 82—92).—From the *E.M.F.* of the cells, $H_2|HCl(M)|AgCl|Ag$, in ethyl alcohol and mixtures of ethyl alcohol and water at 25°, the relative activity coefficients of the acid in these solutions have been determined and the absolute activity coefficients approximately estimated. L. J. H.

Activity Coefficient and Ionic Concentration Product of Water in Sodium and Potassium Chloride Solutions. H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, **47**, 930—940).—From previously recorded measurements of the *E.M.F.* of certain concentration cells containing no liquid junctions (Harned, A., 1920, ii, 664; 1922, ii, 255), the activity coefficients of water in solutions of sodium and potassium chlorides have been calculated and also values for the product $\gamma_{H} \cdot \gamma_{OH}/a_{H_2O}$, γ being the activity coefficient and a the activity. From this it is shown that water passes through a maximum state of ionisation with progressive addition of salts, sodium chloride producing a higher dissociation than the potassium salt. All weak electrolytes yielding ions with high activity coefficients probably produce a similar effect. S. K. T.

Free Energy of Sulphuric Acid in Aqueous Sulphate Solutions. H. S. HARNED and R. D. STURGIS (*J. Amer. Chem. Soc.*, 1925, **47**, 945—953).—The activity coefficients of sulphuric

acid in sulphate solutions are calculated from the *E.M.F.* of cells of the type $H_2|M_2SO_4(c_1),H_2SO_4(c_2)|Hg_2SO_4|Hg$, where M=Na or K, and $H_2|MgSO_4(c_1),H_2SO_4(c_2)|Hg_2SO_4|Hg$, where c_1 is $0{\cdot}1N$ to $1N$ and c_2 is $0{\cdot}1N$ and $0{\cdot}01N$. Measurements are also made with the former cells in which $c_1+c_2=0{\cdot}1N$. S. K. T.

Activity of the Hydroxyl Ion in Concentrated Lyes on the Basis of Electrode and Liquid Potential Measurements. R. Fricke (*Z. Elektrochem.*, 1924, **30**, 580—587).—Measurements of liquid potentials, hydrogen electrode potentials, and mercuric oxide electrode potentials lead to fairly consistent results for the activity of the hydroxyl ion in alkali hydroxides at 30° with concentrations up to about $15N$. It is found that the activity increases relatively slowly up to about $10N$, after which it increases very rapidly. When the concentrations are referred to N-solutions, potassium hydroxide is more active than sodium hydroxide of the same concentration. The increasing activity is attributed in part to lower hydration of hydroxyl ions at higher concentrations. C. H. D. C.

Affinity. T. de Donder (*Compt. rend.*, 1925, **180**, 1334—1337).—A mathematical treatment of affinity from the point of view of thermodynamics. In the Clausius equation, $dA=TdS-dQ \geqq 0$ (S is entropy, T abs. temperature, dQ heat absorbed during a given transformation), dA is identified with affinity. On this basis, the van't Hoff and Le Chatelier theorems are deduced in a generalised form. R. A. M.

Thermodynamic Deductions from the Equation of State for Adsorbed Substances. M. Volmer (*Z. physikal. Chem.*, 1925, **115**, 253—260).—By means of a cyclic process Gibbs' equation is derived, and by combining this with the corrected equation of state (cf. preceding abstract) further equations are derived, similar to those already obtained from kinetic considerations by Langmuir (A., 1918, ii, 430). L. F. G.

Thermodynamics of Surface Actions. L. Gay (*J. Chim. Physique*, 1925, **22**, 115—130).—Theoretical. A description of the general principles underlying the application of thermodynamics to surface actions.

The phase rule as usually formulated involves the assumption that the phases in equilibrium are all at the same pressure, which is not necessarily the case when curved interfacial boundaries are present. If the pressure of each phase is considered as a separate variable, the number of degrees of freedom of a system, in which all the phases are in contact, is independent of the number of phases, and equals $(n+1)$, where n is the number of components. W. H.-R.

Relation between Deviations from Raoult's Law and the Partial Heats of Solution. J. A. V. Butler (*J. Amer. Chem. Soc.*, 1925, **47**, 117—122).—In those cases for which data exist, there is an almost exact proportionality between the deviations

and the partial heats of solution. From statistical theory it is suggested that this linear relation between the two quantities would be explained if the heat of solution is divided between the passage from the interior to the surface and the escape from the surface in definite proportions for each system. L. J. H.

Proposal to Establish a Secondary Thermochemical Standard. W. Swientoslawski (*Bull. Soc. chim.*, 1925, [iv], **37**, 84—89; cf. A., 1924, ii, 39).—A protest against the use of any thermochemical standard (for the combustion of organic substances) other than that accepted internationally, *i.e.*, benzoic acid, except as an auxiliary to prove the purity of the benzoic acid employed in the calibration. L. J. H.

Thermal Method for the Study of Gaseous Systems. G. Piccardi (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 226—229).—The results of experiments on dry air and on nitrogen tetroxide show that the method previously described (A., 1924, ii, 537, 600) gives at least qualitative indications of the changes in the gas which are produced by a rise of temperature. T. H. P.

Heats of Solution of Glycerol. N. de Kolossowsky (*J. Chim. Physique*, 1925, **22**, 83—93).—Using 99% glycerol and a Berthelot calorimeter, the following values have been determined for the molecular heats of solution of glycerol. In water, +1335 cal. for dilutions from 1/140 to 1/200 mol.; in methyl alcohol −370 cal. for a dilution of 1/50 mol.; in an equimolecular mixture of water and methyl alcohol, −417 cal. for a dilution of 1 mol. glycerol to 86 mols. of mixed solvent; in mixtures of water and ethyl alcohol containing 30, 33·83, and 62% ethyl alcohol (by weight), 0, −412, and −337 cal., respectively. The heats of dilution in water and pure or aqueous methyl alcohol are comparatively small. The most probable value for the heat of solution of 1 mol. of anhydrous glycerol in 200 mols. of water is +1450 cal. W. H.-R.

Heats of Solution of Phenols in Water. N. de Kolossowsky and A. Kraeff (*J. Chim. Physique*, 1925, **22**, 94—96).—The following molecular heats of solution in water have been determined, using a Berthelot calorimeter. Phenol, −2762 cal.; *o*-cresol, −3126 cal.; resorcinol, −3636 cal.; quinol, −4446 cal.; pyrogallol, −3911 cal. W. H.-R.

Heats of Solution of Barium Chloride in Aqueous Alcohol. N. de Kolossowsky (*J. Chim. Physique*, 1925, **22**, 97—100).—The heats of solution of anhydrous barium chloride in aqueous solutions of ethyl alcohol containing 20·36 and 33·83% alcohol, are −130 and −944 cal., respectively; the corresponding values for the hydrated salts $BaCl_2,2H_2O$ are −6718 and −7416 cal. The heats of hydration are thus +6588 and +6472 cal. in the two cases, indicating that the addition of alcohol to water lowers the heat of hydration, which in the case of pure water is +7465 cal. W. H.-R.

Theory of Electrolytic Conductivity. O. REDLICH (*Physikal. Z.*, 1925, **26**, 199—205).—The range of applicability of the Debye and Hückel equations (A., 1923, ii, 724) without the introduction of arbitrary constants is considerably extended by the introduction of a single universal constant, which, although possessing a theoretical basis, has to be evaluated from experimental data. This constant, 0·694, is obtained as a correction factor in calculating the ionic radius by means of a modified Stokes' law (Redlich, *ibid.*, 1925, **26**, 155), and is evaluated from conductivity data for potassium chloride. It is valid for all binary electrolytes. An application of Ohm's law to the inter-ionic forces leads to an expression which includes the previously neglected second term in $\sqrt{c}$ of the Debye and Hückel equation, contains no arbitrary constants although it includes the above universal one, and satisfactorily reproduces the conductivities of binary electrolytes up to 0·1*N* concentration.

F. G. T.

Conductivity of Electrolytes. C. W. DAVIES (*J. Physical Chem.*, 1925, **29**, 473—481).—For concentrations below 0·002*N* conductivity data agree with the relation: $\lambda_\infty - \lambda_c = K\sqrt{c}\lambda_\infty$, where K is a constant, c the concentration in g. equivalents per litre, and λ_∞, λ_c the equivalent conductivities of univalent ions. M. B. D.

Precision Determination of the Electrical Conductivities of Concentrated Aqueous Solutions of Calcium Chloride. M. CROWE (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 339).—Determinations of the electrical conductivities of aqueous solutions of calcium chloride at concentrations from 25% to 50% for temperatures between 10° and 30° have been made, the accuracy being estimated as about 0·05%. Details will be published later.

J. S. C.

Theory of Electrolytic Ions. XXIX. Method of Measuring Conductivity by the Use of an Amplifying Tube. R. LORENZ and H. KLAUER (*Z. anorg. Chem.*, 1924, **136**, 121—146).—In the ordinary Wheatstone bridge arrangement for the determination of the conductivity of dilute solutions, the use of an amplifying tube in series with the telephone permits of a much sharper determination of minimum tones. Small changes in the potential of the grid are more highly amplified when the potential approximates to zero, so that a very sudden fall in the intensity of the tone is noticeable as the potential actually reaches zero. When the system contains an unbalanced capacity there must be a compensating condenser in the circuit and the electrodes used should be slightly platinised. Some curves obtained by the use of the apparatus with and without the amplifier are reproduced and a device for comparing tone intensities is described and illustrated.

A. R. P.

Electrical Conductivity of Films. G. TAMMANN and H. BREDEMEIER (*Z. anorg. Chem.*, 1925, **144**, 64—68).—The growth of films on metal surfaces may proceed in accordance with either

a parabolic or an exponential law. In the former case, the concentration of the attacking agent (halogens) falls uniformly throughout the film, and the films show electrolytic conduction, as indicated by polarisation effects; in the second case, the concentration of the attacking agent (oxygen or nitrogen) varies exponentially with the thickness, and the film shows metallic conduction. S. I. L.

Conductivities in Liquid Hydrogen Sulphide Solutions. G. N. QUAM and J. A. WILKINSON (*J. Amer. Chem. Soc.*, 1925, **47**, 989—994).—The conductivities of saturated solutions of substances in liquid hydrogen sulphide (sp. cond. $<1 \times 10^{-11}$ ohm^{-1}) at the temperature of solid carbon dioxide are recorded. Some solutions will not conduct, *e.g.*, those of many organic compounds, ammonium and bismuth chlorides; the latter forms an insoluble thio-compound. The halides of the phosphorus group of elements exhibit better conductivities the higher the atomic weight; halogen acid is probably not formed in these solutions. Halogen solutions conduct well; observations with iodine confirm Walden's explanation of this phenomenon (A., 1903, ii, 408). Progressive introduction of alkyl radicals in ammonium chloride causes a corresponding increase in the conductivity of the solution. Solutions of acetic acid only conduct at the ordinary temperature, whilst the anhydride, the acid chloride and thioacetic acid show a maximum conductivity, and reaction with the solvent occurs. S. K. T.

Transference Numbers of Hydrochloric Acid in Solutions of Ethyl Alcohol. H. S. HARNED and M. H. FLEYSHER (*J. Amer. Chem. Soc.*, 1925, **47**, 92—95).—By comparing the data previously obtained (cf. this vol., ii, 538) with measurements of cells of the type Ag|AgCl|HCl(m_2)|HCl(m_1)|AgCl|Ag, the transference numbers of the hydrogen ion are obtained at 25° for solutions of hydrochloric acid in ethyl alcohol and in 50% ethyl alcohol–water mixtures. L. J. H.

Transport Numbers by the Moving-boundary Method. III. Novel Form of Apparatus. D. A. MACINNES and T. B. BRIGHTON (*J. Amer. Chem. Soc.*, 1925, **47**, 994—999).—A transport apparatus is described in which two sharp boundaries are very simply obtained. Results should not be calculated from the ratios of the boundary movements in very accurate work. S. K. T.

Transport Numbers by the Moving-boundary Method. IV. Transport Numbers of some Chloride Solutions. E. R. SMITH and D. A. MACINNES (*J. Amer. Chem. Soc.*, 1925, **47**, 1009—1015).—An apparatus is described similar to, but smaller than, that previously used (Smith and MacInnes, A., 1924, ii, 727) by means of which correct values for transport numbers are obtained throughout wider ranges of indicator concentrations. Values obtained at 25° in 0·1*N*-chloride solutions were: $N_{Na^+}=0{\cdot}3865$, $N_{H^+}=0{\cdot}8320$, $N_{K^+}=0{\cdot}492$; in 0·2*N*-potassium chloride solution, $N_{K^+}=0{\cdot}4900$. The product of the transport number of the chloride ion and the corresponding equivalent conductivity for the 0·1*N*-

solutions is constant, which shows that these salts have the same degree of ionisation at 25°. This also holds at 18° (MacInnes, A., 1921, ii, 619). This ionisation is considered to be complete, so that the influence of concentration on equivalent conductivity is due to change in mobility rather than in the numbers of ions.

S. K. T.

Transport of Electrolytes. Mobilisation of Ions by Intermolecular Exchanges. W. MESTREZAT and (MLLE.) Y. GARREAU (*Compt. rend.*, 1925, **180**, 1266—1268).—Certain ions have been shown to possess enhanced mobilities under physiological conditions. It is suggested that a mobile ion may be replaced by another of the same sign, taken from the solute on the other side of the membrane. If the salts NaX and NaCl are on either side of a membrane which is penetrated more easily by the anions than the cations, it would seem possible to have chains of the ions of these salts moving in opposite directions with penetration of the membrane by the anions only. Once through the membrane, the anions are temporarily liberated from the electrostatic forces of the molecule; a rearrangement of forces occurs and fresh anions reinforce the chains. Thus, diffusion occurs in cascade fashion. This method of representation combines the concept of the molecular unit (electrostatic forces) with mobility of ions in the living organism. Side by side with small changes in the diffusion of the less mobile ions, it establishes a circulation of the more mobile ions of the same sign, tending towards complete exchange on either side of the membrane. The presence of molecular systems capable of exchanging ions in this way gives a simple conception of rapid transport of anions and of selective effects in the organism.

R. A. M.

Transport of Electrolytes. Velocity of Diffusion through a Membrane and Ionic Selection. W. MESTREZAT and (MLLE.) Y. GARREAU (*Compt. rend.*, 1925, **180**, 1069—1071).—A study has been made of the rates of diffusion of the anions when 0·25*N*-solutions of sodium iodide, sodium nitrate, magnesium sulphate, disodium hydrogen phosphate, and potassium ferrocyanide are dialysed through animal or collodion membranes against distilled water or dilute solutions of sodium chloride (0·01*N*—0·25*N*). The presence of sodium chloride in general increases the velocity of diffusion to an extent of more than 100% and in the case of the ferrocyanide of 1268%. The maximum effect is observed with concentrations of NaCl, which vary inversely as the valency of the anion involved: 0·14*N* for univalent, 0·08*N* for bivalent, 0·05*N* for tervalent, and 0·01*N* for the quadrivalent ions. The observed maximum of diffusion also varies approximately inversely as the valency of the diffusing ion, the concentration of the diffusate being after 2 hrs. 0·043*N* for I' and NO_3' and 0·023*N* for the SO_4'' ion. The large effect produced by a relatively small amount of sodium chloride can only be explained by a concentration of the salt on the outer face of the membrane which modifies the potential difference between it and the liquid and so hinders the passage

backwards of the anions through the membrane. It is significant that the concentration of sodium chloride in the body fluids is close to that found to be the optimum concentration for the diffusion of uni- and bi-valent ions. G. M. B.

Electrode Potentials and the Free Energy of Solvation. J. HEYROVSKÝ (*J. Physical Chem.*, 1925, **29**, 406—409; cf. this vol., ii, 404).—The electrode potential depends, not only on the number of ions in solution, but also on their degree of solvation and therefore on the vapour pressure of the solution. The activity coefficient is therefore expressed mathematically by means of the free energy of solvation. M. B. D.

Electromotive Behaviour of Magnesium. A. SMITS (*Z. Elektrochem.*, 1924, **30**, 223—230).—The values of the potential of magnesium against solutions of its salts, as measured by other workers, are discussed from the point of view of the author's theory of allotropy, and it is shown that the too negative value of the results cannot be accounted for by the formation of a film on the surface of the metal which resists the passage of electrons. It is deduced mathematically that the hydrogen in the hydrogen film on the metal is still in process of formation and that its solubility product is greater than if it were in internal equilibrium. The potential of an amalgamated magnesium electrode against a *M* solution of magnesium sulphate is −1·85 volt. A. R. P.

Influence of Finely Porous Materials at the Liquid Boundaries on Liquid Potential. R. FRICKE (*Z. Elektrochem.*, 1924, **30**, 577—580).—Experimental evidence is adduced that the presence of porous materials, such as the filter-paper pads used by Müller at the liquid boundaries in concentration cells, has an appreciable effect on potential measurements. The measured values are lower than those obtained with a pure liquid boundary, and a time factor is introduced, the *P.D.* gradually increasing over many hours. It is noted that Müller has recently overcome the difficulty connected with his arrangement. C. H. D. C.

Potential Differences between Liquids and Air. A. FRUMKIN (*Kolloid-Z.*, 1924, **35**, 340—342; cf. A., 1924, ii, 462).—Inorganic electrolytes charge the water–air interface either not at all or negatively, the greater the charge the less hydrophile the anion. Organic substances charge the water-surface according to their capillary activity. Comparing concentrations of different substances which correspond with equal adsorptions, it is found that the charge produced per adsorbed molecule varies but slightly with the number of adsorbed molecules. For homologous series, this quantity is independent of the length of the carbon chain. An explanation is based on the Langmuir–Harkins theory of orientation. The Kenrick method of measurement (cf. A., 1896, ii, 460), although convenient and accurate, has its limitations. A new apparatus has been devised capable of measuring the potential difference when the liquid surface is still. The liquid is placed in a rectangular glass vessel and connected to earth through a

calomel electrode. A variable *E.M.F.* is interposed between the calomel electrode and earth; 4—6 mm. distance from the liquid surface is a platinum wire 0·1 mm. thick connected to a quandrant electrometer. The wire is heated to white heat by a very small (2 mm. long) gas flame. Care is taken completely to insulate the gas flame. When the liquid surface is charged the electrometer deflection can be brought back to zero by the introduction of an *E.M.F.* between the calomel electrode and earth. This gives directly the value of the required potential difference. The readings obtained in the course of 1 hr. show variations of less than 10 millivolts and the absolute values agree with those obtained by Kenrick's method. The potential difference between air and water when a unimolecular layer of a substance such as oleic acid or olive oil covers the water-surface has been measured. By varying the surface area a curve is obtained showing the variation of the potential difference with the area occupied per molecule or with the film thickness. As the area occupied by the oil film is decreased, the value suddenly rises sharply to a new value, the curve being very similar to that obtained in investigations on the variation of surface tension with the thickness of the oil film. The author does not accept Langmuir's suggestion of the existence of a "liquid" and "vapour" condition of the film, but suggests that the "liquid" condition of Langmuir corresponds with the formation of molecular complexes or micelles. D. C. J.

Mechanism of the Development of a Potential Difference at the Boundary of Two Phases. D. Reichinstein (*Z. Elektrochem.*, 1924, **30**, 238—246).—Assuming that the partition coefficients of all the ions and electrons are of equal value, the author deduces the following generalisations: a necessary condition for the development of a potential difference at the phase boundary is the existence of a single asymmetry in the homogeneous phase; a symmetrical equilibrium is produced when a solid which sets up a chemical equilibrium between ions and electrons in a finite time is introduced into a solution in which a non-asymmetrical equilibrium is maintained, and, finally, a potential difference is set up at the boundary of two phases if different degrees of asymmetry prevail in both phases in relation to the same electrolytic or electronic dissociation process. A. R. P.

Thermo-electricity of Electrolytes. J. Thiele (*Physikal. Z.*, 1925, **26**, 321—329; cf. Schmidt, A., 1924, ii, 727).—When long strips of quartz are coated with solid salts and heated at one end, suitable contacts being applied at the extremities, the thermo-electric difference of potential is measurable by means of an electrometer. With halides of cadmium, lead, thallium, silver, and copper, also sodium and potassium nitrates, from 300° downwards, the difference of potential is directly proportional to the temperature difference and ranges from 20×10^{-5} volt to 136×10^{-5} volt per 1°. The temperature gradients in successive series of measurements on a given salt, however, show some divergences. In all cases,

the hot end becomes positive, in agreement with the view that cations alone migrate, whilst heavy complex anions remain stationary. Mercuric chloride and iodide show no thermo-electric effect. Similar measurements with aqueous solutions of electrolytes confirm the known fact that the current in that case flows in the opposite direction, the temperature gradients being again linear.

W. A. C.

Decomposition Potentials of Non-aqueous Solutions. W. FINKELSTEIN (*Z. physikal. Chem.*, 1925, **115**, 303—329).—Current–voltage data, between 0 and 9 volts, were obtained for the following solutions: iodine trichloride in bromine, liquid sulphur dioxide, arsenic trichloride, nitrobenzene, dichloroacetic acid, acetic acid; iodine bromide in bromine, liquid sulphur dioxide, arsenic trichloride, nitrobenzene, acetic acid; phosphorus pentabromide in bromine, liquid sulphur dioxide, arsenic trichloride, nitrobenzene; phosphorus oxychloride in bromine; ether tribromide in ether, bromine, chloroform; acetamide in bromine; benzamide in bromine; antimony tribromide in bromine. No polarisation was observed with any of these solutions, *i.e.*, each series of data when plotted gives a straight line passing through the origin. Critical decomposition potentials were observed with the following solutions: dimethylpyrone ditrichloroacetate in benzene and chloroform; dimethylpyrone in liquid sulphur dioxide and arsenic trichloride; arsenic tribromide in ethyl alcohol, liquid sulphur dioxide, nitrobenzene; arsenic trichloride in nitrobenzene; antimony tribromide in nitrobenzene and ethyl acetate; bismuth tribromide in nitrobenzene; phosphorus trichloride in nitrobenzene. As the nature of the solvent had very little effect on the decomposition potential, it was assumed that heats of solution were small. The temperature coefficients of the decomposition potentials of the last-mentioned series of solutions (trihalides in various solvents) were calculated by the Helmholtz formula; experimentally found values for arsenic trichloride in nitrobenzene and antimony tribromide in ethyl acetate were in good agreement. Yellow phosphorus, antimony, and bismuth, respectively, precipitate arsenic from solutions of arsenic trichloride in nitrobenzene. L. F. G.

Reduction Potential of Dicyan-quinhydrone. E. K. RIDEAL (*Trans. Faraday Soc.*, 1925, **27**; Advance proof).—The *E.M.F.* of a cell of the type substituted quinhydrone in 0·1*N*-HCl|0·1*N*-HCl| benzoquinhydrone in 0·1*N*-HCl has been determined. For 1 : 2-dicyanoquinhydrone, the *E.M.F.* is 0·27374 and 0·27224 volt at 0° and 25°, respectively, giving a temperature coefficient of −1·5 mv. for 25°. The corresponding reduction potential of 1 : 2-dicyanoquinhydrone is $\pi_{0.250}$=0·9712 volt, a much higher value than those obtained for the 1 : 4-dichloro or 1 : 4-dibromo substituted compounds.

W. H.-R.

Relation between Energy of Escape of Electrons and Electrochemical Normal Potential. A. GÜNTHER-SCHULZE.—(See ii, 477.)

Electrolytic Deposition of Calcium from Solutions of Calcium Hydroxide in Water, and Calculation of the Normal Potential of Calcium. A. EILERT (*Z. Elektrochem.*, 1925, **31**, 176—180).—An amalgam containing up to 2·4% of calcium may be obtained by the electrolysis of a saturated solution of calcium hydroxide in water, using a platinum anode and a mercury cathode, provided that traces of water are previously removed from the mercury and that the electrolyte is free from suspended particles. The discharge potential of calcium (ϵ_h) in saturated calcium hydroxide solution is found to be −1·81 volts, and from this and other data the normal potential is calculated. The value obtained, −2·57 volts, is in good agreement with Wilsmore's figure, −2·56 volts. N. H. H.

Transfer Resistance. A. L. FERGUSON and G. VAN ZYL (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 145—160).—The concept of "transfer resistance" and in particular the work of Newbery are attacked. A large number of experiments on decomposition potentials have been carried out by both the direct and commutator methods, the influence of such factors as the concentration of the electrolyte, speed of commutator, current density, and the size and nature of the electrode surfaces being studied. The effect of time on the polarisation was largely eliminated by making the measurements several hours after potential was applied or increased. The conclusion is that the differences between the various potentials measured by the two methods are due to sources of error in the commutator method. The discharge potential of an electrode would be the same as the charge potential if the two could be measured at the same instant by the commutator method and both would be the same as the value measured by the direct method. The existence of "transfer resistance" is therefore denied. N. H. H.

Electrical Overvoltage. A. SMITS (*Z. Elektrochem.*, 1924, **30**, 214—223).—A theoretical and mathematical discussion of the application of the author's theory of allotropy to overvoltage is given. The theory assumes that the origin of overvoltage is to be found in the electrodes themselves, which are assumed to consist of molecules, atoms, ions, and electrons in a state of equilibrium and that, when an electrode is placed in contact with an electrolyte, its surface is covered with a liquid film with which the metal is in equilibrium. As an illustration of the theory the case of a cell with electrodes of hydrogen and platinum or palladium is considered. A. R. P.

Effect of Surface Condition on Overvoltage. M. KNOBEL (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 139—144).—Measurements have been made at different current densities of the hydrogen overvoltages for smooth and spongy surfaces of lead, copper, gold, cadmium, platinum, silver, and palladium, and oxygen overvoltages for smooth and spongy nickel and platinum. Arguments are put forward to show that the lowering of overvoltage on the

spongy surfaces is due to the changed nature of the surface and not to the greater magnitude of the area alone. For example, a roughly crystalline surface of silver showed nearly the same overvoltage as a smooth surface whilst a true sponge gave a much lower value. N. H. H.

Anode Effect. C. S. TAYLOR (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 161—171).—An analysis of previous observations of the anode effect in the electrolysis of fused electrolytes and its causes is presented. Any combinations of conditions which permit local overheating at any point of the anode surface may produce the effect. At this point, a gas film is formed and by the diversion of current to other parts of the anode area, which are already in a metastable state, these become overloaded and the result is the practically instantaneous spread of the film over the whole anode surface. For example, a high-resistance film of solid impurity or of frozen electrolyte on certain portions of the anode surface may start overheating at other points. The combination of factors which lead to the effect may, however, differ widely. N. H. H.

Effect of Small Alternating Currents on Some Polarised Electrodes. S. GLASSTONE (*J. Amer. Chem. Soc.*, 1925, **47**, 940—945).—The previously recorded potentials indicating the influence of a small alternating current on cathodic and anodic overvoltages are probably doubtful, mainly owing to the use of a direct method of measurement. By the use of superimposed direct and alternating currents for certain metals in normal sulphuric acid and sodium hydroxide solutions, it is found that the polarisation is reduced in a few cases only. It is suggested for these cases that rapid variation of the current strength, due to the superimposition, causes a diminution in the tension at the metal–gas–electrolyte interfaces, thus favouring bubble formation and retarding the accumulation of active material. The results of Grube and Dulk (A., 1918, ii, 348) and of Goodwin and Knobel (*Trans. Amer. Electrochem. Soc.*, 1920, **37**, 617) are probably not valid. S. K. T.

Effect of Alternating Current on Polarisation during Metal Deposition. N. ISGARISCHEV and S. BERKMANN (*Z. Elektrochem.*, 1925, **31**, 180—187).—The effect of an alternating current on the cathodic and anodic polarisation of nickel during the electrolysis of solutions of nickel ammonium sulphate and of nickel sulphate, with and without the addition of sulphuric acid and of gelatin, has been studied. From the character of the cathodic polarisation curves, it is concluded that there are at least two effective processes, the deposition of the nickel and the evolution of hydrogen. It is highly probable that the alternating current influences strongly only one of these processes and that this influence is largely affected by the frequency. The concentration of hydrogen ions and of gelatin has a considerable effect on the curves. The effect of the alternating current on the anodic polarisation of nickel and on the cathodic polarisation of zinc in solutions of zinc sulphate is not so marked. N. H. H.

Polarisation and Concentration Changes at the Cathode during Electrolysis of Copper Salts. A. R. GORDON (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 116—117).—The observed polarisation values are much greater than those predicted by theory. On starting the current there is an instantaneous initial polarisation π_0, over and above the *CR* drop; during electrolysis the polarisation increases up to the moment at which hydrogen is evolved, in accordance with the equation, $\pi=\pi_0+0{\cdot}188 \log z_0/z$, where z_0 is the concentration of copper in the body of the electrolyte and z its concentration at the cathode. The value of π_0 is apparently dependent on the nature of the surface and previous treatment of the cathode. J. S. C.

Electrolysis with Gas Cathodes. A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1925, **31**, 187—189).—Experiments are described in which solutions of (*a*) copper sulphate, (*b*) copper sulphate and sulphuric acid, (*c*) copper sulphate and sodium sulphate, (*d*) potassium cuprocyanide, (*e*) silver nitrate, (*f*) mercurous nitrate, and (*g*) lead nitrate were electrolysed at low pressures by using the vapour above the solution as the cathode, electrical contact being made by means of a platinum dish suspended 1—2 cm. above the surface of the solution. The anode consisted of a wire of the metal under consideration. The products received on the platinum dish were: (*a*) and (*c*) copper hydroxide, (*e*) silver oxide, (*g*) lead oxide, (*b*), (*d*), and (*f*) nothing. No metal was deposited and therefore no confirmation of Gubkin's results with silver nitrate (*Pogg. Ann.*, 1887, **33**, 114) was obtained. The phenomena are explained by the theory that the electrons streaming from the cathode with much greater velocity than the cations do not discharge these, but ionise the water molecules. The hydroxyl ions then react with the cations forming, *e.g.*, copper hydroxide. If the solution is acid this neutralises the base and no deposit is formed. An extension of the theory explains the absence of deposit in (*d*) and the deposit of copper hydroxide in (*c*).
N. H. H.

Surface Phenomena in Photo-electric Elements with a Fluorescent Liquid. A. GRUMBACH (*Compt. rend*, 1925, **180**, 1102—1105; cf. A., 1923, ii, 108).—The cell Pt|fluorescent or absorbing solution|Pt, under illumination shows an *E.M.F.* due to a modification of the electrode-surface by adsorption of molecules changed by light. Radiation causes two effects, the Becquerel *E.M.F.* and the adsorption *E.M.F.* In aqueous solutions, the latter is always at first opposed to the former; it persists in the dark and finally reaches a value which remains constant until diffusion intervenes. The adsorption effect is independent of electrical conditions, for the variation of electrode potential is a function of illumination and the nature and concentration of the solution. This is shown by experiments with solutions of potassium fluorenesulphonate ($3{\cdot}84 \times 10^{-6}$ g./litre), in which the same limiting *E.M.F.* is observed whether the cell is connected in open circuit or short-circuited during the period of illumination. The

view that the phenomenon is due to the transformation of molecules in the bulk of the liquid under illumination, followed by adsorption, is confirmed by the observation that the same *E.M.F.* is obtained when the light from a mercury vapour lamp is focussed directly on the electrode or on to the liquid above it. R. A. M.

Electronic Theory of the Anodic Behaviour of Metals, especially those exhibiting Passivity Phenomena. U. SBORGI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 315—318).—On the basis of the most recent views concerning the distribution of the electrons in the atoms of different elements (cf. Lewis, "Valence and the Structure of Atoms and Molecules," and Bohr, "Les spectres et la structure de l'atome"), the author shows that each large period of the periodic system may be divided into three portions: (1) Elements preceding the transition elements. The configuration of the kernel is that of the initial noble gas, the kernel and valency are fixed, and the ionisation is of the metallic type, taking place with simultaneous loss of all the valency electrons. (2) Transition elements, with which the kernel and valency are variable, and the ionisation is usually metallic. (3) Elements subsequent to transition elements: pre-metalloids and metalloids. These have fixed kernels with the configuration of that of the final noble gas. The valency is fixed in the elements of the first kind (Zn, Cd), but variable in the remainder, for which also the ionisation is metalloid in type, taking place by partial loss of the valency electrons. The constancy of the valency of zinc and cadmium may be a particular case of the phenomenon that the alteration of valency for all elements of this category usually occurs in double steps, so that for bivalent elements the only ordinary ionisation possible is total ionisation and these elements are thus of fixed valency.

T. H. P.

Electronic Theory of the Anodic Behaviour of Metals, especially of those exhibiting Passivity Phenomena. II. U. SBORGI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 388—392; cf. preceding abstract).—An electronic interpretation is suggested for various anode phenomena. T. H. P.

Behaviour of Diaphragm Electrolysers with Circulation of the Alkali Chloride. IV. F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 135—149).—For the current yield of circulating diaphragm electrolysers in its dependence on the alkali concentration of the cathodic effluent, the author (*ibid.*, 1922, [iii], **28**, 142) derives the expression, $R=1-n/(1+\chi_1/\chi_2)+0{\cdot}0103\chi_{1.2}/(U_{OH}+U_M)(1+\chi_1/\chi_2)C_2$, where n indicates the transport number of the cation of the alkali, χ_1 and χ_2 the respective partial conductivities of the chloride and alkali in the catholyte, $\chi_{1.2}$ the total conductivity of the catholyte, U_{OH} and U_M the respective effective velocities of the hydroxyl and metal ions per 1 volt of potential gradient, and C_2 the concentration of the alkali in the catholyte. Results obtained with electrolysers fed with sodium chloride are now given, and correspond qualitatively, but not

quantitatively, with the above formula; this is doubtless attributable to the uncertainty attending the determination of the ratio χ_1/χ_2. T. H. P.

Behaviour of Diaphragm Electrolysers with Circulation of the Alkali Chlorides. V. F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 181—188).—From data obtained for catholytes from an electrolyser fed with saturated sodium chloride solution, the author calculates the values of the velocity of the hydroxyl ion in the catholyte and of the total linear velocity with which the liquid is displaced normally to the diaphragm. The results show that, in counter-current electrolysers, no loss in yield should be incurred owing to migration of the ions, the losses being due solely to diffusion phenomena; the reason for the great influence of the type of diaphragm on the yield is thus evident. Experiments made with small glass electrolysers containing asbestos diaphragms, the anode being of Acheson graphite and the cathode of iron gauze, show that almost theoretical yields are obtainable, even when the molecular concentration of the sodium hydroxide is comparatively high. T. H. P.

Chemico-physical Investigations on the Catholyte of Diaphragm Electrolysers with Circulation of the Sodium Chloride. F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 150—165).—The results are given of determinations at various temperatures of density, viscosity, and conductivity measurements of (1) sodium chloride solutions of concentrations ranging from N to saturation, (2) sodium hydroxide solutions ranging from N to $6{\cdot}72N$, and (3) solutions containing both the chloride and the hydroxide in proportions varying in accordance with the decomposition occurring in an electrolytic cell supplied with saturated sodium chloride solution. Contrary to theoretical anticipation, the equivalent conductivities of sodium hydroxide solutions, corrected for the viscosity, increase with the concentration of the solution; this result suggests considerable hydration of the ions, the degree of which diminishes as the concentration is augmented. The experimental values of the conductivity of the solutions containing both chloride and hydroxide are in good agreement with those calculated from the values for the separate components. The accord is less satisfactory when the values of the conductivity corrected for the viscosity are compared, owing partly to the anomalous behaviour of the hydroxide referred to above.

In general, the results furnish abundant indication of the great influence of the viscosity of the ions and confirm the observation that the low mobility of the hydroxyl ions in the cathode liquids, in comparison with the value calculated for infinite dilution, is largely responsible for the high current yields given by circulation electrolysers containing diaphragms. T. H. P.

Electrolytic Preparation of Potassium Bromate with Carbon Electrodes. D. T. EWING and H. W. SCHMIDT (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 133—137).—Potassium bromide

solutions were electrolysed using carbon electrodes in place of platinum. Since untreated carbon electrodes disintegrate rapidly the pores were filled with paraffin wax. A depolariser such as potassium dichromate is essential for high yields. The optimum yield was obtained with an anodic current density of 7 amp./dm.^{2} N. H. H.

Critical Increment of Chemical Reactions. W. E. GARNER (*Phil. Mag.*, 1925, [vi], **49**, 463—465).—In the usual interpretation of the Arrhenius constant A, the assumption that the experimental velocity constant K corresponds with the velocity constant of the activation process is unsound. Assuming the momentary formation of complexes between the reacting molecules, it is shown that the activation energy of the reactants may be either greater or less than A. Thus the critical increment is not necessarily the same as the activation energy, and ν calculated therefrom may not coincide with the actual absorption bands of the reactants. C. W. B.

Kinetics of Reactions. [BARON] JÜPTNER (*Kolloid-Z.*, 1925, **36** [*Zsigmondy-Festschr.*], 185—191).—The fundamental distinction between uni- and multi-molecular reactions is discussed and it is shown that the application to gas reactions of Bjerrum's views (*Z. Elektrochem.*, 1911, **17**, 732) gives only approximate agreement with experimental results. The velocity of reactions between gases and solids is shown, by consideration of the reduction of carbon dioxide by different forms of carbon, to depend, not only on the surface density and porosity, but also on the atomic distances in the solid. E. M. C.

Termolecular Collisions resulting from Bimolecular Collisions considered from the Physical and Chemical Points of View. I. Formation of Nitrosyl Chloride. M. TRAUTZ and H. SCHUETER (*Z. anorg. Chem.*, 1924, **136**, 1—47).—The empirical identity of the chemical (formation of an intermediate compound) and the physical (duration of impact) conceptions of ter- and multi-molecular collisions is proved from theoretical considerations. The reaction between nitric oxide and chlorine, which is purely termolecular within wide ranges of temperature and concentration, is shown to proceed in two stages in accordance with the impact duration law, thus: $NO+Cl_2=NOCl_2$ and $NOCl_2+NO=2NOCl$. The velocity constants for each stage of the reaction are in agreement with those deduced from the law of mass action, and the temperature coefficients agree with the requirements of the reaction velocity isochore. The compound $NOCl_2$ cannot be formed by the interaction of nitrosyl chloride and chlorine, but only from nitric oxide and chlorine; it is extremely unstable, and the equilibrium of the reaction by which it is formed lies very close to the left-hand side of the equation above. The heat of formation of nitrosyl dichloride is 7000 cals. ($\pm$700) and its formation and decomposition velocity constants are $1{\cdot}5\times10^{-5}$ and 4×10^{-3}, respectively. The results of this investigation show that all reactions of a higher order than the second which take place in dilute systems of liquids or

gases may be considered as superimposed reactions of the first or second order. A. R. P.

Chemical Reactions in the Glow Discharge. A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1924, **30**, 386—391).—The normal cathode fall in mixtures of gases which do not interact can be calculated by the mixture rule, but in gases which react with each other the curve has a pronounced hump above the line joining the values for each individual gas. The height of this hump in mixtures of oxygen and hydrogen and of oxygen and nitrogen is proportional to the reaction velocity, which is itself proportional to the strength of the current and is independent of the gas pressure. This is explained in the case of the oxygen–hydrogen reaction by the assumption that the reaction is induced by the hydrogen which is decomposed into reactive H^+ and H^- atoms by the discharge; the critical potential of this decomposition is 17·2 volts in the discharge zone and about 8·8 volts outside it. Nitrogen and oxygen react only slightly in the glow discharge, whilst nitrogen and hydrogen do not react at all; in fact, ammonia is completely decomposed by the discharge. A. R. P.

Thermal Theory of Gas Ignition by Electric Sparks. J. D. MORGAN (*Phil. Mag.*, 1925, [vi], **49**, 323—336).—Ignition depends on the raising of a sufficient volume of the combustible gas to a sufficiently high temperature. The incendivity of capacity sparks is, in general, greater than that of inductance sparks. The incendivity of capacity sparks depends on the shape and relative position of the electrodes in a manner to be expected. The energy required for ignition of a given gas by low-voltage inductance sparks is constant over a wide range of values of self-inductance and current, so long as the deviation of the spark is constant. There is no difference between the incendivity of inductance sparks produced in direct and alternating current circuits. Experiments on the ignition of highly inflammable solids by means of short, hot wires shows that the energy required for ignition increases with diminution of rate of heating. Over a wide range, a linear relation exists between the energy and the time during which it is supplied. C. W. B.

Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. III. Effect of Temperature on the Limits. A. G. WHITE (*J. Chem. Soc.*, 1925, **127**, 672—684).—On the assumption that the ignition temperature of a gas mixture at lower-limit concentrations is practically independent of the concentration of the inflammable gas, the lower composition limits for the downward propagation of flame in certain mixtures of air and combustible gas have been determined as previously described (T., 1922, **121**, 1244). The temperature–concentration curves for the upper and lower limits are practically linear, but for acetylene and ethylene the upper-limit concentration figures increase very rapidly at the higher temperatures. Except for hydrogen, the theoretical flame temperature remained approximately constant throughout the whole temperature range at the lower concentration

limit. The upper limits for mixtures of methane and air determined in a narrow tube increase less rapidly with temperature than those determined in a wide tube; this mixture, also, yields practically the same results for horizontal as for downward propagation of flame. S. K. T.

Movement of Flame in Closed Vessels. O. C. DE C. ELLIS and R. V. WHEELER (*J. Chem. Soc.*, 1925, **127**, 764—767).—By means of the apparatus already described (this vol., ii, 590) the assumptions made by Wheeler (T., 1918, **113**, 840) and by Mallard and Le Chatelier (*Ann. Mines*, 1883, [viii], **4**, 379) regarding the propagation of flames in closed spherical vessels are confirmed experimentally. The rate of development of pressure in such experiments is retarded when ignition takes place at the bottom of the sphere instead of the centre; the maximum pressure attained, also, is less. S. K. T.

Thermal Decomposition of Nitrogen Pentoxide. H. S. HIRST (*J. Chem. Soc.*, 1925, **127**, 657—671).—The thermal decomposition of nitrogen pentoxide is shown to be probably a true unimolecular reaction. The measured velocity coefficient agrees with that obtained by Daniels and Johnston (A., 1921, ii, 249); the values found at low initial pressures are not in accordance with Bodenstein's theory (A., 1923, ii, 303). No inhibitor of the reaction was discovered; the temperature coefficient is very large (300% velocity increase for 10° rise) so that there is probably no wall effect. The decomposition of pure nitrogen pentoxide at 80° is practically instantaneous (cf. Daniels, Wulf, and Karrer, A., 1923, ii, 24). S. K. T.

Velocity of Reaction in Mixed Solvents. VIII. Velocity of Formation of certain Quaternary Ammonium Salts. H. MCCOMBIE, H. M. ROBERTS, and H. A. SCARBOROUGH (*J. Chem. Soc.*, 1925, **127**, 753—759).—Measurements of the velocity of formation, k, of quaternary ammonium salts in three different solvent pairs confirm the authors' previous suggestion that when k is a discontinuous function of the composition of the solvent the solvent complex undergoes further complex formation with one of the reactants or reaction products. Addition of that solvent in which the reaction proceeds more slowly causes a large decrease in k except in the case of mixtures of acetone and benzene. S. K. T.

Bromometric Investigations. H. P. KAUFMANN and E. HANSEN-SCHMIDT (*Arch. Pharm.*, 1925, **263**, 32—50).—In addition to a general review of the literature, the following new observations are recorded. The stability of bromine solutions (0·1*N*) depends on the nature of the solvent. Thus, in carbon tetrachloride there is a loss of only 1% after 56 days; in acetic acid the decrease in strength is slightly greater; in carbon disulphide or chloroform it is about 22% in the same time; in methyl or ethyl alcohol, the strength falls rapidly at first, but afterwards less quickly, so that ultimately no further change takes place. In the two alcohols, 7·4% and 67%, respectively, of the active bromine disappears in

the first day. These rates are for the anhydrous solvents; when water is present the action is more rapid. The formation of acid inhibits further action, and, in the case of the alcohols, the addition of certain bromides has the same effect. Thus, if sodium or lithium bromide (12 equivalents) be added to a 0·1*N* solution of bromine in methyl alcohol a very stable preparation is obtained, only 3% of the active bromine having disappeared after 56 days. Calcium bromide is not so active; zinc and stannous bromides are almost indifferent; ferric bromide facilitates the interaction of the bromine and the alcohol. Ethyl alcohol solutions are similarly stabilised, but not so effectively. It is recommended, therefore, to use as a standard a 0·1*N*-solution of bromine in methyl alcohol saturated with sodium bromide.

Various substitutive and additive reactions were investigated. Hexane is not attacked by bromine (0·1*N*-solution) in darkness in carbon tetrachloride, carbon disulphide, or methyl alcohol (as above), and in daylight with measurable rapidity only in carbon tetrachloride. With salicylic acid, substitution takes place (the dibromo derivative being formed) slowly in carbon tetrachloride either in daylight or darkness, more rapidly in methyl alcohol, but here again exposure to daylight or to the light of a mercury vapour lamp scarcely accelerates the interaction. αβ-Di-iodoethylene (Kaufmann and Utzel, A., 1922, i, 213) reacts rapidly with bromine in carbon tetrachloride when the mixture is illuminated, but in darkness scarcely at all. Cinnamic acid takes up two atomic proportions of bromine (from a 0·1*N*-solution) in 1 hour in carbon tetrachloride, 3 hours in carbon disulphide, 24 hours in acetic acid, and 24 hours in methyl alcohol (containing sodium bromide). The rate of addition is affected by the presence of water in the methyl alcohol, and by light, particularly in the case of the carbon tetrachloride. Linseed oil takes up bromine additively only in darkness from carbon tetrachloride solution; when the solution is illuminated substitution reactions also take place. In methyl alcohol, however, there is only addition, and no substitution, either in light or darkness.

The application of these findings to the determination of the enol in keto–enol mixtures, and to the determination of "iodine-numbers" is discussed. W. A. S.

Hydrolysis of Iodine as Measured by the Iodine Electrode. H. D. Murray (*J. Chem. Soc.*, 1925, **127**, 882—885).—The diatomic iodine molecule is assumed to give two oppositely charged ions; hydrolysis then follows from the reaction $I^{\cdot}+H_2O=H^{\cdot}+HIO$. There is in the solution between the iodine and hypoiodous acid molecules and the ions $H^{\cdot}$, $I^{\cdot}$, I', and I_3', an equilibrium which is derivable from the mass-action laws: $[I^{\cdot}][I']/[I_2]=K_1$; $[I'][I_2]/[I_3']=K_2$; $[I^{\cdot}][OH']/[HIO]=K_3$. Hence under conditions where any hydrogen iodide formed is largely dissociated,

$$K_1=([I']^2/[I_2])(\{1+1/K_2\cdot[I_2]\}/\{1+K_u/K_3\cdot 1/[H^{\cdot}]\}).$$

The value of K was measured by means of an iodine–iodide electrode. The normal potential of the iodine electrode at 25° was found to be

0·6204 volt; the value in 0·1*N*-sulphuric acid was 0·6829 volt. At 25° the value of K_1 was $0·97 \times 10^{-8}$, and K_3 $3·2 \times 10^{-10}$. W. T.

Velocity of Ester Formation. P. PETRENKO-KRITSCHENKO, W. BOGATSKY, and N. LUBMAN (*Z. physikal. Chem.*, 1925, **115**, 289—302).—The velocity constants of the reactions between the following alcohols and acids, in benzene solution, at 100°, have been determined: ethyl alcohol, *iso*propyl alcohol, *tert.*-butyl alcohol, benzyl alcohol, benzhydrol, triphenylcarbinol; acetic acid, trichloroacetic acid, hydrochloric acid. The generally accepted view that the velocity is greatest with primary and least with tertiary alcohols is correct only for the reactions with acetic acid. In each series of alcohols, the velocity constant for the reaction with trichloroacetic acid is greatest with primary and least with secondary alcohols; with hydrochloric acid the velocity constant is greatest for tertiary and least for primary alcohols. L. F. G.

Thermal Decomposition of Derivatives of Ethyl Oxalacetate. A Unimolecular Reaction. D. L. WATSON (*Proc. Roy. Soc.*, 1925, **A, 108**, 132—153).—The thermal decomposition of ethyl ethoxyoxalacetate, oxalpropionate, and oxalsuccinate between 140° and 200° as represented by the equation, $CO_2Et{\cdot}CO{\cdot}CHR{\cdot}CO_2Et = CO + CO_2Et{\cdot}CHR{\cdot}CO_2Et$, follows the unimolecular law. Ethyl oxalacetate itself also loses carbon monoxide in accordance with this equation, but a simultaneous condensation process occurs at the temperatures investigated. The decomposition of ethyl phenyloxalacetate is autocatalytic. The above changes are practically unaffected by solvents or acids. These investigations are shown to afford no evidence in support of the radiation theory as developed by Lewis and Perrin. Various theoretical considerations are discussed. J. S. C.

Kinetics of the Reaction between the Halogens and Saturated Aliphatic Ketones in Dilute Aqueous Solution. F. O. RICE and C. F. FRYLING (*J. Amer. Chem. Soc.*, 1925, **47**, 379—384).—Chlorine, bromine, and iodine react with acetone in dilute aqueous solution with the same velocity and have the same temperature coefficient of velocity, supporting the view that the mechanism of the reaction consists of a slow reaction between acetone and hydrogen ion followed by a rapid reaction involving the halogen. Pinacolin and iodine react with less than half this velocity but all other ketones investigated react at the same, or at a greater rate. This does not support the hypothesis that the slow change is an enolisation of the ketone. The reactions between different ketones and iodine all have the same temperature coefficient. L. J. H.

Velocity of the Addition of Hydrogen Chloride to Quinone in Methyl Alcohol. EBERT (*Z. Elektrochem.*, 1925, **31**, 209; cf. this vol., ii, 408).—A correction; $\log k = 1·160 + \log[H^+] + \log[Cl^-] - 1·61([H^+]+[Cl^-])^{\frac{1}{2}}$. N. H. H.

Kinetics of Hæmoglobin. III. Velocity with which Oxygen combines with Reduced Hæmoglobin. H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1925, **A**, **107**, 654—683).—The investigation deals with (1) the order of the reaction, (2) the relation between the velocity-coefficients and the equilibrium-constant, and (3) the effect of p_H, temperature, light, and salt content upon the reaction-velocity. The methods adopted were similar to those used in studying the rate of dissociation of oxy-hæmoglobin (cf. A., 1923, ii, 746). The velocity of reaction was independent of the methods of preparation of the solutions. The measurement, at different cross-sections of the velocity apparatus, was made by means of the reversion spectroscope. The time for half completion of the reaction was between 0·01 and 0·001 second. By comparing the results obtained with two widely different rates of flow, the velocity apparatus was shown to be adequate for dealing with such high velocities. The velocity coefficients with different concentrations of reactants at p_H 7 and at p_H 10 to 11 showed the reaction to be bimolecular. A further test of the correctness of the equation $d(O_2\overline{Hb})/dt=k_1(O_2)(\overline{Hb})-k(O_2\overline{Hb})$ was obtained by comparing the value of the equilibrium constant, as calculated from the dissociation curve, with that obtained from the ratio of the two velocity coefficients. The experiments showed that the dissociation curve, in dilute solution, is of a hyperbolic character, and that the quotient of the velocity coefficients is equal, within the limits of error, to the equilibrium constant. Change of salt concentration, hydrogen-ion concentration, or of temperature was found to have no marked effect on the reaction velocity. The low temperature coefficient both at p_H 7 and p_H 10 (little more than unity for 10° rise) suggested that the reaction might be a photochemical one, but experiment showed that this is not so. In view of the small effect of p_H on k_1, the effect of p_H on the equilibrium constant must be mainly ascribed to its influence on the reduction velocity coefficient. The possible existence of aggregates in solution is discussed, and it is concluded that the presence of such aggregates will not affect the velocity of oxygen uptake so long as the part of the hæmochromogen grouping which combines with oxygen is sharply localised and far removed from the part of the grouping which forms aggregates. The low temperature coefficient of the reaction may be explained by assuming that every collision of oxygen with this localised portion results in combination. L. L. B.

Space Velocity of Transformation of the Modifications of Sulphur. W. FRAENKEL and W. GOEZ (*Z. anorg. Chem.*, 1925, **144**, 45—59).—Assuming that transformation originates at a number of points and spreads outwards from them with constant linear velocity (at the same temperature and for the same substance), it is shown that the amount of substance changed in unit time increases with the square of the time, until the boundaries of the changed areas meet; the transformation velocity becomes constant and finally diminishes. The curve for total amount of substance changed thus rises at first with the third power of the time, gradually

flattens, and then falls; the S-curve is accepted as the characteristic of a true transformation in and throughout the solid phase. The volume–time diagrams, plotted by aid of the air dilatometer, for the change monoclinic to rhombic sulphur at temperatures somewhat above normal and for rhombic to monoclinic at 100°, conform to this curve. The temperature for maximum formation of transformation centres in supercooled monoclinic sulphur was found to be −20°; the change to the rhombic form was also observed microscopically, being inaugurated by means of carbon disulphide or rhombic crystals, and the linear velocity measured. S. I. L.

Transformation Velocity of Ammonium Nitrate. A. SIEVERTS (*Z. anorg. Chem.*, 1925, **144**, 60—63).—The characteristic S-curve for transformation throughout a solid (cf. preceding abstract) was obtained, and the transformation temperature of 32·1° observed by Early and Lowry confirmed (T., 1919, **115**, 1387). S. I. L.

Theoretical Force and Co-volume of Explosives. E. BURLOT (*Compt. rend.*, 1924, **179**, 968—970).—The experimental values of f do not agree with those calculated from the formula $f=P_0V_0T/273$, the discrepancy being as great as 22% in the case of ballistite. The differences are attributed to the cooling of the gas by the walls of the bomb and the fact that a given pressure which is developed within a few thousandths of a second has not the same crushing effect as when the pressure is developed slowly. H. J. E.

Theoretical Force of Explosives. H. LE CHATELIER (*Compt. rend.*, 1924, **179**, 971—972; cf. Mallard and Le Chatelier, A., 1883, ii, 542, 844; 1884, ii, 549).—Burlot's experiments show that the values determined by Mallard and Le Chatelier for some specific heats should be modified, but sufficient data are not yet available for fixing the new values. The errors are in part due to the assumption that the specific heat of a gas is independent of the pressure, but at low temperatures, when internal pressures are not negligible, this is not the case. Errors in the methods of pressure measurement are also indicated, but these to some extent counteract each other. H. J. E.

Rate of Dehydration in the System Water–Alumina. M. GUICHARD (*Bull. Soc. chim.*, 1925, [iv], **37**, 381—389).—Determination of the constitution and nature of hydrates, by determination of constant weight at constant temperature, is inapplicable in the case of the hydrates of alumina and other gelatinous substances in which some or all of the contained water is adsorbed. However, curves showing the rate of dehydration with constantly increasing temperature differentiate between combined and adsorbed water. Alumina obtained by precipitation in the cold undoubtedly contains chemically combined water, and evidence is obtained for the existence of the hydrates $Al_2O_3,3H_2O$ and $Al_2O_3,2H_2O$. Alumina from boiling solutions contains only adsorbed water. The catalytic activity of alumina in promoting chemical processes involving the

removal of the elements of water appears to be purely an adsorption phenomenon. J. S. C.

Rapidity of Dehydration at Increasing Temperature. M. GUICHARD (*Bull. Soc. chim.*, 1925, [iv], **37**, 62—67).—On dehydrating precipitates at a slowly increasing temperature, a period of constant weight is obtained for a time for each definite hydrate, whilst adsorbed water is driven off continuously. The method is superior to that of dehydration at constant temperature in that it avoids recording false equilibria due to the rate of loss in water decreasing with the water content in cases of absorbed water. L. J. H.

Decomposition of Malic Acid by Sulphuric Acid. E. L. WHITFORD (*J. Amer. Chem. Soc.*, 1925, **47**, 953—968).—The decomposition of active and inactive malic acid by 100% sulphuric acid is a unimolecular reaction and is uninfluenced by the nature of the walls of the containing vessel. The reaction is greatly inhibited by water, many sulphates (especially those of sodium, potassium, and silver), acetic acid, dimethylpyrone, and large amounts of sulphur trioxide; dissolved hydrogen chloride and copper sulphate have no influence. The logarithm of the velocity constant is a linear function of the "molality" of the inhibitor, as is also the case for formic and oxalic acids (cf. Schierz, A., 1923, ii, 230; Lichty, A., 1907, ii, 445; 1909, ii, 38). The temperature coefficient of the reaction is large (3·72) and falls off slightly when water is added in increasing amounts (cf. Dhar, A., 1924, ii, 746). It is suggested that the reaction proceeds as follows: $C_4H_6O_5+H_2SO_4 \rightleftharpoons C_4H_6O_5,H_2SO_4 \rightleftharpoons H_2SO_4+CO+H_2O+C_3H_4O_3$ (formylacetic acid). The action of inhibitors is completely explained on Taylor's theory of negative catalysis (A., 1923, ii, 399). S. K. T.

Velocities of Crystallisation of Gypsum and Preparation of a Plaster of Great Resistance to Compression. L. CHASSEVENT (*Compt. rend.*, 1925, **180**, 1029—1031; cf. A., 1924, ii, 483).—By means of measurements of the electrical conductivity of the solution, the velocities of crystallisation of $CaSO_4,2H_2O$ from supersaturated solution have been determined at temperatures from 16° to 80°. The velocity of crystallisation falls as the temperature approaches 60°, above which temperature seeding the solution with the dihydrate is practically without effect. If the solution is supersaturated with respect to $CaSO_4,0{\cdot}5H_2O$ at these temperatures, crystallisation is rapid to a point between the solubilities of the two hydrates and then proceeds extremely slowly. A plaster of high density (2·18) and great hardness is obtained by mixing plaster of Paris with the amount of water theoretically necessary for production of the dihydrate, compressing the mass at 80°, and then allowing it to set at laboratory temperature. G. M. B.

Effect of Various Factors upon the Velocity of Crystallisation of Substances from Solution. J. D. JENKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 903—922).—The velocity of crystallisation at 0° of solutions of carbamide and of naphthalene in methyl

alcohol was investigated by a thermometric and by a rapid refractometric method. The presence of collodion strongly inhibits the crystallisation of naphthalene and converts it from a process of the first into one of the second order; it also suppresses deposition on the (110) faces of the crystals, thus causing elongation to a needle form. Addition of water (up to 13%) and of benzene (7%) has practically no influence. No inhibitors were found for the crystallisation of carbamide from methyl alcohol; above a certain point, increase in the amount of initial supersaturation causes an increase in the rate of crystallisation, possibly because of the spontaneous formation of fine crystals at the time of seeding.

The velocity coefficient k, for the crystallisation of carbamide from mixed and pure solvents is related to the viscosity, η, of the latter by the relation: $k\eta^{0\cdot59}$=constant; this expression is not in harmony with the diffusion explanation of crystallisation. The results, generally, indicate that the influence of inhibitors is not due to capillary action, but to the formation of stable adsorption complexes (cf. Marc, A., 1912, ii, 336). The influence of temperature on the velocity of crystallisation of acetanilide from two different solvents is accounted for by the lower viscosities of the media at the higher temperature.

Lactose hydrate crystallises only slowly from water because of its slow formation in solution; the process is greatly accelerated by a little ammonia. Preliminary experiments with ammonium nitrate in various solvents indicate that the velocity of solution tends to be more susceptible to the viscosity of the medium than the velocity of crystallisation, though other factors also intervene.

A solvate compound of carbamide, $(NH_2)_2CO,CH_3\cdot OH$, was isolated as rhomb-shaped plates, unstable above 10°, which rapidly lost methyl alcohol in the air. S. K. T.

Kinetics of Cellulose Production. S. Arrhenius (*Z. Elektrochem.*, 1924, **30**, 375—376).—Comparative tests on the solubility of the cellulose and encrustants of wood in the usual technical solvents—sodium hydroxide, sodium sulphide, and "sulphate liquor"—show that the reactions are unimolecular. The cellulose and the encrustants appear to be converted into soluble intermediate compounds with great velocity and the reaction constants of these depend on the concentration of the solution and on the temperature, the encrustants dissolving much more rapidly than the cellulose at the lower temperatures. Sodium sulphide retards solution of the cellulose and increases the rate of solution of the encrustants. [Cf. *B.*, 1925, 395.] A. R. P.

Corrosion Phenomena in Aluminium. E. Maass and W. Wiederholt (*Z. Metallk.*, 1925, 115—121).—Aluminium is more readily attacked by alkaline solutions than by acids of equivalent strength, but in neither case is the rate of solution dependent on the concentration of the hydroxyl or hydrogen ions, although it is markedly influenced by the nature of the other ions present as it is in solutions of neutral salts. Of the cations, potassium has the

greatest accelerating action, followed by sodium, ammonium, calcium, and magnesium. Of the anions, chloride is the most corrosive, producing generally a loosely-adherent oxide deposit and severe local pitting. Sulphates and nitrates, on the other hand, have only a slight corrosive action as a more tenacious deposit of hydroxide is usually formed in these solutions. Carbonates are almost as strongly corrosive as the corresponding hydroxides. The rate of attack of aluminium by 0·1*N*-acids decreases with the acid in the following order: sulphurous, hydrochloric, nitric, sulphuric, oxalic, acetic, tartaric acids; except in the case of sulphurous acid, where no action is visible, the corrosion is uniformly accompanied by the evolution of hydrogen from the surface of the metal. With alkalis, the gradual formation of a protective coating slowly retards corrosion. Pure water has no action on aluminium, but a slight attack occurs when a current is passed between two aluminium electrodes. Hydrogen peroxide rapidly destroys a sheet of the metal. [Cf. *B.*, June 26th.] A. R. P.

Reaction between Potassium Persulphate and Potassium Iodide in Gelatin Sols. S. O. Rawling and J. W. Glassett (*J. Physical Chem.*, 1925, **29**, 414—420).—The reaction between potassium persulphate and potassium iodide to give potassium sulphate and iodine is accelerated by the presence of gelatin. Some of the iodine liberated reacts with the gelatin. The accelerating effect is not due to the influence of catalysts present as impurities in the gelatin. The acceleration is increased to a maximum by acids and decreased by alkalis. Acceleration still occurs when the gelatin is at its isoelectric point and also when the solutions are kept at 39°, so that the effect is not due to the gel form. The acceleration is either caused by an organic catalyst in the gelatin or by adsorption of the reacting ions on the gelatin particles. M. B. D.

Autoxidation and Anti-oxygenic Action. XVI. Location of the Catalytic Property in the Oxidisable Part of the Molecule of the Catalyst. C. Moureu, C. Dufraisse, and P. Lotte (*Compt. rend.*, 1925, **180**, 993—998; cf. A., 1924, ii, 841).—Comparative experiments on the autoxidation of furfuraldehyde, acraldehyde, heptaldehyde, benzaldehyde, styrene, and turpentine in the presence of small quantities of various sulphur compounds show that in general the catalytic action of a molecule R·S·R′ is greatly diminished or entirely suppressed if the oxidised form R·SO_2·R′ be substituted. Thus the autoxidation of furfuraldehyde is inhibited by traces of methyl, ethyl, or phenyl sulphides, or of propane-β-diethylthiol, whilst dimethyl- and diethyl-sulphones, diphenyl sulphoxide, sulphonal, and trional have no such effect. On the other hand, in the case of the autoxidation of acraldehyde, the positive catalytic action of methyl and ethyl sulphides and the negative action of propane-β-diethylthiol are both practically suppressed when the corresponding sulphones are substituted for the parent sulphides. The conclusion is reached that the catalytic activity is due to the oxidisability of the sulphur atom in the active substances. G. M. B.

Classification of Reactions Taking Place in the Presence of a Contact Substance. W. SWIENTOSLAWSKI (*J. Chim. phys.*, 1925, **22**, 73—76).—Theoretical. Reactions in the presence of a contact substance are divided into two classes according as equilibrium is attained or not. If the reacting substances are in contact with the catalyst for a time sufficient to establish equilibrium, the final state is independent both of the nature of the catalyst and of the series of reactions by which the equilibrium is established. If, however, the substances are removed from the catalyst before equilibrium is attained, the products of reaction may differ both qualitatively and quantitatively according to the particular catalyst and the exact nature of the intermediate reactions. W. H.-R.

Theory of the Catalytic Surface. H. S. TAYLOR (*Proc. Roy. Soc.*, 1925, **A**, **108**, 105—111).—Previous investigations (A., 1924, ii, 668) lead to the conclusion that some modification of the Langmuir concept (A., 1922, ii, 629) is necessary. The concept of the catalytic surface to which the varying capacity of the surface to adsorb and to promote catalytic change has led is set forth in reference to the action of metallic nickel in effecting catalytic hydrogenation. Whilst *X*-ray examination shows that metallic catalysts possess the definite lattice structure of the crystalline material, there are, on the surface, groups of atoms in which the crystallisation process is incomplete. The surface is to be regarded as composed of atoms in varied degrees of saturation by neighbouring metal atoms, varying from those one degree less saturated than interior atoms to those which are held to the solid surface by a single constraint only, and it is by this constraint alone that these outermost atoms differ from gaseous metal atoms. These atoms can attach to themselves or adsorb three molecules, the linking between which and the nickel atom is identical with that obtaining in nickel carbonyl. This concept introduces a mechanism whereby both constituents of a hydrogenation process may be attached to one nickel atom and obviates the necessity, inherent in the Langmuir scheme, of having both reactants adsorbed on adjacent elementary spaces. The idea of metallic atoms detached to varying extents from the normal crystal lattice is in harmony with observations on such catalytic surfaces. The phenomenon of catalyst-poisoning is discussed. The amount of surface which is active catalytically is determined by the nature of the catalysed reaction. J. S. C.

Catalytic Actions at Solid Surfaces. XII. Particles of a Catalyst which participate in Chemical Change. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1925, **A**, **108**, 111—120).—The results of investigations on the toxic action of the mucilaginous and other impurities of whale oil on nickel catalyst during hydrogenation accord excellently with the views of Taylor (preceding abstract). The points at which isolated or semi-isolated nickel atoms are supposed to exist correspond with the "active patches" previously suggested by the present authors (*Trans. Faraday Soc.*, 1922, **17**, 670). The inactivation of the catalyst by means of impurity depends on the covering up of the active

particles by toxic material, the active patches being thus rendered inaccessible to unsaturated compound or hydrogen. Taylor's views are critically discussed and extended. The attraction between the unsaturated organic molecule and unsaturated nickel atom is held to be strong enough to loosen the nickel atom from its adjacent atom or atoms so that when catalytic change actually occurs the nickel atom loses all contact with its neighbours. For the moment, there may exist, actually apart from the solid surface, a combination of nickel, unsaturated compound, and probably hydrogen as well. This is a much more definite conception of the "intermediate complex" than has yet been advanced. The relative rôles played by unsaturated compound and hydrogen are discussed, and it is shown that the theoretical postulates advanced are in agreement with experiment. J. S. C.

Catalytic Reactions at Solid Surfaces. XIII. Some Factors Controlling Selective Hydrogenation: Terpene Derivatives. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1925, **A**, **108**, 121—131).—Previous work on the subject is reviewed in an attempt to connect the process of selective hydrogenation with some determining factor relative to the association between unsaturated compound and the acting atom of the metal (cf. preceding abstract). The normal course is the complete hydrogenation of any unsaturated system which has become definitely associated with an active atom of metal, and hence when selective hydrogenation of a diethylenic substance occurs one unsaturated centre only is associated with the metal at the moment catalytic change occurs. The extent to which factors other than unsaturation itself control the selective nature of the process is indicated by observations on the hydrogenation of acids instead of esters, the predominating affinity between the acid radical and the metal exerting a marked influence on the development of association between the latter and the ethylene groups. The work of Lebedev, Kobliansky, and Yakubchik (this vol., i, 350) shows that the rate of hydrogenation of various ethylene derivatives depends on the degree of substitution, and that in binary mixtures of substances each containing an ethylene linking, the less highly substituted is hydrogenated in preference to the other. Applying the latter generalisation to previous observations on the course of hydrogenation of various terpene derivatives (A., 1922, ii, 41), the positions of the ethylene linkings in a number of these substances have been fixed. J. S. C.

Synthesis of Water over Nickel and Copper Catalysts. A. T. LARSON and F. E. SMITH (*J. Amer. Chem. Soc.*, 1925, **47**, 346—355; cf. Pease and Taylor, A., 1922, ii, 148, 701).—The synthesis of water over reduced nickel is essentially similar to that over copper. In each case, a stable oxide is formed which retards the catalytic action. The essentially catalytic reaction appears to be of the nature of an alternate oxidation and reduction. L. J. H.

Activity of Contact Substances. I. Catalytic Synthesis of Water by the Platinum Metals and their Alloys. H. REMY and B. SCHAEFFER (*Z. anorg. Chem.*, 1924, **136**, 149—183).—The catalytic

activity of the platinum metals and their binary alloys with each other has been compared by passing a volume of a diluted mixture of 2 vols. of hydrogen and 1 vol. of oxygen over the metal until a visible amount of water was produced. The activity of the catalyst was markedly influenced by previous treatment with oxygen or hydrogen alone. After exposure to oxygen, the activity of the metals decreased in the order: iridium, palladium, platinum, whilst osmium, ruthenium, and rhodium were inactive. After exposure to hydrogen, the activity with mixtures of oxygen and hydrogen diluted with excess of hydrogen decreased in the order: osmium, iridium, platinum, rhodium, whilst ruthenium and palladium were inactive, whereas when the diluent was nitrogen the corresponding order was: osmium, platinum, palladium, rhodium, whilst ruthenium and iridium were inactive. On the other hand, alloys of the metals behaved quite differently; thus in the last-named case osmium–platinum alloys were only very slightly active, although each metal separately was very active, and rhodium–ruthenium alloys were exceedingly active, although rhodium itself was only slightly active and ruthenium, alone, inactive. Addition of ruthenium to palladium or iridium and exposure of the alloys to hydrogen results in greatly increased activity. A. R. P.

Influence of Gas Content on Catalysis with Platinum. G. KÄB (*Z. physikal. Chem.*, 1925, **115**, 224—232).—A method of forming deposits of platinum-black by electrical dispersion of the metal in atmospheres of different gases is described. The rate of catalytic decomposition of formic acid was studied. The activity was inhibited if the atmosphere in which dispersion took place contained hydrogen, carbon monoxide, or oxygen, the inhibiting effect due to oxygen being greatest and that due to hydrogen least; nitrogen has no effect on the activity. Platinum-black prepared in a hydrogen or carbon monoxide atmosphere can be activated by pumping away the gas, or, in the case of hydrogen, by the action of atmospheric oxygen or of ozone. The electrode potentials, against dilute sulphuric and formic acids, of specimens of platinum-black saturated with hydrogen are displaced in the noble direction if the metal is inactive, the displacement being the greatest with the most inactive preparations (cf. Hofmann and Ebert, A., 1917, ii, 25). L. F. G.

Interaction of Hydrogen and Carbon Dioxide on the Surface of Platinum. C. R. PRICHARD and C. N. HINSHELWOOD (*J. Chem. Soc.*, 1925, **127**, 806—811).—The interaction of carbon dioxide and hydrogen has been investigated from 870° to 1122°. The reaction was made irreversible by the absorption of the water formed, and was shown to go to completion; the product consisted entirely of carbon monoxide. With a constant pressure of carbon dioxide, the rate was found to be proportional to the pressure of hydrogen, at least up to 300 mm. When the pressure of hydrogen is kept constant, the rate is at first proportional to the pressure of carbon dioxide, and then passes through a maximum when the pressure of carbon dioxide is about double that of hydrogen. Carbon monoxide has only a slight retarding influence. The course of the

reaction is nearly unimolecular when the gases are present in equimolecular proportions. The rate of reaction increases 2·85 times for 100° rise in temperature. The poisoning effect of carbon dioxide at high pressure points to its strong adsorption, which, however, is not the case, hydrogen being much more strongly adsorbed. It is therefore assumed that the catalytic activity is localised in certain active points, and the relative adsorbability of the gases on the active points bears no relation to that on the total surface. The results obtained are in accordance with the equation $d[CO]/dt=k[H_2]\sigma(1-\sigma)$, where σ is the fraction of the active surface covered with carbon dioxide. W. T.

Catalytic Oxidation of Ammonia. P. PASCAL and E. DECARRIÈRE (*Mém. Poudres*, 1924, **21**, 68—86).—The temperature at which oxidation begins depends on the form of the platinum catalyst, but not on the ammonia content or velocity of the gas. These temperatures are 145° for corrugated platinum foil, 170° for foil crumpled into pellets, 240° for wire gauze, and 240° for wire in plug form. The yield of nitrogen oxides increases to a maximum with increasing temperature, then falls, and is negligible above 900°. With increasing curvature of the catalytic surface, the optimum temperature rises steadily from 650° to 775°, and the maximum yield sinks from 100% to 75—80%. Thus, pellets of crumpled foil are better than wire, and spongy platinum on a soluble support is the least advantageous. In the case of pellets, the yield is slightly increased by increasing the proportion of oxygen in the air, an optimum content being about 25% of oxygen. Ammonia losses are due principally to formation of nitrogen, apart from cases in which oxidation is only partial owing to too low a temperature or imperfect contact with the catalyst. W. T. K. B.

Influence of Gaseous Impurities on the Yield in the Catalytic Oxidation of Ammonia. P. PASCAL and E. DECARRIÈRE (*Mém. Poudres*, 1924, **21**, 87—105).—Hydrogen sulphide causes a progressive decline in activity of the platinum catalyst proportional to the quantity of the impurity present, the activity gradually increasing again when the impurity is removed. Acetylene differs from hydrogen sulphide and hydrogen phosphide (cf. *J.S.C.I.*, 1922, 214A, 291A) in causing a momentary increase in yield followed by a decrease depending in extent on the absolute quantity of impurity that has passed over the catalyst. The yield continues to decrease even when the actual proportion of acetylene present is diminished and for some time after all acetylene has been eliminated. The main cause of the decreased yield with hydrogen sulphide and acetylene is the rise in temperature due to the combustion of the impurity. W. T. K. B.

Catalytic Oxidation of Ammonia by Air in Contact with Platinum–Palladium Alloys. E. DECARRIÈRE (*Bull. Soc. chim.*, 1925, [iv], **37**, 412—421; cf. A., 1919, ii, 463; 1924, ii, 169).—The catalytic oxidation of ammonia by air in presence of platinum–palladium alloys containing 0·5% and 5%, respectively, of palladium has been investigated at various temperatures. Although the

efficiencies of the alloys as catalysts are somewhat reduced after their first employment, the effect is fairly small in the case of high (8—10%) concentrations of ammonia; the alloy containing 0·5% of palladium is preferred to platinum. [Cf. *B.*, 1925, 352.]

J. S. C.

Efficiency of Catalysts [in Oxidation of Ammonia]. A. T. Schlœsing (*Mém. Poudres*, 1924, **21**, 106—126).—The yield is expressed by the ratio of the quantity of nitric acid produced to that theoretically obtainable from the ammonia in the gas before passing over the catalyst, both being expressed in terms of the same volume of nitrogen present. Samples may be taken before and after being passed over the catalyst by means of evacuated bottles, but a better arrangement is to remove a steady stream of gas continuously over a period of time and concurrently at both points. A special type of absorbing vessel is described, the gas before the catalyst being drawn through one absorber containing *N*-sulphuric acid and a second containing potassium pyrogallate, and the gas after the catalyst being drawn through three absorbers, the first two with sodium hydroxide (slightly weaker than *N*) and the third with potassium pyrogallate. In both cases, the volume of residual nitrogen is measured. There is no loss of accuracy if the second alkaline absorber in the nitric acid determination and the pyrogallol absorber in the ammonia determination are omitted, the volume of nitrogen in the latter case being calculated from that of the air collected. Various corrections and precautions are discussed.

W. T. K. B.

Synthesis of Nitric Acid by Ostwald's Process. P. Pascal (*Mém. Poudres*, 1924, **21**, 1—67).—Calcium cyanamide does not suffer loss of nitrogen on storage, but there is a gradual absorption of atmospheric moisture accompanied by incipient polymerisation to dicyanodiamide. When heated in autoclaves with an alkali, dicyanodiamide liberates ammonia, although not so readily as calcium cyanamide, and the final reaction products include tricyanotriamide and ammeline melanurate. A maximum liberation of ammonia and minimum formation of nitrogenous secondary products is obtained by using in the autoclave a solution containing 16 g. of sodium hydroxide per litre, the average yield being 96%. The oxidative efficiency of the platinum catalyst depends on the ammonia content of the gas, a sharp maximum being observed. It also deteriorates with age, gaseous impurities (*e.g.*, hydrogen phosphide and hydrogen silicide) and, particularly, dust being detrimental. There is also an optimum value for the velocity of the gas passing over the catalyst, and it is important to maintain a low temperature in the absorbing towers. Losses may be reduced to almost zero by using an alkaline spray in the towers, sodium nitrite and nitrate being formed in about equal quantities as long as the liquid is alkaline and sodium nitrate alone occurring when it becomes acid. On the three stages of the process, a net yield of 87% should be attainable with the plant described. [Cf. *B.*, 1925, 444.]

W. T. K. B.

Catalytic Decomposition of Nitrous Oxide on the Surface of Gold: a Comparison with the Homogeneous Reaction. C. N. HINSHELWOOD and C. R. PRICHARD (*Proc. Roy. Soc.*, 1925, **A**, **108**, 211—215).—The decomposition occurring on the surface of heated gold wires follows the simple unimolecular law and is shown to be a true surface reaction rather than a reaction occurring in a small zone of heated gas. The value of E in the expression $d \log k/dT = E/RT^2$ is 29,000 cal./g.-mol. The mechanism of the process is discussed and compared with that of the homogeneous reaction (A., 1924, ii, 751) and of the reaction at the surface of platinum (this vol., ii, 310). J. S. C.

Reaction Velocity of Oxygen with Solutions of some Inorganic Salts. III. Catalytic Oxidation of Sulphites. W. REINDERS and S. I. VLES (*Rec. trav. chim.*, 1925, **44**, 249—268; cf. this vol., ii, 308).—The results of Titov (A., 1904, ii, 113) have been confirmed and extended. An examination of the velocity of oxidation at various hydrogen-ion concentrations showed that cupric and ferric ions exert catalytic activities between $p_H 4$ and $p_H 12$, reaching a maximum within this range, whilst nickel and cobalt are only active in alkaline solutions. In ammoniacal solutions, no oxidation occurs except in presence of copper salts; under these conditions, the reaction is unimolecular, the concentration of oxygen having very little influence, and the velocity being proportional to the concentration of the copper catalyst. Without addition of any catalyst, the reaction velocity is a maximum for p_H 10, but this is probably due to presence of traces of copper; by extrapolation from the results obtained with increasing quantities of copper, the amount of the latter in the distilled water used was found to be $3{\cdot}2 \times 10^{-7}$ mol. per litre, a probable proportion. The catalytic activity of nickel and cobalt in alkaline solutions is ascribed to the hydroxides, but no regularities could be observed. S. I. L.

Effect of Water and of Carbon Dioxide on the Catalytic Oxidations of Carbon Monoxide and Hydrogen by Oxygen. A. B. LAMB and W. E. VAIL (*J. Amer. Chem. Soc.*, 1925, **47**, 123—142).—The retarding effect of water vapour on the catalytic oxidation of carbon monoxide and hydrogen by the oxygen of the air in contact with "hopcalite" (manganese dioxide and cupric oxide) was measured over a considerable range of temperatures and partial vapour pressures of water and compared with the water content of "hopcalite" in equilibrium with moisture under the same conditions. The activity is only slightly dependent on the temperature, being mainly determined by the equilibrium water content of the catalyst. The temperature coefficient of activity of very dry "hopcalite" for the oxidation of carbon monoxide is also small, and the initial activity of the very dry material for the oxidation of hydrogen is very high. Larger amounts of water vapour, carbon dioxide, and nitrogen affect the two reactions (oxidation of hydrogen and carbon monoxide) equally for each gas and to about the extent expected from the relative absorbabilities of the three gases. L. J. H.

Organic Reactions at the Surface of Titania. Adsorption of certain Gases by Titania. F. BISCHOFF and H. ADKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 807—826; cf. A., 1924, ii, 159).—Mixtures of acetic acid with varying proportions of formic acid were passed over titania at 300—350°. The formation of acetaldehyde (cf. Sabatier and Mailhe, A., 1912, i, 238) was not observed. The catalytic activities of various samples of titania in decomposing butyl alcohol (at 430°), ethyl alcohol (at 400°), ethyl ether (at 430°), and ethyl acetate (at 450°) were compared. Those derived from titanium chlorides and from alkyl titanates by hydrolysis are reproducible as regards catalytic activity, whilst those from sodium titanate behave irregularly. The results obtained are in accord with the hypothesis previously advanced to explain the mechanism of catalysis at the surface of alumina (A., 1924, ii, 159), the surface state of the titania being influenced by the size and shape of the groups previously attached to the titanium atom. The decomposition of ethyl alcohol into ethylene at the surface of titania does not take place through the intermediate formation of ether. The formation of saturated hydrocarbons by the decomposition of alcohols or ether at the surface of titania is due to auto-oxidation and reduction, which takes place either between two molecules of alcohol or between two parts of the ether molecule, with simultaneous formation of an aldehyde. The decomposition of formic acid at the surface of titania dried below 300° proceeds with formation of carbon monoxide and water exclusively, whilst ignited titania gave considerable proportions of carbon dioxide and hydrogen. The total rate of decomposition of the acid was the same with the two catalysts, and it is concluded that the latter reaction is due to secondary adsorption. The adsorption of carbon dioxide, ethylene, ethane, and hydrogen by various samples of titania was determined at 20° and 97°, and was found to be independent of the relative catalytic activities of the samples. No relationship was observed between the relative activities of a catalyst for different reactions and its absolute activity as measured by the amount of material undergoing decomposition. F. G. W.

Carbon Monoxide, a Product of Electrolysis. A. F. O. GERMANN (*Science*, 1925, **61**, 70—71).—The specific conductivity of carbonyl chloride at 25° is $0{\cdot}007 \times 10^{-6}$. Electrolysis of a solution of aluminium chloride in carbonyl chloride results in the evolution of carbon monoxide and chlorine. A. A. E.

Pseudohalogens. I. L. BIRCKENBACH and K. KELLERMANN (*Ber.*, 1925, **58**, [*B*], 786—794).—Measurement of the decomposition potentials of the corresponding potassium salts in aqueous solution allows the halogen and pseudohalogens to be arranged in the sequence, TeCN, SeCN, I, SCN, CN, Br, N_3, Cl, OCN, F, in which there does not appear to be any direct relationship between affinity and atomic or molecular weight. In absolute ethyl-alcoholic solution the values found are those appropriate to the corresponding halogen or pseudo-halogen acids, the cation not appearing to exert any influence.

Electrolysis of solutions of potassium cyanate in the lower alcohols with a flowing mercury cathode yields a solution containing *oxycyanogen* $(OCN)_2$. The compound has not been isolated in the homogeneous state, but its solution has a halogen-like odour, liberates iodine from potassium iodide, and dissolves copper, zinc, and iron without evolution of gas. The action of oxycyanogen on methyl alcohol gives formaldehyde and cyanic acid; the latter compound yields with methyl alcohol methyl carbamate, which is converted by cyanic acid into methyl allophanate. Preliminary experiments establish the possibility of isolating oxycyanogen by the action of a halogen on silver cyanate in an organic solvent at a low temperature.

Selenocyanogen, $(SeCN)_2$, cannot be obtained by the electrolysis of solutions of potassium selenocyanate in methyl alcohol, since such solutions decompose with precipitation of selenium. It is prepared by shaking a solution of iodine in ether, chloroform, or carbon tetrachloride with an excess of pure silver selenocyanate at a temperature not exceeding 10° and evaporation of the filtered solution in a vacuum. It is a yellow, crystalline powder which can be preserved in a vacuum, but becomes red in a few hours when exposed to air. It exhibits the properties typical of halogens. Pure potassium selenocyanate is prepared by heating a mixture of potassium cyanide and selenium with anhydrous ethyl alcohol for several hours and subsequently evaporating the alcoholic solution in a vacuum; it is transformed into silver selenocyanate by means of silver acetate. H. W.

Electrolytic Production of Magnesium (from Fused Mixtures containing the Oxide). O. Ruff and W. Busch (*Z. anorg. Chem.*, 1925, **144**, 87—113).—The solubilities of magnesium oxide in fused mixtures of the chlorides, sulphides, and fluorides of the alkali and alkaline-earth metals have been examined; only the fluorides dissolve it freely, and of these only the lithium, calcium, and magnesium compounds can be employed. The ternary diagram for these three was constructed from experimental data, the ternary eutectic being found to melt at 665° and to have the composition, LiF, 56·2; CaF_2, 15·2; MgF_2, 28·6%. To meet the necessary temperature conditions for electrolysis, this eutectic must be employed; the solubilities of magnesium oxide in this are 0·16% at 700°, 0·07 at 800°, 0·17 at 900°, and 0·12% at 1000°. The solubilities of lithium oxide and calcium oxide in the same eutectic were also determined; the first is almost insoluble, the latter more soluble than magnesium oxide. Addition of oxides, sulphides, chlorides, or other fluorides did not raise the solubility of magnesium oxide in the fused mass. Electrolysis of the oxide dissolved in the molten eutectic was investigated; below 725° compact metal could not be obtained, above 775° the metal diffused in the mass. Between 725° and 775° a compact rod of magnesium was obtained, the current efficiency reaching 90% with a density of 1000 amp./dm.^{2} and a potential of 6—8 volts; the accumulation of oxygen in the cathode chamber reduced the efficiency greatly in other cases. S. I. L.

Production of Metallic Magnesium from Fused Salts. W. G. HARVEY (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 229—241).—The electrolytic production of magnesium from the chloride and oxide is described. The chloride hexahydrate is dehydrated by heat, an equal quantity of sodium chloride and a little ammonium chloride being added to prevent the formation of oxychloride. The fused mass contains 10% of magnesium oxide and melts at 620°. Electrolysis is carried out at 675—725° in steel pots (cathodes) using graphite anodes. Metallic sodium is not formed if the electrolysis is stopped when the concentration of the magnesium chloride falls to 10%. Metallic magnesium floats on the electrolyte, a thin film of which protects it from oxidation. The metal is purified by remelting, but cannot be freed entirely from the chloride, which leads to subsequent corrosion of the metal. The oxide process overcomes this difficulty. Magnesium oxide dissolves (0·1%) in a fused mixture of equal parts of magnesium and barium fluorides containing sufficient sodium fluoride to give fluidity at 950°. The primary reaction is electrolysis of the fluoride, but this is reformed by reaction between the fluorine and dissolved magnesium oxide. The latter is added from time to time to maintain the concentration. The metal after remelting contains 99·9% Mg, and is permanent owing to the absence of hygroscopic impurities. [Cf. *B.*, 1925, 406.] C. S.

Zinc Arc as a Means of Reduction. A. STOCK, A. BRANDT, and H. FISCHER (*Ber.*, 1925, **58**, [*B*], 643—657; cf. Stock and Praetorius, A., 1913, ii, 46).—The apparatus consists of a very thin-walled glass flask the stopper of which supports two brass rods which carry the lower, fixed and the upper, movable electrodes and a glass T-piece serving for the introduction of an indifferent gas and a resistance thermometer. The arc is formed beneath the liquid under investigation. The apparatus is immersed in a cooling bath which is kept stirred by a mechanical agitator, figured and described in the original. The behaviour of zinc and graphite electrodes in the presence of carbon disulphide is described in detail. The optimum yield of carbon subsulphide, C_3S_2, amounting to almost 50% of that obtainable according to the scheme $3CS_2+4Zn \rightarrow C_3S_2+4ZnS$ is secured by the use of a zinc anode and carbon cathode at 0°. The reaction is not merely a thermal change between carbon disulphide and zinc vapour in which the arc serves as a source of heat, since carbon subsulphide is not produced with an alternating current arc. With silicon tetrachloride, the best conditions are found in the use of a stationary aluminium cathode and movable zinc anode at −55° to −15°. The main reaction consists in the production of zinc chloride and silicon, whereas a minor portion of the silicon tetrachloride is converted into hexachlorodisilane, m. p. +2·5° (instead of −1° as recorded previously). Under similar conditions at −60° to +10°, phosphorus trichloride yields mainly yellow phosphorus and zinc chloride, phosphorus dichloride, P_2Cl_4, m. p. −28°, being formed in minor quantity (cf. Besson and Fournier, A., 1910, ii, 121). Boron trichloride is converted chiefly into boron; to a small extent

a new *chloride*, B_2Cl_4, b. p. 0°/44 mm., m. p. about −100°, is produced which could not be freed completely from silicon tetrachloride present to a small extent in the initial boron trichloride. It decomposes slowly at the atmospheric temperature into boron and boron trichloride, is decomposed by sodium hydroxide according to the equation, $B_2Cl_4+3H_2O=B_2O_3+4HCl+H_2$, and with water yields a moderately stable compound in which the B·B group remains intact.

The action of sodium amalgam on the chlorides of silicon, boron, or phosphorus leads almost exclusively to the production of the respective non-metal. Phosphorus trichloride appears to react slowly with mercury with intermediate formation of the dichloride, by which the metal is greatly attacked. H. W.

Preparation of Electrolytic Mercurous Chloride in Saturated Potassium Chloride for Use in the Calomel Electrode. W. W. Ewing (*J. Amer. Chem. Soc.*, 1925, **47**, 301—305).—Mercurous chloride is made electrolytically in saturated potassium chloride solution, the stirrer being arranged to sweep the surface of the mercury, thus removing the calomel as formed. The saturated potassium chloride solution of the anolyte is connected to the catholyte by inverted U-tubes containing *N*-potassium chloride solution, the open ends bearing semi-permeable membranes made from filter-paper soaked with collodion. The cathode is of copper, and the catholyte is saturated cupric chloride solution. The method gives a dependable quality of calomel mixed with finely divided mercury and avoids washing and shaking. The *E.M.F.* of the cell Hg+HgCl|HgCl in satd. KCl|HgCl in *N*-KCl|HgCl+Hg is 0·0388 volt at 25°. The electrode potential of the saturated potassium chloride calomel half-cell is −0·2446 volt on the hydrogen scale at 25° and its temperature coefficient is 0·0002 volt per degree from 20° to 30°. L. J. H.

Electrolytic Reduction of Tungstic Acid in Hydrochloric Acid Solution. O. Collenberg and J. Backer (*Z. Elektrochem.*, 1924, **30**, 230—238).—At a platinum cathode solutions of alkali tungstates in concentrated hydrochloric acid (containing the oxychloride WO_2Cl_2) are reduced quantitatively to derivatives of quinquevalent tungsten, whereas reduction proceeds further at a mercury, lead, or tin cathode. Above 16°, sodium tungstate gives quantitative yields of tervalent tungsten derivatives at the base metal cathode, but below 16° reduction is not so complete; potassium tungstate is completely reduced only at a lead cathode. During reduction, the colour of the solution changes first to blue when the tungsten is in the quinquevalent form, and this colour slowly fades on further reduction, yielding eventually a yellowish-green or red solution of tervalent tungsten. The yellowish-green solution is always obtained above 35°; it contains compounds of the type $R'_3W_2Cl_9$. The red solution is obtained at 16° and contains compounds of the type $R'_2(WCl_5,H_2O)$ which are unstable, changing on keeping or warming to compounds of the first-named type.

A. R. P.

Photosensitive Formation of Water from its Elements in the Presence of Chlorine. R. G. W. NORRISH and E. K. RIDEAL (*J. Chem. Soc.*, 1925, **127**, 787—797).—The formation of water in the gaseous system hydrogen–chlorine–oxygen on illumination by visible radiation is governed by the relationship $d[H_2O]/dt=k[Cl_2][O_2]$. It is independent of the partial pressure of hydrogen between the limits tested (0·16—0·9 of the total pressure). The result is consistent with the hypothesis that activation of the oxygen is first brought about by contact with chlorine molecules activated by absorption of light. The activated oxygen molecules then combine with hydrogen molecules to form water. The anticatalytic effect of oxygen on the formation of hydrogen chloride is regarded as due to the direct intervention of oxygen in the hydrogen–chlorine reaction chains, resulting in the formation of water. With the photosensitive decomposition of ozone by chlorine, and the activation of hydrogen by resonating mercury atoms, this reaction falls into the simplest class of photochemical sensitisation. W. T.

Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. A. J. ALLMAND, P. W. CUNLIFFE, and R. E. W. MADDISON (*J. Chem. Soc.*, 1925, **137**, 822—840).—Chlorine in water is considerably hydrolysed according to the equation $Cl_2+H_2O=HClO+H^{\cdot}+Cl'$. The addition of chlorides, and especially of hydrochloric acid (which suppress the hydrolysis), retards its photodecomposition; this indicates that the hypochlorous acid molecule is more photosensitive than the chlorine molecule. The hypochlorous acid decomposes to give hydrogen chloride and oxygen. The production of molecular oxygen and of chloric acid would then be due to secondary reactions, the latter being formed as a result of the hypochlorous acid molecules acting as acceptors for oxygen atoms. The addition of sodium acetate and disodium hydrogen phosphate (salts of acids the dissociation constants of which, though small, are appreciably greater than those of hypochlorous acid) suppress the concentration of hydrogen ion but form no hypochlorites. The effect of these salts (especially the latter) was to increase the yield of chloric acid from 61 to 83%, supporting the idea of the primary product of photolysis being oxygen atoms and that these with hypochlorous acid formed chloric acid. The suppression of chlorine ions by the addition of mercuric chloride (to form $HgCl_4^{\cdot\cdot}$) was not found effective. The addition of hydrochloric acid, which would decrease hydrolysis, should considerably decrease the yield of chloric acid; the yield decreased, but much less rapidly than expected if solely produced by the interaction of the primarily formed oxygen and hypochlorous acid (calculation based on Jakowkin's hydrolytic constant, A., 1899, ii, 736). Hence hypochlorous acid is probably one of the intermediate products of reaction of photoactivated chlorine molecules and water, this then acting as an acceptor for the oxygen. Chlorides and sulphuric acid also lower the yield of chloric acid. Their effects vary and various ions seem to have specific effects. Manganous sulphate and cobalt sulphate gave side reactions. The evolution

of oxygen in the reaction is subject to marked supersaturation effects. W. T.

Action of Light on Chlorine Dioxide. H. Booth and E. J. Bowen (*J. Chem. Soc.*, 1925, **127**, 510—513).—Dry gaseous chlorine dioxide on exposure to light is converted into chlorine heptoxide to the extent of about 60%; the latter forms a red liquid, b. p. about 80°, which becomes colourless on continued exposure. Chlorine monoxide and another unknown oxide are probably intermediate products. Dry chlorine dioxide (diluted with carbon dioxide) prepared in the dark is stable towards heat; after the addition of chlorine monoxide it gives thermal decomposition curves identical with those obtained with illuminated gas. S. K. T.

Action of Ultra-violet Light on Carbon Dioxide and Water. C. W. Porter and H. C. Ramsperger (*J. Amer. Chem. Soc.*, 1925, **47**, 79—82).—Experiments on the formation of formaldehyde by the action of ultra-violet light on mixed water vapour and carbon dioxide gave negative results. L. J. H.

Photochemical Studies. III. Reaction between Nitrogen and Hydrogen in Presence of Mercury Vapour: Resonance Radiation of Mercury. W. A. Noyes, Jun. (*J. Amer. Chem. Soc.*, 1925, **47**, 1003—1009).—Gaseous hydrogen and nitrogen combine to form ammonia in presence of mercury vapour with the possible formation of traces of hydrazine also; the reaction is probably of the first order with respect to hydrogen. The important factor appears to be the dissociation of hydrogen caused by the first resonance radiation of mercury (cf. Compton and Turner, A., 1924, ii, 639). Kuhn's results were qualitatively confirmed (A., 1924, ii, 249). The number of molecules of ammonia formed is of the same order as the number of quanta in the incident radiation (cf. Moore and Noyes, A., 1924, ii, 748). S. K. T.

Photochemistry of Silver Compounds. J. Eggert and W. Noddack (*Z. Physik.*, 1925, **31**, 942—948).—The absorption of pure silver chloride emulsion was determined with particular attention to the reflected light, using an Ulbricht hollow sphere photometer. For 365 $\mu\mu$ 1 mol. of silver chloride was decomposed by one quantum. For Valenta printing-out-paper emulsion, the same quantum relation was found to be probable. The sensitivity of this emulsion for green light is greatly increased by previous exposure to blue light, whereby an adsorption compound of silver and silver chloride is formed which in turn is decomposed by the green light. The behaviour of emulsions of silver chloride, bromide, and iodide is compared. E. B. L.

Silver Halide Emulsions and the Law of Photochemical Equivalence. J. Eggert and W. Noddack (*Z. Physik*, 1925, **31**, 922—941).—A critical examination of the divergence between the results of other workers and those contained in the previous paper (cf. preceding abstract), particularly as regards the shape of the curve relating amount of silver reduced and time of exposure

of the Valenta emulsion. The initial portion of the curve is found to be straight and not S-shaped. E. B. L.

Leptology of the Silver Bromide Grain. T. T. BAKER (*Brit. J. Phot.*, 1925, **72**, 248).—The *X*-ray crystal patterns of (1) silver bromide made by direct precipitation in water, (2) silver bromide precipitated in presence of iodide, *i.e.*, the so-termed silver iodobromide, (3) silver bromide precipitated from silver ammonium nitrate, and (4) silver bromide emulsified in gelatin and the crystals grown to be about 500 times their original sensitivity, are identical. There is no indication of silver iodide in the silver iodobromide. The change in spectral sensitivity of silver iodobromide compared with that of pure silver bromide may be due to the presence of silver iodide, which need not, however, take part in the photochemical change. It is suggested that in a sensitive emulsion the silver iodide is adsorbed in a colloidal form on the surface of the silver bromide grains. In certain types of photographic emulsion the presence of iodide retards growth of the silver bromide crystals. Whatever the function of the iodide may be, the evidence is stated to support the view that photographic sensitisation is due to substances deposited on the grain surfaces. W. C.

[Photographic] Ripening Process. LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 137—144; cf. *B.*, 1925, 150).—Both acid and basic dyes exert a protective action on silver bromide, as can be shown by their preventing the ripening of a highly disperse silver bromide–gelatin emulsion by ammonia. The effect is independent of the charge on the silver bromide. Bromo-chloride emulsions are very resistant to fogging on warming. The effect is probably due to the small grain-size and consequent greater protective action of the gelatin. Emulsions prepared by adding the silver salts to the halide solution give a higher speed than emulsions prepared in the reverse order, but they develop an intense fog in a digestion time which gives no trace of fog in emulsions prepared by adding the halides to the silver salts. The effect is due to the different environment during precipitation, the grains prepared in excess of halide solution containing less gelatin than those prepared in the reverse manner. The grain size in each emulsion pair is the same. If the amount of colloidal silver adsorbed by silver bromide is increased above a certain limit, no more silver is adsorbed, and the protecting power of the silver bromide for the silver already adsorbed is decreased, owing to the excess silver preventing the silver bromide shrinking and protecting the silver (cf. *Kolloid-Z.*, 1911, **8**, 97). This explains the greater effect of oxidising agents in decreasing the sensitivity of an emulsion after exposure to light. [Cf. *B.*, June 26th.] W. C.

Action of Light on Silver Bromide. H. STOCK (*Z. wiss. Phot.*, 1925, **23**, 132—136).—A criticism of results obtained by Stromberg (*J.S.C.I.*, 1923, 953A), showing that no valid conclusions can be reached from them, and indicating certain essential factors for experiments of this nature. [Cf. *B.*, June 26th.] W. C.

History and Theory of the Latent Image. II. LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 122—132; cf. *B.*, 1925, 151).—The three important new reactions which depend on the complicated colloid-chemical nature of the latent image are: the "Keimblosslegung" (nucleus exposure), dependent on the part of the silver of the latent image occluded in the silver halide grains, which is uncovered and made active by treatment with solvents for silver halide; "nucleus isolation," which is due to an adsorption replacement of the soluble part of the latent image as a result of treatment with acid-bromide-dye mixtures, and "nucleus activation," which is due to peptisation of the soluble portion of the latent image by treatment with alkali. [Cf. *B.*, June 26th.] W. C.

Blackening of a Photographic Film by *X*-Rays. J. K. ROBERTSON and J. T. THWAITES (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 99—102).—The degree of blackening produced on a photographic plate may be expressed by an expression of the type It^p, where I is the intensity of the light, t the time of exposure, and p a constant. For ordinary visible light, p has the value 0·86. By means of a wedge method the value of p has been determined for *X*-rays and has been found to be of the order of unity. J. S. C.

Kinetics of Photochemical Processes in Dyes. A. PREDWODITELEFF and N. NETSCHAJEWA (*Z. Physik*, 1925, **32**, 226—235).—The initial rates of the bleaching of cyanine and pinacyanol in collodion show a periodicity which is dependent on concentration. This does not apply if the solutions are sufficiently dilute, for which the rate of bleaching is in accordance with the formula for a unimolecular reaction. E. B. L.

Photolysis of Dibasic Acids. VOLMAR (*Compt. rend.*, 1925, **180**, 1172—1173).—Berthelot (A., 1914, ii, 602) showed that photolysis of one carboxyl group in oxalic acid occurs with radiation of 0·3μ and that shorter waves, λ=0·2μ, were required for the decomposition of the product. The changes are expressed better by the schemes $R(CO_2H)_2 \rightharpoonup CO_2+RH(CO_2H)$; $RH(CO_2H) \rightharpoonup CO_2+RH_2$ than by $R(CO_2H)_2 \rightharpoonup 2CO_2+RH_2$. The latter reaction requires radiations of wave-length 0·18μ, since the radiations not absorbed by quartz do not effect the change. Near ultra-violet radiation causes partial photolysis. Using 0·01*M*-solutions of dibasic acids subjected to the light of a quartz mercury lamp, oxalic and malonic acids yielded formic and acetic acids, respectively. Succinic acid gave a trace of propionic acid, whilst glutaric acid gave no butyric acid. In the last case, only 0·13 c.c. of carbon dioxide was set free in 4 hrs. Thus the active wave-length is greater the nearer the carboxyl groups. Oxalic acid, by reason of its special constitution, has the maximum sensitivity towards light. As the side-chain lengthens the mutual influence of the carboxyls diminishes, so that from succinic acid onwards the groups behave as if they were single, and photolysis only occurs at wave-lengths shorter than 0·21μ, as in monobasic acids. The results are in accord with the law of photochemical equivalence. R. A. M.

Photochemistry of Complex Compounds. I. R. SCHWARZ and H. WEISS (*Ber.*, 1925, **58**, [*B*], 746—755).—Hexamminecobaltic chloride, nitropentamminecobaltic chloride, *cis*- and *trans*-dinitrotetramminecobalt, the two forms of trinitrotriamminecobalt, and *cis*-tetranitrodiamminecobalt are hydrolysed in aqueous solution at a rate which is inappreciable in the dark, but is greatly accelerated by light. The cobalt separates, except from dilute solutions, in which it remains as sol, as brownish-black cobaltic hydroxide, whereas the nitrito residue passes into the ionic form. Attempts to determine the latter iodometrically in an atmosphere of carbon dioxide gave results which were not sufficiently reproducible for measurements of the kinetics of the change, which is therefore followed by determination of the electrical conductivity of the solution. Sodium hexanitritocobaltiate is too unstable in solution to yield accurate measurements. For hexamminecobaltic chloride, the conductivity method is unsuitable, since there is not a considerable difference between the conductivity of the complex and that of the products of its hydrolysis; in this case, therefore, the reaction is studied in acid solution, in which the acid titer gradually diminishes in consequence of the ammonia liberated. The photochemical decomposition of the nitritoamminecobalt compounds is an irreversible action of the first order in which the maximum action of light is observed in all cases in the ultra-violet at 366 $\mu\mu$. Increase in the number of nitro groups in the nucleus diminishes the photochemical stability; trinitrotriamminecobalt occupies an intermediate position by reason of its electrically neutral nucleus. Among stereoisomeric salts, the *trans* compound is photochemically the more stable. The velocity of reaction is about 1½ times as great in acid as in neutral solution and is largely independent of the hydrogen-ion concentration. H. W.

Chemistry of High Temperatures. H. VON WARTENBERG (*Z. Elektrochem.*, 1924, **30**, 351—356).—Chiefly speculative. After reviewing some of the principal reactions of compounds of the commoner elements between 2000° and 3000°, the author speculates on the probable course of certain reactions above 5000°. A. R. P.

Induced Reactions and Diabetes from the Point of View of Induced Oxidation. N. M. MITTRA and N. R. DHAR (*J. Physical Chem.*, 1925, **29**, 376—394).—Although mercuric chloride is not reduced by solutions of sodium arsenite alone, yet in the presence of another reducing agent such as sodium sulphite, sodium phosphite, or formic acid, it is reduced by both simultaneously. Similarly, it is possible to oxidise solutions of sodium nitrite, potassium oxalate, sodium arsenite, or nickelous hydroxide by air or oxygen when in the presence of sodium sulphite, which in its turn is itself oxidised. The amount of oxidation of nickelous hydroxide induced by the presence of cobaltous hydroxide increases with the concentration of sodium hydroxide to a maximum and then falls with further increase in alkali. Dextrose can be oxidised by passing air through solutions which also contain sodium sulphite. These induced oxidations are due to the formation of active oxygen

molecules in one reaction, which are then capable of reacting with the second substance present. Diabetes is due to insufficient oxidation of dextrose and fat in the human body, and the action of insulin etc. is to induce this oxidation in a similar manner to the reactions which have been investigated. The author suggests that iron preparations should be helpful in the treatment of diabetes.

M. B. D.

Reduction of Metals from their Salts by Means of Other Metals in Liquid Ammonia Solution. C. A. KRAUS and H. F. KURTZ (*J. Amer. Chem. Soc.*, 1925, **47**, 43—60).—When a metallic salt is added to a solution of a more electropositive metal in ammonia, precipitation of the metal (from the salt), either alone or as a compound with the other, may occur. The theory of the various possible cases is fully discussed. Salts of mercury, cadmium, zinc, tin, lead, antimony, bismuth, and thallium reduced thus by sodium all give compounds with sodium, but silver is precipitated alone. Some of the intermediate compounds of sodium with mercury, tin, and lead are not stable in contact with the solutions, but decompose to compounds poorer in sodium. Mercuric ethyl chloride, by the same treatment (with excess of sodium), gives the compound NaHg, identical with that obtained by reducing ordinary mercury salts. Data are also given for the reduction of some salts by calcium, compounds being obtained. Numerical data suggest the formation of compounds having the formulæ NaCd, $NaZn_4$, Na_4Sn, Na_4Pb, Na_3Tl_2, CaAg, Ca_7Zn, Ca_3Hg_2, Ca_2Pb_3, Ca_5Sn. L. J. H.

Double Salts formed by Sodium and Potassium Carbonates. J. W. BAIN (*Univ. Toronto, Sch. Eng. Res. Bull.*, 1925, **5**, 123—124).—Attempts to prepare crystals of the supposed double salt, $K_2CO_3,3Na_2CO_3,10H_2O$ (cf. Bain and Oliver, A., 1917, ii, 87), by the evaporation of solutions of varying concentration at temperatures above 35° have proved unsuccessful, and the isothermal diagram of the solubilities of potassium and sodium carbonates at 40° exhibits no indication of a double salt, unless the intersections are very obtuse. When heated under the microscope, the double salt,

$$K_2CO_3,Na_2CO_3,12H_2O,$$

yields small needles at 35°, but these appear to consist of $Na_2CO_3,2H_2O$. T. H. P.

Interaction of Sodium Chloride and Alumina. F. H. CLEWS (*J. Chem. Soc.*, 1925, **127**, 735—739).—The following reactions occur when sodium chloride and alumina are heated together: (*a*) $4x\text{NaCl}+y\text{Al}_2\text{O}_3+x\text{O}_2=2x\text{Na}_2\text{O},y\text{Al}_2\text{O}_3+2x\text{Cl}_2$; (*b*) $2x\text{NaCl}+y\text{Al}_2\text{O}_3+x\text{H}_2\text{O}=x\text{Na}_2\text{O},y\text{Al}_2\text{O}_3+2x\text{HCl}$; (*c*) $4\text{HCl}+\text{O}_2=2\text{H}_2\text{O}+2\text{Cl}_2$. Reaction (*b*) always predominates, the chlorine being due to (*c*) rather than (*a*). The yield of hydrogen chloride and chlorine passes through a maximum as the proportion of sodium chloride increases. Reaction (*b*) is practically complete above 1000° when water is continuously supplied. Equilibrium in the solid phase at 830° is imperfectly attained when the quantities of water and hydrogen chloride are varied. The stability of sodium aluminate

with reference to hydrogen chloride decreases rapidly when the molecular ratio $Al_2O_3 : Na_2O$ is less than 10 : 1 at 1045° or 12 : 1 at 830°. For the complete interaction of alumina and sodium chloride in the presence of water excess of the first-named is more important than excess of water. S. K. T.

Complexes with Two Unsymmetrical Co-ordination Valencies. F. L. Hahn and H. Wolf (*Z. anorg. Chem.*, 1925, **144**, 117—127).—It is proposed to substitute for the phrase "having the co-ordination number *n*" the description "*n*-numbered." A four-numbered complex should give rise to *cis-trans* isomerism or optically active isomerides, according to the disposal of the co-ordination linkings. In this class, the following double salts have been examined: *ammonium copper o-sulphobenzoate*, bluish-green rosettes, anhydrous, the *ammonium cadmium* salt,

$$(NH_4)_2[Cd{\cdot}C_6H_4(CO_2)(SO_3)],2H_2O,$$

and the *ammonium zinc* salt ($+1{\cdot}5H_2O$); *dipyridine copper sulphoacetate*, and the *diammonium sulphoacetates* of *copper*, *zinc*, *nickel*, and *cobalt*; the *manganese* and *cadmium* salts of this series partly dissociate in solution. The simple *sulphoacetates* of potassium, *sodium*, and ammonium (anhydrous), *magnesium*, *zinc*, *cadmium*, *cobalt*, and *nickel* (with $3H_2O$), *copper* ($+1H_2O$), and *manganese* ($+2H_2O$) are described. Determinations of molecular weights by the cryoscopic method in aqueous solution indicate that copper sulphobenzoate and the sulphoacetates of zinc, cadmium, and manganese are all considerably dissociated; the apparent absence of dissociation of copper sulphoacetate is attributed to equilibrium between association and dissociation. The equivalent conductivities of some of the simple sulphoacetates are recorded.

A number of *compounds* of 2-acetamidopyridine with the sulphates, chlorides, and nitrates of bivalent heavy metals have been prepared. S. I. L.

Effect of Colloids in the Displacement of Lead and Copper from their Salts by Zinc. L. T. M. Gray (*J. Chem. Soc.*, 1925, **127**, 776—780).—In the presence of colloids (gelatin, gum arabic, and glue) the size of the lead crystals deposited diminishes fairly steadily throughout, but the cohesive power increases up to a certain point and then diminishes; this maximum was not shown in the case of gum arabic. This effect on the cohesive power is ascribed to a film of adsorbed colloid. The same results were obtained in the case of copper and gelatin. In the experiments on copper with glue, the decrease in the size is apparently the decisive factor. The deposit deteriorates with time of contact owing to the continued adsorption of the colloid. The best deposits were obtained with a concentration of 0·0020—0·0026*M* copper sulphate and in the presence of 0·6—0·8% of boric acid. Mechanical cleaning of the zinc strip with fine emery paper gave better results than treatment with acid or alkali. W. T.

Ageing of Metallic Hydroxides. R. Fricke (*Z. Elektrochem.*, 1924, **30**, 393—396).—Gallium hydroxide, precipitated by the calculated amount of alkali, always retains more water than corresponds

with $Ga_2O_3,3H_2O$, even after prolonged drying in the air. The actual proportion of water retained varies with the method and conditions of preparation; less water is retained the higher the temperature of precipitation and the longer the precipitate is washed. The solubility of the compound in alkali hydroxide solutions decreases with decreasing water content and with increasing alkali concentration of the solution. A cold saturated solution of freshly-precipitated gallium hydroxide in alkali hydroxide solution slowly deposits gallium hydroxide on keeping. Potassium hydroxide dissolves less gallium hydroxide than does sodium hydroxide and a greater proportion of the gallium is precipitated on keeping. The colour of ferric hydroxide varies considerably with the method of precipitation; this is apparently due to the varying amounts of water retained by the precipitate, light coloured precipitates retaining a greater proportion of water than those more deeply coloured.

A. R. P.

Lanthanum Thallous Sulphates. F. Zambonini and G. Carobbi (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 278—283; cf. this vol., ii, 222).—Investigation of the system lanthanum sulphate–thallous sulphate–water shows the existence at 25° of the *compounds*: $La_2(SO_4)_3,4{\cdot}5Tl_2SO_4$; $La_2(SO_4)_3,3Tl_2SO_4$; $La_2(SO_4)_3,Tl_2SO_4,2H_2O$.

T. H. P.

Transformations of Carbon Monoxide under the Influence of the Silent Electric Discharge. E. Ott (*Ber.*, 1925, **58**, [*B*], 772—775).—The primary change of carbon monoxide under the influence of the silent electric discharge proceeds according to the scheme $4CO = C_3O_2+CO_2$. The carbon suboxide subsequently becomes polymerised to a degree which depends on the intensity of the discharge; in a 10-tube Siemens ozoniser it yields an ochre-yellow deposit, whereas in a single tube the deposit is dark brown and resembles that obtained by the thermal decomposition of carbon monoxide.

H. W.

Interaction of Carbon Dioxide and Hydrogen in the Corona due to Alternating Currents of High Frequency. R. W. Lunt (*Proc. Roy. Soc.*, 1925, **A**, **108**, 172—186).—With a frequency $1{\cdot}5 \times 10^7$, approximately equimolecular mixtures of carbon dioxide and hydrogen interact in the corona to give a water-gas equilibrium. The same result is obtained by exposing mixtures of carbon monoxide and water vapour to the discharge. Experiments in which the carbon dioxide content of the initial gas mixture was varied over the range 11—100% show that in the range $CO_2 < 50\%$ some of the carbon monoxide is reduced to methane, but in no case was it possible to detect formaldehyde or formic acid.

J. S. C.

Oxides, Metals, and Carbides at High Temperatures. O. Ruff (*Z. Elektrochem.*, 1924, **30**, 356—364).—A review of the reactions of oxides and carbides of some of the commoner and rarer metals such as thorium, zirconium, calcium, silicon, and tungsten, together with speculations on the probable behaviour of some of these compounds at very high temperatures. Alumina

and zirconia are more resistant to reduction above 2000° than are thoria and silica, but both are readily attacked by lime and magnesia at this temperature. Lists of m. p. of refractory oxides, carbides, and metals are given and the mechanism of the formation of calcium carbide and of its reactions at high temperatures is discussed.

A. R. P.

Silicates. W. EITEL (*Z. Elektrochem.*, 1924, **30**, 364—370).—A review of the work of other investigators on the systems SiO_2–Al_2O_3, MgO–SiO_2, CaO–SiO_2, CaO–Al_2O_3–SiO_2, diopside–anorthite–albite, anorthite–forsterite–quartz, SiO_2–K_2SiO_3–H_2O, $CaCO_3$–nepheline. A bomb furnace for the examination of the equilibrium between carbonates and silicates under pressure is described and illustrated.

A. R. P.

Silicates. III. Action of Magnesium, Calcium, and Barium Oxides on Silicates at High Temperatures and the Preparation of Metallic Iron from Silicates. G. TAMMANN and C. F. GREVEMEYER (*Z. anorg. Chem.*, 1924, **136**, 114—120).—Orthoclase, leucite, nepheline, hornblende, and willemite were heated at temperatures up to 1000° with magnesium, calcium, and barium oxides equivalent to the silica content of the mineral. Magnesium oxide had no action on any of the minerals, calcium oxide reacted slowly above 500° with all, the reactions with leucite and nepheline being the most energetic. Barium oxide attacked silicates containing alumina at 275° and those free from alumina at 350°; the action was much more energetic when the barium oxide contained a small proportion of water, but in no case was complete decomposition obtained and in no case did fusion ensue at 1000°, the particles of mineral simply becoming coated with a protective layer of partly fused barium compound. Fusion of hornblende at 1400° with barium oxide equivalent to the silica content and with carbon sufficient to reduce the iron resulted in the production of 62% of the theoretical quantity of iron together with a fluid barium silicate slag.

A. R. P.

Fusion of Rare-metal Ores. I. Pyrosulphate Fusion of Titanium Ores. G. W. SEARS and L. QUILL (*J. Amer. Chem. Soc.*, 1925, **47**, 922—929).—Complete decomposition of rutile and dissolution of the titanium content are only obtained when at least 12·5 parts of sodium pyrosulphate are used to 1 part of ore. A higher ratio is required when elements with high-melting sulphates are present. Sufficient pyrosulphate must be used to keep the fused mass below 700°, since above this temperature normal titanium sulphate is converted into an insoluble basic salt; this behaviour is probably common to all the less basic rare metals. Sodium pyrosulphate is somewhat more efficient than the potassium salt.

S. K. T.

Rare Earths. XVIII. Preparation and Properties of Cerium-free "Misch Metal." A. P. THOMPSON and H. C. KREMERS (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 207—212).—Cerium-free "misch metal" was prepared by removing cerium from

a rare-earth mixture by precipitation as CeO_2 and electrolysing the fused chlorides of the remaining metals in iron cells with carbon anodes. Two products, *A* and *B*, were obtained, the percentages of iron being 11·8 and 32·0, respectively. The metal is white, tarnishes in air, and is brittle; m. p. *A*, 975°; *B*, 1050°; d^{15}, *A*, 6·96; kindling temperature, *A*, 195°; *B*, 280°. The metal is pyrophoric and *A* shows a lower kindling temperature than a sample of commercial "misch metal," despite the absence of cerium. N. H. H.

Rare Earths. XIX. Preparation and some Properties of Metallic Cerium. H. C. Kremers and H. Beuker (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 213—230).—Cerium free from iron was prepared by electrolysing the fused chloride in graphite cells with carbon anodes. The metal corrodes easily in dry air. It is highly malleable and ductile. The following physical constants were redetermined: d^{15} (in absolute alcohol) 6·77; Brinell hardness (500 kg. weight) 21; heat of combustion 1·661 cal./g.; kindling temperature, 165°. The pure metal is moderately pyrophoric; it shows promise as a means of removing oxygen from partially evacuated tubes. N. H. H.

Dehydration of Ammonium Nitrate. T. L. Davis and A. J. J. Abrams (*J. Amer. Chem. Soc.*, 1925, **47**, 1043—1045).—The results of Pelouze's experiments on heating ammonium nitrate with sulphuric acid (*Ann. Chim. Phys.*, 1841, [iii], **2**, 47) may be explained by assuming the intermediate formation of nitroamide. Further experiments are described in support of this view; lower yields of nitrous oxide are obtained when meta- or ortho-phosphoric acid is used in place of sulphuric. S. K. T.

Interaction of Nitrogen Sulphide and Sulphur: Nitrogen Persulphide. F. L. Usher (*J. Chem. Soc.*, 1925, **127**, 730—735).—Sublimation of nitrogen sulphide containing free sulphur over silver gauze at about 125° yields a film of a ruby-red compound which turns deep blue on keeping (½ hr.—2 days) or on warming at 50°, and behaves like blue nitrogen sulphide (Burt, T., 1910, **97**, 1171). Nitrogen sulphide free from sulphur yields directly the blue compound, from which the ruby compound could never be obtained. These modifications are considered to be produced from different intermediate volatile nitrogen sulphides, the one giving rise to the ruby compound being formed by the decomposition of *nitrogen persulphide*, NS_2, by silver. Nitrogen persulphide is obtained as a dark red liquid, resembling bromine, and solidifying to a pale yellow solid at the temperature of solid carbon dioxide, by subliming nitrogen sulphide with sulphur at 125° in the absence of silver gauze. It has a penetrating odour like that of iodine and can be distilled unchanged in a vacuum. At the ordinary temperature it decomposes slowly into sulphur and yellow nitrogen sulphide. Water decomposes it into ammonium salts and free sulphur. It is more volatile than the sulphide N_4S_4; hydrogen sulphide decolorises an ethereal solution with probable formation of a thio-acid of nitrogen. S. K. T.

Synthetic Praseodymiferous Chlorovanadinite. G. CAROBBI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 311—315).—Fusion of a mixture of 10 g. of lead vanadate, 2 g. of lead chloride, and 1 g. of praseodymium vanadate results in the formation of a crystalline chlorovanadinite containing praseodymium vanadate (3·34%) in place of part of the lead vanadate, $3(Pb, Pr)_3(VO_4)_2,PbCl_2$. The fact that, under these experimental conditions, quinquevalent praseodymium isomorphous with quinquevalent vanadium is incapable of existence, fails to support the arrangement of the rare earths in the periodic system proposed by Prandtl and Grimm (A., 1924, ii, 615). T. H. P.

Preparation of Intermetallic Compounds by the Wet Method. A. MAZZUCCHELLI and A. VERCILLO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 233—235; cf. A., 1924, ii, 119).—A 35% solution of antimony trichloride in dilute hydrochloric acid (1 : 1) is practically inert towards copper at the ordinary temperature, but at 100° deposits on it a thin, adherent, metallic film, which stops further action. If, however, the liquid contains a considerable amount of cuprous chloride, the action at 100° becomes continuous and leads to the formation of the compound, Cu_2Sb. Under similar conditions, treatment of tin with a mixture of cuprous and stannous chlorides yields an alloy with Sn : Cu=1 : 6, possibly consisting of the compound Cu_3Sn covered with granules of copper; antimony trichloride and tin give the alloy Sb_2Sn; arsenic trichloride and copper, the compound As_2Cu_3; telluric chloride and copper, a compound having the composition Te_3Cu_2, but consisting probably of a mixture of TeCu or $TeCu_2$ with tellurium; tellurium chloride and lead give, not the compound PbTe, but pure tellurium. Neither bismuth chloride and antimony nor antimony chloride and bismuth yield antimony–bismuth alloys. The results obtained are discussed in relation to the considerations advanced by Mylius and Fromm (A., 1894, ii, 235). T. H. P.

Reactions in Liquid Hydrogen Sulphide. G. N. QUAM (*J. Amer. Chem. Soc.*, 1925, **47**, 103—108).—A simple method of preparing pure liquid hydrogen sulphide is described. The reactions of a large number of organic and inorganic substances in contact with liquid hydrogen sulphide over a long period of time (months) and over a wide temperature range (usually at the ordinary temperature) are described, the substances being tabulated as regards their solubility and/or reactivity. Many reactions took place very slowly. Oxidising salts all react and cause the separation of free sulphur. The existence of the hydrate, $H_2S,6H_2O$ (Scheffer and Meijer, A., 1919, ii, 502), is confirmed. Dry sulphur dioxide reacts vigorously with liquid hydrogen sulphide; bismuth trichloride forms the *compound* BiSCl. L. J. H.

Reducing Action of Sodium Hyposulphite in Alcoholic Solution. L. EYMER (*Rev. gén. Mat. Col.*, 1925, **39**, 96—97).—When cotton dyed with a red direct cotton dye or indigo is introduced together with 5 c.c. of water into a boiling mixture of 50 mg.

of dry sodium hyposulphite and 15 c.c. of alcohol, the resulting mixture continues to boil smoothly, hydrogen sulphide is evolved, and the cotton is completely decolorised. Under similar conditions, the alcohol being replaced by an equal volume of water, the resulting mixture commences to boil vigorously, sulphur dioxide is liberated, but no decolorisation of the dyed cotton occurs. The effect of the alcohol is evident only when the reducing mixture contains 70—95% of alcohol, but decolorisation occurs most easily in 82% alcohol, and is probably due to its solvent action on the products of decomposition. The addition of alcohol to an aqueous solution of sodium hyposulphite does not increase its reducing action on dyed cotton. A. J. H.

Preparation of Selenides from Hydrogen Selenide and Solutions of Metallic Salts. L. MOSER and K. ATYNSKI (*Monatsh.*, 1925, **45**, 235—250; cf. Fonzes-Diacon, A., 1900, ii, 345, 348, 402, 405, 546, 730; 1901, ii, 22, 60, 100).—Pure hydrogen selenide, prepared by the action of hydrochloric acid on magnesium selenide in an apparatus specially devised to prevent admixture with air, was continuously passed into an enclosed volume of water. Solutions of metallic salts were added drop by drop to the saturated solution, which was mechanically stirred. Under these conditions, the metallic selenides were always produced in the presence of excess of hydrogen selenide and no excess of metallic ions (which frequently act as reducing agents) were at any time in the solution. In this way, deposition of metal and formation of complexes and double salts which might veil the primary reaction were avoided. In the purification and analysis of the selenides so obtained, air was carefully excluded at every stage, the operations of filtration, washing, and dissolving being always carried out in an indifferent atmosphere. Analytical results showed that previously described selenides were often mixtures containing selenium to which the ascribed colour is due (the sodium and potassium selenides described by Berzelius as red are actually pure white). The following *selenides* are described: *ferrous*, FeSe, black, becoming brown by oxidation in air; ferric selenide could not be prepared in the pure state; *manganous*, MnSe, reddish-yellow (cf. Fonzes-Diacon, *loc. cit.*); *nickelous*, NiSe, black; unlike the sulphide, it shows no tendency to form a colloidal solution; *cobaltous*, CoSe, similar to that of nickel; *zinc*, ZnSe, lemon-yellow, decomposes on drying. Selenides of chromium, aluminium, and uranium cannot be prepared in the wet way; Berzelius' statement that a dark red aluminium selenide is formed from hydrogen selenide and a solution of an aluminium salt is inaccurate. *Molybdenum*, $MoSe_3$, dark brown, dissolves in alkali sulphides and selenides with formation of double salts. *Tungsten*, WSe_3, black; *thallium*, Ti_2Se, bluish-black. Silver, Ag_2Se, black, unstable, losing selenium on drying, soluble in alkali hydroxides, sulphides, and selenides; forming complex compounds. *Mercuric*, HgSe, black (double *salt* $HgCl_2,2HgSe$); with solutions of mercurous salts, a mixture of mercuric selenide and selenium is precipitated. *Lead*, PbS, black, on account of its insolubility

and the speed of reaction of lead salts with hydrogen selenide, is preferred to the silver salt for both detection and determination of the gas. *Bismuth*, Bi_2Se_3; *cuprous*, Cu_2Se, from a solution of a potassium cuprous salt, brown or black (cf. Fonzes-Diacon, *loc. cit.*); oxygen converts the selenide into $CuSeO_3$. *Cupric*, CuSe, black, becomes green by oxidation in air. *Cadmium*, CdSe, dark brown, is moderately stable (yellow double *salt*, 3CdSe, CdI_2). *Arsenious*, As_2Se_3, dark reddish-brown, unstable, is soluble in alkali selenides, ammonium carbonate, and ammonium hydroxide, with formation of dark brown complex compounds. *Arsenic*, As_2Se_5, brownish-red, is similar to the trisulphide. *Antimonious*, Sb_2Se_3, dark brown, is soluble in alkali sulphides and selenides. Antimonic selenide could not be prepared. *Stannous*, SnSe, black, is fairly stable; *stannic*, $SnSe_2$ is dark reddish-brown. *Aurous*, Au_2Se, black, is very unstable (complex *potassium* salt). *Auric*, Au_2Se_3, black. *Platinic*, $PtSe_2$, black, unstable, forms complex salts with alkali sulphides and selenides; *palladous*, PdSe, is dark brown. In general, the metal selenides correspond in composition with the sulphides, are much less stable, oxidise quickly in air, and cannot be dried without decomposition. The deeper colour of the selenides compared with the sulphides is attributed to the higher atomic weight of selenium. A. C.

Double Selenates of Thallous Selenate and the Selenates of Bivalent Metals. L. C. Lindsley and L. M. Dennis (*J. Amer. Chem. Soc.*, 1925, **47**, 377—379).—Double *selenates* of the formula $Tl_2SeO_4,M''SeO_4,6H_2O$ with *copper*, *cobalt*, *nickel*, *magnesium*, and *manganese* were prepared and analysed. They are isomorphous with the corresponding double sulphates, the acute angles being about 40′ greater with a corresponding decrease in the obtuse angles. L. J. H.

Dithiomolybdates. H. ter Meulen (*Chem. Weekblad*, 1925, **22**, 218—220).—Ammonium dithiomolybdate is readily obtained pure by the method of Krüss (A., 1884, 1268). When boiled with dilute hydrochloric acid, it yields molybdenum trisulphide:— $3(NH_4)_2MoO_2S_2+6HCl=2MoS_3+MoO_3+6NH_4Cl+3H_2O$; the oxysulphide, MoO_2S, is obtained by the action of sodium sulphide on the oxychloride in absolute alcohol. If acetic acid is used in place of hydrochloric to decompose the dithiomolybdate, stable colloidal solutions of the trisulphide are obtained. The fusion of sodium carbonate and the trisulphide or tetrathiomolybdate also yields the dithio compound, $MoS_3+2Na_2CO_3=Na_2MoO_2S_2+Na_2S+2CO_2$. S. I. L.

Silicododecatungstic Acid. E. O. North and G. D. Beal.—(See ii, 607.)

Potentiometric Study of the Reaction between Chlorine Water and Iodide Ion. E. Müller and D. Junck (*Z. Elektrochem.*, 1925, **31**, 206—209).—The potentiometric titration of chlorine water with potassium iodide and *vice versa* cannot be carried out with great accuracy, since chlorine escapes during the titration. A series of such titrations has, however, served to throw light on

the course of the reaction between chlorine and iodide ion. In the titration of chlorine water with potassium iodide alone or in the presence of sulphuric acid, the curve shows two breaks which correspond with the reaction $3Cl_2+I'+3H_2O=IO_3'+6HCl$, followed by $IO_3'+5I'+6HCl=3I_2+3H_2O+6Cl'$. In the presence of hydrochloric acid, the reaction proceeds in the three stages: $3Cl_2+I'+3H_2O=IO_3'+6H^{\cdot}+6Cl'$; $IO_3'+2I'+3Cl'+6H^{\cdot}=3ICl+3H_2O$; $ICl+3I'=3I_2+3Cl'$. In the titration of potassium iodide solution with chlorine water, alone or in the presence of sulphuric acid, two breaks are observed, the first corresponding with complete displacement of the iodine and the second with the reaction $I_2+6H_2O+5Cl_2=2IO_3'+12H^{\cdot}+10Cl'$. In the presence of hydrochloric acid, the reactions are $I_2+Cl_2=2ICl$; $2ICl+4Cl_2+6H_2O=2HIO_3+10H^{\cdot}+10Cl'$. N. H. H.

Potentiometric Study of the Reduction of Iodate with Iodide. E. MÜLLER and D. JUNCK (*Z. Elektrochem.*, 1925, **31**, 200—206).—An accurate potentiometric titration of the reduction of potassium iodate with potassium iodide in the presence of hydrochloric acid may be made provided that the acid concentration is not too high. With low concentrations of acid, the curves show one break corresponding with complete reduction. With intermediate concentrations, two breaks are observed, which correspond with the consecutive reactions (i) $IO_3'+2I'+6H^{\cdot}+3Cl'=3ICl+3H_2O$ and (ii) $3ICl+3I'=3I_2+3Cl'$. Titrations could therefore be made with 0·4 of the usual quantity of iodide, but since with higher concentrations of acid low results are obtained for both breaks, it is considered safer to work with low concentrations and titrate to the stage of complete reduction. These complications are avoided to a very large extent if sulphuric acid be used, since its range of permissible concentration is greater and the formation of iodine chloride is impossible. In the reverse titration of iodide with iodate, the presence of too much hydrochloric acid obscures the stage of complete reduction, but on further addition of iodate a good value is obtained for the completion of the reaction corresponding with (i) above. Here also the use of sulphuric acid is recommended, however.

In the titration of potassium periodate with potassium iodide in sulphuric acid and in low concentrations of hydrochloric acid, only one break, corresponding with complete reduction, is observed, and it is more marked in the first instance. With high concentrations of hydrochloric acid, there are two breaks, corresponding with the stages $IO_4'+3I'+8H^{\cdot}+4Cl'=4ICl+4H_2O$ and $4ICl+4I'=4I_2+4Cl'$. The reverse titration gives results analogous to those observed with the iodate. N. H. H.

Reduction of Permanganic Acid by Arsenious Acid and Mechanism of the Oxidation of Manganous Salts to Permanganic Acid. A. TRAVERS (*Bull. Soc. chim.*, 1925, [iv], **37**, 456—471).—Permanganic acid is reduced by arsenious oxide in presence of sulphuric or nitric acid to a manganic salt and manganese dioxide. In presence of hydrofluoric, phosphoric, or arsenic acid the

whole of the manganese may be converted into the corresponding manganic salt. Reduction to manganous salts occurs in presence of a considerable excess of arsenious oxide.

Manganic fluoride, orthophosphate, metaphosphate, and *orthoarsenate* are described. Aqueous solutions of these salts are quite stable in presence of the corresponding acids. The fluoride is very slightly ionised in aqueous solution.

The oxidation of manganous salts to permanganates in presence of silver nitrate and ammonium persulphate has been investigated. On mixing cold concentrated solutions of silver nitrate and ammonium persulphate, a crystalline precipitate, $3Ag_2O_2,AgNO_3$, is obtained, which in acid solutions evolves ozone and oxidises manganous salts to permanganates. The oxidation may be effected by persulphate alone in presence of hydrofluoric, phosphoric, or arsenic acid, or of sulphuric or nitric acid to which a little hydrofluoric acid has been added. If the acidity of the oxidising medium is considerable, the process is reversed, the permanganic acid being reduced to manganous salt. Excess of an alkali fluoride arrests the oxidations at the stage of manganic salts, the double salts of the type $MnF_3,2NaF$ resisting all attempts at further oxidation.

Evidence is brought forward in favour of the view that silver peroxide or ammonium persulphate in presence of acids furnishes ozone, which is responsible for the oxidation. The subsequent reduction in strongly acid solutions is attributed to the action of hydrogen peroxide resulting from the decomposition of Caro's acid, which is formed in appreciable amounts in such solutions.

J. S. C.

Influence of Neutral Salts on the Reaction between Ferric Chloride and Stannous Chloride. W. F. Timofeev, G. E. Muchin, and W. G. Gurevitsch (*Z. physikal. Chem.*, 1925, **115**, 161—176).—Neutral salts accelerate the oxidation of stannous chloride by ferric chloride. The effects of dilute solutions of sodium, potassium, and ammonium ions of the same concentrations, and of barium ions of half these concentrations, are equal, the action here thus depending solely on the valency of the ions. The acceleration due to cadmium chloride is, however, much less. The effect of continued additions of sodium chloride is not proportional to the amounts added. The reaction velocity at first increases rapidly, but afterwards slowly approaches a limiting value, attained in saturated sodium chloride solution; at the same time, the reaction changes slowly from the third to the second order. The temperature coefficient of the reaction and its change on additions of sodium chloride has been ascertained.

L. F. G.

Potassium Chlororuthenites. R. Charonnat (*Compt. rend.*, 1925, **180**, 1271—1273; cf. Howe, A., 1902, ii, 86; 1904, ii, 490, 665; Miolatti, A., 1902, ii, 246; Gutbier, A., 1921, ii, 457; Aoyama, A., 1924, ii, 771; Krauss, A., 1924, ii, 196, 770, 772; Charonnat, A., 1924, i, 706).—The complex salts of ruthenium and potassium chlorides with water which could not be formulated on Werner's theory are not, in fact, anomalous. The brown salt, $K_2Ru^{III}Cl_5,H_2O$,

and the red salt, $K_2Ru(H_2O)Cl_5$, are not isomerides, but differ in respect of ruthenium valency. The brown salts contain less water than is indicated by the formula; the alkali salts are not transformed by chlorine into hexachlororuthenates. The red salts are only formed from the brown ones by the prolonged action of reducing agents; they lose a molecule of water between 140° and 180°, and are easily converted into hexachlororuthenates by chlorine. The red salts are, in fact, aquochlororuthenites, $[Ru^{III}(H_2O)Cl_5,]X_2$, and the brown salts are hydroxychlororuthenates, $[Ru^{IV}(OH)Cl_5]X_2$. The valency of the ruthenium in the red salt is settled by its preparation from potassium ruthenotrioxalate, $[Ru^{III}(C_2O_4)_3]K_3$. The brown but not the red salts liberate iodine from potassium iodide and hydrochloric acid. R. A. M.

Production of Active Hydrogen. H. Copaux, H. Perperot, and R. Hocart (*Bull. Soc. chim.*, 1925, [iv], **37**, 141—153).—Several substances were tested as a means of measuring activation, tungsten trioxide proving the best. The extent of reduction suffered is measured by direct titration (Fontès and Thivolle, cf. A., 1923, ii, 264). Electrical activation is very small at atmospheric pressure. Activation by passage over a catalyst did not occur (cf. Mitchell and Marshall, T., 1923, **123**, 2448). L. J. H.

Preparation of Hydroxylamine. C. De W. Hurd and H. J. Brownstein (*J. Amer. Chem. Soc.*, 1925, **47**, 67—69).—Hydroxylamine is formed in butyl alcohol solution from the hydrochloride and sodium butoxide; after filtration from sodium chloride, the hydroxylamine is crystallised by cooling in an ice–salt mixture. The yield is 50%. Methods of recovery of the remainder are suggested. L. J. H.

Preparation of Nitroxyl Chloride and Bromide and their Action on Grignard's Reagent. N. Zuskine (*Bull. Soc. chim.*, 1925, [iv], **37**, 187).—Nitroxyl chloride, NO_2Cl, may be prepared by the action of phosphorus oxychloride on nitric acid; nitroxyl bromide by passing nitrogen dioxide and bromine vapour over a catalyst of calcined bone at 200—250°. With Grignard's reagent, the corresponding nitrogen compounds are not formed, but, *e.g.*, diphenyl with some chlorinated (or brominated) benzene. L. J. H.

Large-scale Preparation of Sodium Amalgam in the Laboratory. R. R. Read and C. Lucarini (*Ind. Eng. Chem.*, 1925, **17**, 480).—The amalgam is prepared by adding the mercury to the melted sodium under toluene. A steel mercury flask is used from which the top has been cut and two holes bored in it (for a thermometer and stirrer and for introduction of the mercury). The top is replaced after introduction of the sodium and toluene and before applying heat. D. G. H.

Magnetic Ferric Oxide. H. Abraham and R. Planiol (*Compt. rend.*, 1925, **180**, 1328—1329).—Ferric oxide can be prepared in two interconvertible forms, magnetic and non-magnetic.

The ordinary oxide (colcothar) is red and non-magnetic. The other form is brownish-yellow and nearly as strongly ferromagnetic as magnetite. The red oxide is reduced at 500° by hydrogen or carbon monoxide to magnetite, Fe_3O_4. This burns in air to give the non-magnetic ferric oxide; slow oxidation by a current of air at 200—250° gives the magnetic variety, which is stable at the ordinary temperature. The magnetic property is not lost at 600°, but at 700° transformation to the red, inactive form is rapid and complete. The two ferric oxides, magnetic and non-magnetic, may correspond with two series of ferric salts. R. A. M.

Rare Earths. XX. Preparation and Properties of Metallic Neodymium. H. C. KREMERS (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 221—227).—Reduction of neodymium chloride by means of sodium gave an impure metal powder. Electrolysis of the oxide in fused cryolite gave alloys containing much aluminium. A fused mixture of neodymium fluoride and potassium fluoride in proportions corresponding with the cryolite molecule was used as solvent for the oxide, but gave bad yields. Larger quantities of the metal containing 3% of iron were prepared by electrolysis of the fused chloride with small amounts of sodium chloride in an iron cell. The first product of electrolysis is the subchloride, $NdCl_2$, which is subsequently reduced to the metal. The metal, d^{15} 7·05, is silver-white, tarnishes in air, and is attacked by hot water and dilute acids. Its kindling temperature is 270°, and the metal is not pyrophoric. It readily alloys with iron, aluminium, nickel, and copper. [Cf. *B.*, 1925, 407.] C. S.

Spectroscope Lighting Unit. R. C. FREDERICK and E. R. WEBSTER (*Analyst*, 1925, **50**, 234—235).—The apparatus is specially designed for the spectroscopical examination of blood, particularly with regard to suspected carbon monoxide poisoning. The cell containing the blood is held by a wire spring arrangement in front of a small pocket torch with dry battery, of the shape of a fountain pen of exaggerated diameter, and this is firmly secured in a retort stand. In order to provide a comparison spectrum, the whole apparatus is duplicated and clamped at the necessary angle.
D. G. H.

Monochromatic Illuminator for Gas Flames. H. B. GORDON (*J. Amer. Chem. Soc.*, 1925, **47**, 1045—1046).—The metallic salt is placed in a porcelain trough with perforated sides surrounding the air holes of a Bunsen burner and is vaporised into the air supply of the burner by an electrically heated wire. S. K. T.

Electrical Heating Apparatus in the Laboratory. A. H. W. ATEN (*Chem. Weekblad*, 1925, **22**, 174—182).—The advantages of electrical heating, and the methods of constructing heating plates, water-baths, crucible furnaces, muffle furnaces, drying ovens, water ovens, stills, extraction apparatus, and electric welding apparatus are described. The methods of calculating the resistances

and currents required and the temperatures attainable are illustrated. A heating element for use in cutting wide glass tubing is described.
S. I. L.

Decomposition Apparatus. E. REMY (*Chem.-Ztg.*, 1925, **49**, 392).—Destruction of organic matter, by heating the substance in 20% hydrochloric acid and adding potassium chlorate in small portions until the reaction is complete, is carried out in a flask provided with a stoppered side tube and thermometer. The flask is fitted with a reflux condenser which carries a wide tube containing a mixture of 2 parts of soda-lime and 1 part of sodium thiosulphate which prevents the escape of chlorine. F. B.

Method of Viscosimetry with Variable Velocity of Flow. Velocity Function of the Viscosity of Disperse Systems. III. R. AUERBACH (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 252—259).—A new form of viscosimeter is described for studying the relationship of viscosity to the hydrostatic pressure. The liquid flows from a graduated tube, 150 cm. long, through a capillary tube and tap into a wide open reservoir level with the lower readings of the graduated tube. Other taps above and below the capillary are provided for convenience in manipulation. The height of the liquid is read at frequent intervals. For details of construction and numerical treatment reference should be made to the original paper. The large number of readings rapidly obtained with a single passage through the capillary is advantageous for systems which undergo viscosity changes on mechanical treatment. The viscosity of a 1% gelatin solution agreed with Ostwald's equation for lower hydrostatic pressures, but approximated to Poiseuille's law for higher pressures. E. M. C.

Distilling Flask for Corrosive Liquids. L. SATTLER and B. R. MORTIMER (*Ind. Eng. Chem.*, 1925, **17**, 495).—The upright side arm of a Claisen type distilling flask is modified to allow a short thermometer to hang from the stopper, whilst the stopper of the flask is hollow with 0·5-mm. tubing sealed to either end to allow of inert gas being slowly bubbled into the flask. The distilling side arm has an inner seal to prevent contamination.
D. G. H.

Modified Claisen Vacuum Distillation Apparatus. R. A. PETERS (*Proc. Physiol. Soc.; J. Physiol.*, 1924, **59**, xxvii).—The apparatus embodies two main points: (1) the bottom of the distilling column is so designed that flasks of different capacity can be fitted rapidly by rubber Gooch crucible cones; (2) a tap of large bore is placed in the delivery tube. By closing this tap before disconnecting the distilling flask the vacuum in the receiver can be maintained. CHEMICAL ABSTRACTS.

Mercury Distillation Apparatus. J. WETZEL (*Chem.-Ztg.*, 1925, **49**, 373).—The mercury is boiled in a flask, condenses in the air-cooled pear-shaped neck, and runs down into an annular channel at the bottom of the neck, from which it flows into a receiver.

The apparatus is suitable for small quantities of metal and may be used equally well at normal or low pressures. S. K. T.

Apparatus for Evaporating under Diminished Pressure Liquids that "Bump." H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1925, [ii], **109**, 345—346).—A stout, wide tube is fitted on the outside with a conical cap carrying a bulb and another ground-on fitting to connect, by means of a cock, with the vacuum pump. The apparatus is heated by a closed oil or other suitable bath and the whole is mounted on a shaking machine, with flexible connexions to the gas etc. "Bumping" and spirting are prevented by the shaking and, as the cap fits on outside the tube, there is no contamination of the contents with grease or other sealing medium. The dry residuum is easily removed. W. A. S.

Platinum-Resistance Thermometry at Low Temperatures. M. S. VAN DUSEN (*J. Amer. Chem. Soc.*, 1925, **47**, 326—332).—The equation

$$t=(1/\alpha)\{(R/R_0)-1\}+\delta\{(t/100)-1\}t/100+\beta\{(t/100)-1\}t^3/100^3,$$

obtained by the addition of a single term to the Callendar equation, expresses accurately the resistance of platinum as a function of temperature on the thermodynamic scale throughout the range 0° to −190°; R is the resistance at $t°$, R_0 the resistance when $t=0$, and α, δ, and β are constants, dependent on the purity of the platinum and determined by a calibration at or near the b. p. of oxygen in addition to the usual points in melting ice, boiling water, and boiling sulphur. L. J. H.

Flame Analysis. O. C. DE C. ELLIS and H. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 760—764).—An apparatus is described for photographing flames at any desired interval after initiation. The camera shutter consists of a large, slotted wheel which is revolved at any desired speed so that rapidly successive images of the flame are obtained on the same plate; the flame is simultaneously photographed in a revolving-film camera, this latter serving both as a chronograph and to record the speed of the flame, since the reflexions from an electrically vibrated tuning fork are recorded on the film at the same time. S. K. T.

Laboratory Apparatus. W. STEINKOPF [with W. OHSE and K. BUCHHEIM] (*J. pr. Chem.*, 1925, [ii], **109**, 347—351).—Cyanogen bromide is conveniently and safely prepared (cf. Scholl, A., 1896, i, 585) in a litre bottle fitted with a stopper carrying a stirrer, dropping-funnel, and thermometer. The reaction being finished, the stopper is replaced by another carrying a tube leading into another similar bottle, also stoppered and fitted with a calcium chloride tube. The leading tube is of T-shape, and is provided with a ramrod so that it can be cleared if it becomes plugged with solidified cyanogen bromide. The first bottle is then surrounded by water at 70—80°; the second is surrounded by ice. Only the vent (the calcium chloride tube) need be (loosely) connected with the draught. If anhydrous cyanogen bromide is required, tubes

containing calcium chloride and sodium wire, in that order, are inserted in the leading tube and are gently warmed.

To prevent the side tube of the still becoming plugged when substances that readily solidify are distilled under diminished pressure, the arm is surrounded by an electrically heated coil of resistance wire both above and below the cork, connexions through the latter being made with thick tinned copper wire.

Soxhlet extractions may be carried out at the b. p. of the solvent in the ordinary apparatus by surrounding it first with a sheet of thin asbestos board and then with a coil of resistance wire, electrically heated. W. A. S.

Combustion Micro-bomb and Micro-calorimeter. II. W. A. Roth and R. Lassé (*Z. Elektrochem.*, 1924, **30**, 607—609).—Using the combustion bomb already described (A., 1924, ii, 748) with a more suitable thermometer, the error in the determination of heats of combustion is reduced to about 0·04%. In the case of benzoic acid, it is difficult to obtain complete combustion, but the results, when suitably weighted, give an accurate mean value. C. H. D. C.

Identity of "Alumen" in Pliny's Natural History. K. C. Bailey (*Nature*, 1925, **115**, 764).

Mineralogical Chemistry.

Chemical Composition of the Earth. H. S. Washington (*Amer. J. Sci.*, 1925, [v], **9**, 351—378).—From a consideration of the composition of meteorites and rocks, the velocity of earthquake waves at different depths, and the density and compressibility of minerals and rocks, some conclusions are reached as to the distribution of matter within the earth. The following zones are deduced: central core, consisting of nickel-iron, Fe 90·67, Ni 8·50%, corresponding with meteoric iron (3400 km. thick); lithosporic shell consisting of patches of silicates in a sponge of metal, corresponding with pallasites (700 km.); ferrosporic shell, corresponding with meteoric stones (700 km.); peridotitic shell (1540 km.); basaltic shell (40 km.); and granitic shell or surface crust (20 km.). The volume, mass, and chemical composition are calculated for each of these zones, and the composition of the earth as a whole is deduced as: Fe 39·76 (31·82 as free metal, and 7·94 in silicates), O 27·71, Si 14·53, Mg 8·69, Ni (free) 3·16, Ca 2·52, Al 1·79, S 0·64, Na 0·39, Co 0·23, Cr 0·20, K 0·14, P 0·11, Mn 0·07, C 0·04, Ti 0·02, total 100·00. There is an excess of iron for combination with silicon and oxygen. This composition is compared with that of the sun and the average composition of the earth's crust (cf. this vol., ii, 63). L. J. S.

Mica Group. A. N. WINCHELL (*Amer. J. Sci.*, 1925, [v], **9**, 309—327).—Isomorphism depends not on the valency but on the atomic volumes of the elements. Fluorine, chlorine, or hydroxyl may "proxy" for (rather than replace) oxygen; potassium does not proxy for hydrogen, nor titanium for silicon. The best available analyses of biotite are calculated to percentages of atoms (omitting O, H, F). The atomic percentages are Si, 31·8 to 38·5 (*i.e.* 5/16 to 6/16); Al, 12·7—25% (2/16—4/16), Mg+Fe″ +Mn 16·5—36·8% (3/16—6/16), K (+Na+Ba+Ca) 12·5% (2/16). The series therefore ranges from $H_4K_2Mg_6Al_2Si_6O_{24}$ to $H_4K_2Mg_5Al_4Si_5O_{24}$. Here titanium and ferric iron proxy for magnesium; if they proxy for aluminium the second term would be $H_2K_2Mg_3Al_6Si_5O_{24}$, but this does not agree quite so well with the analyses. The several analyses are plotted on a square diagram at the four corners of which are $H_4K_2Mg_6Al_2Si_6O_{24}$ (phlogopite), $H_4K_2Mg_5Al_4Si_5O_{24}$ (eastonite), and the corresponding iron compounds $H_4K_2Fe_6Al_2Si_6O_{24}$ (annite), and $H_4K_2Fe_5Al_4Si_5O_{24}$ (siderophyllite). The optical data (α, γ, and $\gamma-\alpha$) plotted on the same diagram show appreciable increases in these values only for the members richer in iron. Variations in the optic axial angle are perhaps more closely connected with the relative amounts of hydroxyl and fluorine. L. J. S.

Mica Group. II. A. N. WINCHELL (*Amer. J. Sci.*, 1925, [v], **9**, 415—430; cf. preceding abstract).—The "heptaphyllite" system, with seven atoms in the nucleus, *e.g.*, KAl_3Si_3 or KAl_2Si_4, is represented by four end-members, muscovite $H_4K_2Al_6Si_6O_{24}$, polylithionite $H_4K_2Li_6Si_6O_{18}$, phengite $H_4K_2Al_4Si_3O_{25}$, and protolithionite $H_4K_2Fe''_3Al_4Si_5O_{22}$, which are placed at the corners of a tetrahedron. The majority of the plotted analyses fall on or near two of the surfaces of the tetrahedron, and are representative of two three-component systems, muscovite–polylithionite–protolithionite and muscovite–protolithionite–phengite, which are referred to respectively as the lepidolite and muscovite systems. There are no series of mixed crystals between the two main groups of micas—the octophyllite or biotite and the heptaphyllite or muscovite–lepidolite systems. In the former the optic axial plane is parallel to the plane of symmetry (010) with $\rho<v$, and in the latter it is perpendicular with $\rho>v$. L. J. S.

Occurrence of Palladium and of Rhodium in British Guiana. J. B. HARRISON (*Off. Gazette, Brit. Guiana*, May 3, 1924, No. 181).—The diamond-bearing gravels near Oewang, near the Kaieteur gorge, Potaro River, yield a black concentrate of ilmenite sand with specks of gold and a few minute grains (total weight 44 mg.) of a white metal. This is malleable but somewhat brittle, and is slowly dissolved by hot strong nitric acid or aqua regia, giving a rose-red solution. A small quantity of ammonium chloro iridate was separated, and the tests indicate the presence of palladium and rhodium in variable amounts in the different grains. One grain from this locality has been identified as platinum (Spencer, *Min. Mag.*, 1924, **20**, 186, 217). L. J. S.

Occurrence of Palladium Amalgam (Palladium Mercuride) in British Guiana. J. B. HARRISON and C. L. C. BOURNE (*Off. Gazette, Brit. Guiana*, Feb. 27, 1925, No. 71).—A further small supply of the white metal as fragments and nuggets up to 12 g. has been found in the diamond-washings of the Kangaruma district, Potaro River. These have *d* 13·33—15·82 and lose in weight when heated, with further losses on successive heatings up to about 1400°. The residual metal (34·8—45·6%) is porous with *d* 10·0—11·0 (after hammering, 11·33—11·9), and consists of palladium with traces of rhodium, platinum, and gold. It was afterwards found that the loss is due to mercury (54·4—65·2%). A re-examination of the material previously described as palladium and rhodium (preceding abstract), also showed the presence of much mercury; and it is suggested that that described as " allopalladium " (Spencer, *Min. Mag.*, 1924, **20**, 217) is also the same. The material is hard (scratching rolled nickel), crystalline, and denser than palladium or mercury. L. J. S.

Radioactive Minerals as Geological Age Indicators. H. V. ELLSWORTH (*Amer. J. Sci.*, 1925, [v], **9**, 127—144).—Previous work on the determination of the age of minerals by the ratio of the lead to the total uranium and thorium contents is discussed and new data are recorded. A theory is proposed accounting for the variations in the composition of uraninites etc., according to which all minerals containing the oxide UO_2 undergo self-oxidation at a rate depending on the rate of disintegration of the uranium and thorium. S. K. T.

Analytical Chemistry.

Portable Gas Analysis Apparatus. H. D. MURRAY (*J. Chem. Soc.*, 1925, **127**, 769—770).—A gas burette is connected by means of a three-way tap to a sparking chamber provided with a mercury reservoir; this is similarly connected to a pipette having two in-leads, one, through which the gas is drawn, reaching to the bottom of the bulb. Suitable absorbents are drawn up into the pipette as required; the analyses are carried out in the usual way. S. K. T.

Burette for Micro Gas Analysis. J. A. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1925, **47**, 109—112).—A simple form of apparatus is described for the micro-analysis of quantities of mixed gases up to 20 mm.^{3}, with an absolute accuracy of about 0·1% on 10 mm.^{3} A calibrated tube of 0·3 mm. bore is connected to a small adsorption bulb above, and also has a bulb below, whilst U-tubes at each end contain some confining liquid (mercury or water). An analysis cannot be vitiated on account of a gas bubble parting from the rest in the measuring tube as bubbles can always be collected again in one or other of the bulbs. L. J. H.

Fusion Mixture for Isopycnometric Analysis. E. CLERICI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 329—332; cf. A., 1922, ii, 578).—Further mixtures of thallium salts have now been prepared which allow of the separation of minerals of all specific gravities between 1 and 5·4. For values below 5, solutions of thallium formate, either with or without the malonate, are preferable. Fused mixtures of thallium formate and fluoride have specific gravities up to 5·38 at 100° and up to 5·4 at 110°. T. H. P.

Destruction of Organic Matter by Hydrogen Peroxide: Its Use in Toxicology. G. MAGNIN (*J. Pharm. Chim.*, 1925, [viii], **1**, 333—336).—In the detection and determination of inorganic poisons in viscera etc., the organic matter is destroyed by warming on the water-bath with a 30% solution of hydrogen peroxide, preferably in the presence of a little sodium hydroxide. The liquid is then acidified, filtered, and treated with sulphur dioxide, the excess of which is removed on the water-bath. C. P. S.

Theory of certain Electrometric and Conductometric Titrations. E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 332—337).—A mathematical analysis, from the point of view of the mass action law, of the location of the end points obtained in hydrogen electrode and conductivity titrations. In electrometric titration, if either the acid or the base is weak, inaccuracies in the end-point (0·3% in the most unfavourable case studied) arise. If the dissociation constant of one is less than 10^{-11}, the other being strong and the total concentration normal, no inflexion will be obtained. In conductometric titration the limits (of dissociation constant) before the inflexion disappears are wider, but the error in the end-point is much greater. When both K_a and $K_b=10^{-6}$, the "break" in the curve occurs about 2% before the true end-point. In general, the electrometric method gives results rather nearer the true end-point. L. J. H.

Behaviour of Electrodes of Platinum and Platinum Alloys in Electrometric Analysis. I. Dissimilar Electrodes. R. G. VAN NAME and F. FENWICK (*J. Amer. Chem. Soc.*, 1925, **47**, 9—19).—Two dissimilar inert electrodes show an abrupt difference of potential at the end-point of an oxidimetric titration. This is primarily a time effect due to the different rates at which they approach equilibrium, magnified by the large increase in the sensitivity of equilibrium potentials to a given change in concentration near the end-point. The end-point thus indicated agrees within the equivalent of 0·5 c.c. of 0·1*N*-titrant with that obtained from the single-potential curve of either electrode. A freshly-ignited platinum electrode immersed in a solution of silver nitrate usually acquires the electromotive behaviour of silver, apparently owing to an invisible coating of silver. L. J. H.

Behaviour of Electrodes of Platinum and Platinum Alloys in Electrometric Analysis. II. Polarised Electrodes. R. G. VAN NAME and F. FENWICK (*J. Amer. Chem. Soc.*, 1925, **47**, 19—29; cf. preceding abstract).—For electrometric analysis, two electrodes

polarised by a constant potential of 0·2—1 volt applied with 20,000 ohms resistance in series with the electrodes is recommended. The potential difference between the electrodes is slight during the titration, but becomes large abruptly at the end-point when the electrode reaction is nearly reversible before the end-point and largely irreversible after it, and is large at first, but vanishes abruptly at the end-point in the converse case. The difference in the end-point from that indicated by the break in the potential curve of a single electrode is usually negligible. The end-point break in titrations employing the potential of a single electrode may often be improved by polarising this with respect to an auxiliary electrode. L. J. H.

Application of Three-electrode Valves in Electrometric Titrations. W. D. TREADWELL and C. PAOLONI (*Helv. Chim. Acta*, 1925, **8**, 89—96).—The apparatus of Goode (A., 1922, ii, 307) is modified so that a conductivity cell can be used for electrometric titrations instead of a hydrogen electrode. The conductivity cell is connected to a source of alternating current of about 11 volts and any changes in conductivity are made to affect the potential of the grid. The anode potential of the valve is 26·3 volts and the titration is followed by means of a millivoltmeter in the anode circuit. Titration curves are given for hydrochloric acid with brucine and barium hydroxide and with a mixture of sodium hydroxide and sodium carbonate. M. B. D.

Electrometric Titration with the use of Quinhydrone. H. NIKLAS and A. HOCK (*Z. angew. Chem.*, 1925, **38**, 407—409).—The hydrogen of a platinum–hydrogen electrode may be replaced by quinhydrone added to the solution to be tested, the quinhydrone being decomposed into quinone and quinol, giving a definite hydrogen partial pressure. The value of p_H is $2·04+p/0·0577$, where p is the measured potential in volts; the method is accurate between p_H 2·05 and p_H 8·0. Above this value, an error is introduced through the oxidation of quinol and its increased dissociation. Within these limits, the method is much more rapid than the standard one. [Cf. *B.*, June 26th.] C. I.

Spectrophotometric Determination of p_H. F. VLÈS (*Compt. rend.*, 1925, **180**, 584—586; cf. Brode, A., 1924, ii, 346).—The determination of p_H from the intensity of absorption at the absorption bands of an indicator, as hitherto described, involves a tedious empirical calibration against a series of standard buffer solutions for each new concentration of indicator used. From a consideration of the absorption constants of the two tautomeric forms supposed to be in equilibrium, and of the ionic dissociation of the indicator, it is shown that where the p_H value is not extremely small it should be a simple function of the absorption ratio, and independent of the concentration of indicator, so that the calibration should be unnecessary. This is found to be the case with "normal" indicators such as cresol-red and bromothymol-blue, where the results are always correct to the first decimal place for p_H. Crystal-

violet and methyl-red, on the other hand, are classed as " abnormal," there being a marked deviation from the simple relationship expected, which is attributed to the presence of a third component. G. M. B.

Colorimetric Determination of Hydrogen-ion Concentration. E. RICHARD (*J. Pharm. Chim.*, 1925, [viii], **1**, 328—333).—Equal volumes of an appropriate one-colour indicator are added to the liquid under examination and to 0·01*N*-sodium hydroxide solution. After 2—3 mins., the colours are compared in a colorimeter, and the p_H is calculated from one of the formulæ : $p_H=p_K+\log E/(e-E)$ or $p_H=p_K-\log (e-E)/E$ (according as $E/(e-E)$ is greater or less than unity), where E is the colorimeter reading for the sodium hydroxide solution, e that for the solution being examined, and p_K is a constant depending on the indicator used. Constants and ranges of seven indicators are tabulated. C. P. S.

Potassium Ferritripyrocatecholoxide as an Indicator for Acidimetry and Alkalimetry. K. BINDER (*Z. anal. Chem.*, 1925, **66**, 1—13).—Potassium ferritripyrocatecholoxide dissolves in water to a red solution which remains unchanged with alkalis but turns violet with a small amount of acid owing to hydrolysis of the acid salt first formed, with the production of potassium aquoferridipyrocatecholoxide, which is decomposed to a green compound with more acid and finally yields a ferric salt. Addition of alkali to this yellow solution produces the same colour changes in the reverse order. For use as an indicator, a 1·25% solution of the red salt in freshly boiled, distilled water is prepared and 10 drops of this are required for *N*-acids, 5 drops for 0·5*N*-acids, and 1 drop for 0·1*N*-acid; the neutral tint is reddish-violet. The indicator has the same range of usefulness as phenolphthalein, and is just as sensitive to carbon dioxide; the alkali used therefore must be freed from carbonates with barium hydroxide. For the determination of ammonia, an excess of standard acid is added to the solution, which is then titrated with alkali to a violet colour. The indicator is useful for titration of the weaker organic acids, but cannot be used with pyridine. As the compound oxidises readily, it must be stored away from the air and alkaline solutions must be titrated without delay. Directions are given for the preparation of the compound (cf. A., 1912, i, 184, 445). A. R. P.

Salt Errors of Indicators in Solutions Poor in Electrolytes. I. M. KOLTHOFF (*Rec. trav. chim.*, 1925, **44**, 275—278).—Most indicators show a too acid reaction in solutions containing only small quantities of electrolytes. The apparent p_H as shown by buffer solutions and the actual p_H determined by means of the hydrogen electrode are tabulated for various solutions and indicators and the appropriate corrections given to an accuracy of 0·05 to 0·1 in the p_H value. The widest deviations are shown by phenol-red and bromophenol-blue, the smallest by cresol-red, bromocresol-purple and neutral-red. The indicators recommended for colorimetric determination of p_H in dilute solutions of electrolytes are α-naphthol-

blue, cresol-red, neutral-red, bromothymol-blue, bromocresol-purple, methyl-red, and methyl-orange. S. I. L.

Use of *p*-Nitrobenzoic Acid as an Acidimetric Standard. W. M. THORNTON, jun., and D. GETZ (*Amer. J. Sci.*, 1925, [v], **9**, 176—180).—*p*-Nitrobenzoic acid is an accurate primary acidimetric standard, its advantages being ease of purification, compactness, and high molecular weight. Before titration, the weighed acid is dissolved in a large excess of boiling alcohol to prevent subsequent precipitation; phenolphthalein is used as indicator. S. K. T.

Determination of Chlorides by Calorimetric Titration. Titration of Mixtures of Cyanide and Halides. P. M. DEAN and E. NEWCOMER (*J. Amer. Chem. Soc.*, 1925, **47**, 64—67).—The slightly modified method of Dean and Watts (A., 1924, ii, 421) is applicable with fair accuracy to single salts, but with mixtures only complete precipitation is indicated. Thus organic halogen compounds reduced by sodium in liquid ammonia do not give solutions which may be determined in this way, as some cyanide is simultaneously formed. L. J. H.

Test for Bromine. R. LORENZ, E. GRAU, and E. BERGHEIMER (*Z. anorg. Chem.*, 1924, **136**, 90—94).—A delicate reagent for the detection of bromine is made by dissolving fluorescein, twice crystallised from 80% alcohol, in cold 35% acetic acid and applying this solution to a loose filter-paper, which is then allowed to dry in the air and preserved away from light. The neutralised solution to be tested is placed in a round flask, so that it reaches to the bottom of the neck, and 5 c.c. of a strong solution of potassium permanganate and 0·02 c.c. of strong sulphuric acid are added. A piece of the test-paper is then affixed to the under side of the stopper, which is replaced in the flask and the whole set aside in the dark for 15 mins. A red coloration on the paper indicates the presence of bromine; the test will detect 0·01 mg. of potassium bromide in 50 c.c. of water or in a saturated solution of sodium chloride. A. R. P.

Iodometric Methods based on the Formation of Cyanogen Iodide. IV. R. LANG (*Z. anorg. Chem.*, 1925, **144**, 75—84).—Since cyanogen bromide is not easily affected by reducing agents, bromides may be accurately determined by oxidation with iodate in acid solution in presence of cyanide, the excess of iodate being titrated with hydrazine in acid solution ($IO_3' + 2Br' + 3HCN + 3H^{\cdot} = ICN + 2BrCN + 3H_2O$). The time required for oxidation may be diminished by addition of a small quantity of alkali chloride. The oxidation may also be effected with permanganate, excess of the latter being removed with nitrite (in sulphuric acid solution) or a ferrous salt (in phosphoric acid solution), the latter being preferred; potassium iodide is then added and the liberated iodine titrated with thiosulphate. Small quantities of chloride do not interfere. Several modifications suitable for the titration of bromides and iodides together are described. Periodate is not so suitable for the method as iodate, although it is satisfactory in presence of suitable amounts of hydrochloric acid and bromide for direct oxidation of iodides;

periodate may also be used in the determination of cyanide and thiocyanate together ($CNS' + IO_4' = ICN + SO_4''$). S. I. L.

Detection of Traces of Iodides. F. B. WADE (*Ind. Eng. Chem.*, 1925, **17**, 470).—The salt, sprinkled on a damp filter-paper impregnated with starch solution, is exposed to chlorine. D. G. H.

Determination of Small Amounts of Iodine as Iodide and Iodate. N. A. LANGE and L. A. WARD (*J. Amer. Chem. Soc.*, 1925, **47**, 1000—1003).—The alkaline sample, containing 0·01—0·10 mg. of iodine, is evaporated with hydrogen peroxide to oxidise nitrites, filtered, and the filtrate, rendered neutral to litmus, partly evaporated and divided into two parts. *o*-Tolidine in alcohol is added to each, one being previously saturated with hydrogen sulphide to reduce iodate to iodide and the excess removed. Hydrogen peroxide is then added to each solution and also to a series of ten standard potassium iodide solutions treated with *o*-tolidine solution as above. After 5 mins., the bluish-green colour which develops is matched with the standards. Comparison cannot be made after 10 mins. Interfering substances (*e.g.*, chlorides and bromides in concentrations exceeding 1500 parts per million, salts of heavy metals) may be eliminated by distilling the sample with steam in acid solution with ferric sulphate, the liberated iodine being absorbed in sodium hydroxide solution. The lower limit of the test is 6—7 parts per million. S. K. T.

Iodometric Titrations. M. DIMITROV (*Z. anorg. Chem.*, 1924, **136**, 189—192).—In order to economise potassium iodide the standardisation of thiosulphate solutions may be carried out satisfactorily as follows: a definite quantity of the solution is treated with a small crystal of potassium iodide and a slight excess over the stoicheiometrical quantity of potassium iodate required to produce sufficient iodine to react with the thiosulphate; the solution is then titrated very slowly with a standard solution of hydrochloric acid, adding starch towards the end of the titration. By using this method, a titration requires only 0·05 g. instead of 2 g. of iodide. A. R. P.

Detection and Determination of Small Quantities of Fluorine. R. J. MEYER and W. SCHULZ (*Z. angew. Chem.*, 1925, **38**, 203—206).—The fluoride solution is concentrated, acidified with strong acetic acid, and treated with excess of 1% lanthanum acetate solution. Solid ammonium acetate is added in large excess and the whole is warmed. After a time, depending on the amount of fluorine present, a flocculent precipitate of lanthanum fluoride deposits, which becomes pulverulent when kept or heated. The amount of lanthanum acetate adsorbed by this precipitate is corrected for by heating it with ammonium acetate and acetic acid solutions, washing, and weighing before and after gentle heating, which converts the normal acetate into oxide without affecting the fluoride. Precipitation by calcium and thorium salts is shown to be

unsatisfactory for the determination of small quantities of fluorine. [Cf. *B.*, June 26th.] S. K. T.

Determination of Nitrogen in Oil, Coke, and Proteins. H. TER MEULEN (*Rec. trav. chim.*, 1925, **44**, 271—274).—The material is thoroughly mixed with seven times its weight of sodium carbonate and heated in a current of hydrogen saturated with water vapour at 100°. The whole of the nitrogen is converted into ammonia, which is determined in the usual way. Proteins give figures by this method generally slightly higher than those obtained by the Kjeldahl method, but pure organic substances give figures corresponding exactly with the theoretical. S. I. L.

Determination of Nitrogen [in Explosives]. M. MARQUEYROL [with L. CHENEL, FRIEDERICH, D. FLORENTIN, KOEHLER, and P. LORIETTE] (*Mém. Poudres*, 1925, **21**, 326—379).—The Schlœsing method with various modifications and the Lunge nitrometer method, as applied to the determination of nitrogen in nitrates and nitric esters, are discussed and compared in detail. The latter is preferred. C. I.

Determination of Nitrous Vapours. A. T. SCHLŒSING (*Mém. Poudres*, 1924, **21**, 127—132).—Details are given for the use of special absorption vessels (cf. this vol., ii, 566). These vessels are of ⊔-shape, the two vertical limbs being connected near the top by a horizontal tube. Sufficient absorbing liquid (about 30 c.c.) is used just to fill this connecting tube, through which the gas bubbles. The gas is drawn forward by means of a water-jacketed aspirator, each bubble being in contact with the absorbent for about 1·5 to 2 minutes. A known quantity of standard alkali is placed in the absorber and is titrated back at the end of the test. W. T. K. B.

Reactions for Nitrates and Nitrites. S. VÁGI (*Z. anal. Chem.* 1925, **66**, 14—16).—In the presence of an equal volume of concentrated sulphuric acid, solutions of nitrates and nitrites give a yellow colour with 2% alcoholic benzidine, but nitrites only give a yellow colour with an acetic acid solution of benzidine. Chlorates and ferric chloride also give a yellow colour with alcoholic benzidine in the presence of sulphuric acid, but may be distinguished from nitrates and nitrites by the red colour produced with the same reagent in the presence of hydrochloric acid, which destroys the yellow colour due to nitrates and nitrites. A 1% aqueous solution of sodium 8-amino-α-naphthol-3 : 6-disulphonate or of sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate gives an orange-coloured solution and α-naphthol-5-sulphonic acid a wine-red colour with nitrates in 50% sulphuric acid. Nitrites, chlorates, and ferric chloride give the same reactions in more dilute sulphuric acid. An acetic acid solution of sodium 8-amino-α-naphthol-3 : 6-disulphonate gives a citron-yellow colour with nitrites. A. R. P.

Reactions of Nitrates and Nitrites. S. VÁGI (*Z. anal. Chem.*, 1925, **66**, 101—104).—A 1% solution of the following reagents in 50% acetic acid gives characteristic colours with dilute nitrite

solutions (the figures in brackets denote minimum concentration of nitrite in mg. per litre for colour to be visible in 40 c.c. of the test solution): pyrogallol, reddish-brown, changing to yellow on keeping (0·1); pyrocatechol, reddish-brown (0·1), becoming green then colourless with ammonia; quinol, intense yellow (5·0); orcinol (0·33% solution), intense bright yellow (1·0); resorcinol (0·25% solution), bright yellow (1·0). A solution of 1 g. of α-naphthol and 0·5 g. of sulphanilic acid in 100 c.c. of glacial acetic acid and 300 c.c. of water gives an orange-yellow solution with nitrites (0·1) becoming rose-red with ammonia. The colour with a corresponding β-naphthol solution is pale yellow, and with pyrocatechol rose-red (0·1). A solution of 1 g. of benzidine and 1 g. of sodium 8-amino-α-naphthol-3 : 6-disulphonate in 400 c.c. of 20% acetic acid gives a yellowish-brown solution with nitrites which becomes rose-red (0·1) in 1 hr. Nitrates give a green colour with a 1% solution of pyrocatechol in strong sulphuric acid and a violet-brown colour with a corresponding pyrogallol solution; nitrites give a similar reaction. A. R. P.

Determination of Phosphorus in the Presence of Vanadium. G. W. Gray and C. D. Garbutt (*J. Iron and Steel Inst.*, May 1925; [Advance proof]).—The material is dissolved in a mixture of nitric and hydrochloric acids, the silica removed, the iron separated with ether, and the phosphorus precipitated as magnesium ammonium phosphate in the presence of citric acid; the precipitate is dissolved in nitric acid and the phosphorus determined as phosphomolybdate. M. E. N.

Detection of Silicic Acid. R. Lorenz and E. Bergheimer (*Z. anorg. Chem.*, 1924, **136**, 95—96).—For the detection of silicic acid in distilled water or sodium chloride solutions, the solution is heated at 80° and treated with 1 c.c. of a solution of 8 g. of potassium molybdate in 100 c.c. of 1 : 1-nitric acid. The green colour of the potassium silicomolybdate solution so formed is compared with that of a standard prepared from a solution of sodium silicate. A. R. P.

Rapid Determination of Carbon in Organic Compounds. H. D. Wilde, jun., and H. L. Lochte (*J. Amer. Chem. Soc.*, 1925, **47**, 440—446).—The substance (80—200 mg.), preferably in compressed tablet form, is burned in a small calorimetric bomb in the presence of oxygen at 25 atm. pressure, and 0·5*N*-barium hydroxide solution, the carbonate being subsequently determined volumetrically. If complete combustion is not attained, the substance may be placed in powder form in a weighed gelatin capsule, allowance being made for the carbon dioxide produced by combustion of the latter. Liquids may also be analysed by using a gelatin capsule. Halogen compounds give appreciable amounts of oxyhalogen derivatives, which impair the accuracy of the results. This is circumvented by adding hydrazine hydrate and aluminium to the alkali from the bomb in an evacuated apparatus, distilling with hydrochloric acid and collecting the carbon dioxide evolved in standard alkali solution. Sulphur can be determined gravimetri-

cally in the solution from the bomb as sulphate. The results are as accurate as those obtained by Liebig's method. F. G. W.

Micro Determination of Potassium in Blood Serum and Other Fluids. F. LEBERMANN.—(See i, 714.)

Substitute for Cobalt Glass. J. MEYER (*Helv. Chim. Acta*, 1925, **8**, 146—148).—Marked superiority is claimed for the use of a gelatin filter dyed with crystal-violet over that of blue glass in the flame test for potassium in presence of sodium. The preparation of the filter is described. M. J.

Separation and Determination of the Alkali Metals, using Perchloric Acid. III. *n*-Butyl Alcohol and Ethyl Acetate as Mixed Solvents in the Separation and Determination of Potassium, Sodium, and Lithium. G. F. SMITH and J. F. ROSS (*J. Amer. Chem. Soc.*, 1925, **47**, 1020—1026).—A mixture of equal volumes of *n*-butyl alcohol and ethyl acetate is shown to be satisfactory for the separation of perchlorates of sodium and potassium, potassium and lithium, and sodium and lithium subsequent to the separation of potassium. In the first case, two separations are necessary (cf. A., 1923, ii, 182; this vol., ii, 436, 437). S. K. T.

Determination of Calcium in Blood by Tisdall's Method. E. P. CLARK and J. B. COLLIP.—(See i, 713.)

Critical Studies on Methods of Analysis. XV. Magnesium. L. A. CONGDON and G. VANDERHOOK (*Chem. News*, 1925, **130**, 241—243, 258—261, 273—276).—The use of sodium salts as precipitants in the methods of determining magnesium as magnesium ammonium phosphate or arsenate gives more nearly correct results than the use of ammonium salts, probably owing to slight adsorption of part of the precipitant by the precipitate which counterbalances loss due to the slight solubility of the precipitate. Weighing the precipitate in each case after ignition to pyrophosphate is preferable to an indirect determination by alkalimetric or iodometric processes. [Cf. *B.*, June 26th.] A. R. P.

Determination of Magnesium in Presence of Aluminium. F. L. HAHN (*Z. anorg. Chem.*, 1925, **144**, 142—144; see Jander and others, *ibid.*, **142**, 329).—The method of determining magnesium in presence of large quantities of aluminium by precipitating as magnesium ammonium phosphate in presence of tartaric acid, which holds aluminium in solution, whilst found to give exact results by some workers, has been found unsuitable by the author, and is not recommended. S. I. L.

Reagent for Aluminium. L. P. HAMMETT and C. T. SOTTERY (*J. Amer. Chem. Soc.*, 1925, **47**, 142—143).—The supposed precipitate of aluminium hydroxide is dissolved in hydrochloric acid and ammonium acetate solution containing ammonium aurintricarboxylate. After lake formation (crimson for aluminium) has taken place, the solution is made alkaline with ammonia solution containing

ammonium carbonate. This removes interfering lakes formed from chromium and alkaline-earths. Ferric iron must first be removed. L. J. H.

Gravimetric Determination of Aluminium and its Separation from Manganese by the Use of "Infusible White Precipitate." B. SOLAJA (*Chem.-Ztg.*, 1925, **49**, 337—338).—The solution is neutralised with ammonia, ammonium chloride is added, and the mixture digested overnight with a quantity of "infusible white precipitate" ($ClHg{\cdot}NH_2$) equal to ten times the amount of alumina present. The precipitate is collected, washed with cold water, and ignited to alumina. The process effects complete separation of aluminium from manganese in one operation and the precipitated aluminium hydroxide filters more readily than that produced by ammonia. [Cf. *B.*, June 26th.] A. R. P.

Alkalimetric Determination of Aluminium Salts and Free Acids in the Presence of One Another. T. SABALITSCHKA and G. REICHEL (*Arch. Pharm.*, 1925, **263**, 193—196).—Excess of sulphuric acid in a solution of aluminium sulphate may be determined by titration with potassium hydroxide, using as indicator either the colouring matter of pæonies (red in acid, colourless in aluminium sulphate solution containing no excess of acid) or sodium alizarinsulphonate. By the method of Stock (A., 1900, ii, 247, 315)—titration with alkali in the presence of barium chloride, using phenolphthalein as indicator—the total amount of acid in the solution (*e.g.*, excess acid and acid equivalent to aluminium) may be found, the difference between total and excess acid showing the amount of aluminium present. Stock's method applies only to the sulphate and chloride, but, *e.g.*, the acetate is converted into the sulphate by treatment with excess of strong sulphuric acid. After evaporation to fuming, the residue is dissolved in water and diluted to a known volume. Part of the solution is then examined for excess acid by titration with alkali, using the pæony indicator, until colourless. Another part is treated with barium chloride and titrated with alkali, using phenolphthalein, to redness, then heated to boiling to remove the colour, and re-titrated to rose colour, the total titration giving the total acid. The pæony indicator is prepared by heating the red petals of *Pæonia peregrina*, Mill., var. *officinalis*, Retz, and *P. arborea*, Don., with 90% alcohol. Excess of this indicator gives a bad end-point. B. F.

Potentiometric Standardisation of Potassium Permanganate Solution with Sodium Oxalate. C. DEL FRESNO (*Z. Elektrochem.*, 1925, **31**, 199—200).—Potassium permanganate may be standardised potentiometrically with sodium oxalate at 70°. The end-point is sharply marked and is the same as in the chemical titration. N. H. H.

Separation of Iron, Chromium, Aluminium, and Phosphoric Acid from Zinc, Nickel, Cobalt, and Manganese, and Determination of the Last Four Elements. K. K. JÄRVINEN (*Z. anal. Chem.*, 1925, **66**, 81—100).—The ordinary methods of

separating iron, chromium, aluminium, and phosphoric acid from the members of the ammonium sulphide sub-group by means of ammonia, barium carbonate, or sodium acetate have to be repeated several times owing to adsorption of the monoxides by the sesquioxide precipitate. This may be overcome and a complete separation obtained in one operation, in the case of iron, or two, in other cases, by the following procedure. The chloride solution is neutralised with ammonium carbonate until a faint permanent precipitate forms and boiled with 2 g. of ammonium sulphate. The boiling solution is treated with 4 g. of sodium nitrite and cooled; the precipitate contains all the iron and phosphoric acid and most of the aluminium and chromium. After filtering and washing, the filtrate is boiled with a further 1 g. of sodium nitrite to remove any remaining sesquioxide. For the separation of zinc, cobalt, nickel, and manganese from the filtrate, successive precipitations with hydrogen sulphide under pressure in 0·035*N*-hydrochloric acid, 2% acetic acid and 2% ammonia are recommended. The precipitates in each case are converted into sulphate for weighing. The zinc sulphate should be tested colorimetrically by thiocyanate for the presence of traces of cobalt. [Cf. *B.*, June 26th.] A. R. P.

Gravimetric Determination of Iron and a Rapid Method for Dissolving Ignited Iron Oxide. N. A. TANANAEV (*Z. anorg. Chem.*, 1924, **136**, 184—188).—Ferric oxide obtained by the ignition of a precipitate of hydroxide produced by the addition of ammonia to a solution of ferric sulphate, chloride, or nitrate invariably retains traces of water even after heating for 1 hr. over a blast burner. Analyses of pure iron wire by this method gave results as much as 2% too high, but more nearly correct figures were obtained if the ignited oxide was moistened with nitric acid, dried, and again heated as before. Evaporation of a solution of ferric nitrate to dryness followed by calcination of the residue also gave correct results. Strongly ignited ferric oxide may be dissolved readily in 1 : 1-hydrochloric acid if a few drops of a solution of stannous chloride are added from time to time. A. R. P.

Separation of Nickel and Copper from Iron. E. G. R. ARDAGH and G. M. BROUGHALL (*Univ. Toronto, Sch. Eng. Res. Bull.*, 1925, **5**, 227—235).—Conditions are given for the complete separation of nickel and copper from ferric hydroxide by means of ammonia and ammonium sulphate or chloride. The method is applicable to ores containing these three metals. [Cf. *B.*, 1925, 381.] T. H. P.

Detection and Determination of Nickel by Means of α-Furildioxime. B. A. SOULE (*J. Amer. Chem. Soc.*, 1925, **47**, 981—988).—Aqueous or alcoholic solutions of α-furildioxime give a red precipitate, $C_{22}H_{14}O_6N_4Ni$, from slightly ammoniacal solutions of nickel salts and may be used in place of α-dimethylglyoxime for the detection (1 in 6×10^6) and determination of this metal. In quantitative work, the precipitate may be weighed directly, or ignited to nickelous oxide, or dissolved and the metal determined by electrolysis or by a cyanide titration. Ferrous iron must be

absent; ammonio-cobaltous ions must be oxidised with hydrogen peroxide. In presence of manganic salts, acetic acid and sodium acetate must be added (cf. Brunck, A., 1907, ii, 582, 989).
S. K. T.

Carbon Error in the Quantitative Deposition of Nickel and Iron from Complex Oxalate Electrolytes. P. K. FRÖLICH (*Analyst*, 1925, 50, 224—230).—No conditions were found under which nickel could be deposited from oxalate electrolytes without contamination by organic matter, but in the case of iron the metal is not contaminated at the beginning of the reaction, and contamination can be sufficiently retarded to allow of quantitative deposition by the addition of ammonium chloride. [Cf. *B.*, June 26th.] D. G. H.

Determination of Vanadium. W. HARTMANN (*Z. anal. Chem.*, 1925, **66**, 16—23).—The vanadium solution, whether obtained by dissolving the substance in acids or by an alkali fusion, is evaporated with sulphuric acid until fumes are evolved, hydrochloric acid is added, and the evaporation repeated to reduce the vanadic acid to vanadyl salt. After dilution and heating at 70°, the vanadium is determined by titration with permanganate which has been standardised against a pure vanadium compound or against a similar material to that analysed, but of known vanadium content. If oxalic acid or other similar substance is used as standard, the vanadium results are always a little too high, but may be corrected by multiplying by 0·9915. Details are given of the methods used in analysing ferrovanadium and commercial vanadium pentoxide. [Cf. *B.*, 1925, 381.] A. R. P.

Determination of Antimony. V. AUGER (*Ann. Chim. analyt.*, 1925, **7**, 100).—Of the methods for determining antimony proposed by Ecke (A., 1924, ii, 705), the first is worthless for both chemical and arithmetical reasons, and the second will fail in the presence of much copper. [Cf. *B.*, 1925, 430.] D. G. H.

Fluorescence as a Criterion of Purity in Organic Compounds. E. BAYLE and R. FABRE (*J. Pharm. Chim.*, 1925, [viii], **1**, 248—253).—The spectrophotometric curves defining the colour of the fluorescence of a substance (cf. A., 1924, ii, 583) are shown to be criteria of the purity of the latter. The curves exhibit peaks which gradually attain a stable maximum position as the impurities are removed. S. K. T.

Rapid Determination of Phenols in Essential Oils, using Small Quantities of Material. L. RETI (*Chem.-Ztg.*, 1925, **49**, 306).—On shaking 0·5 or 1·0 c.c. of the oil with 3—5% sodium hydroxide solution in an absorption vessel ("phenolometer") constructed like Gerber's butyrometer, and centrifuging the mixture a good separation is obtained; the diminution in volume, corresponding with the amount of phenol present, can be read with great accuracy to 0·01 c.c. [Cf. *B.*, 1925, 424.] A. C.

Test for Pentoses. P. THOMAS (*Bull. Soc. Chim. biol.*, 1925, **7**, 102—112).—When an aqueous solution of a pentose, or of com-

plex derivatives containing a pentose, is poured carefully on to a 0·3% solution of β-naphthol in concentrated sulphuric acid, a deep blue (ultramarine) ring is formed; the colour is intensified on gentle shaking and diffuses into the acid, the original ring of colour becoming greenish-brown. The reaction appears to be characteristic of pentoses and does not occur with the other sugars, aldehydes, and ketones examined. The blue colour seems to be due to direct combination between the pentose and β-naphthol, and does not involve the intermediate formation of furfuraldehyde. The latter gives an intense orange-red colour with β-naphthol, above which a green ring forms, but no blue colour is produced.

C. T. G.

Reducing Action of Dextrose on Copper Salts in Alkaline and Acid Solution. P. FLEURY and P. TAVERNIER (*Bull. Soc. Chim. biol.*, 1925, **7**, 331—335).—The reducing action of dextrose on copper salts is influenced in acid solution (Barfoed's copper acetate reagent) by the presence of many chlorides, mannitol, and the concentration of the copper, whilst in alkaline solution (Bertrand's reagent) all alkaline and alkaline-earth salts, as well as mannitol, have a retarding effect. [Cf. *B.*, 1925, 417.]

D. G. H.

Interaction of Dextrose and Methylene-blue in an Alkaline Medium. E. KNECHT and E. HIBBERT (*J. Soc. Dyers Col.*, 1925, **41**, 94—95).—The possibility of over-reduction of methylene-blue in the reaction between this dye and dextrose in an alkaline medium is avoided, and the reaction is thereby made available for the determination of dextrose, by acidifying the product within a few seconds after the commencement of the reaction. A mixture containing sodium hydroxide, dextrose, and methylene-blue is boiled in an atmosphere of carbon dioxide, or preferably nitrogen, excess of hydrochloric acid is quickly added, and the excess of methylene-blue titrated in the usual way with titanous chloride and iron alum. Thiocarmine-*R* in the presence of rosinduline-*B* and sodium tartrate is quantitatively reduced by titanous chloride before the latter dye is affected. [Cf. *B.*, 1925, 348.] A. J. H.

Determination of Volatile Organic Acids. A. BOHANES (*Chem. Listy*, 1925, **19**, 121—123).—The time of distillation of volatile organic acids may be reduced by the addition of glycerol (50 c.c. to 100 c.c. of liquid to be distilled) with or without water. The temperature must not materially exceed 120°, and if necessary the operation is finished in a current of steam. [Cf. *B.*, June 26th.]

D. G. H.

Determination of Formic Acid in Blood and Urine. F. DE EDS.—(See i, 713.)

Detection of Ethyl Phthalate in Ethyl Alcohol. J. T. RALEIGH and S. U. MARIE (*J. Amer. Chem. Soc.*, 1925, **47**, 589—590).—Detection of ethyl phthalate in ethyl alcohol by evaporating the sample to dryness with dilute sodium hydroxide solution, and

fusing the residue with resorcinol, is untrustworthy, as the aqueous extract of the fused mass still shows a fluorescence, although of a slightly different colour, in the absence of ethyl phthalate. A suggested alternative is to evaporate the sample to a small volume and pour the residue into a large volume of very dilute sodium hydroxide solution. The presence of ethyl phthalate is indicated by a turbidity, but the test is not conclusive. F. G. W.

Chemical Nature of Fats. I. Iodine Super-value of Fatty Oils and Unsaturated Fatty Acids. B. M. MARGOSCHES, L. FRIEDMANN, and W. TSCHÖRNER.—(See i, 629.)

Determination of Formaldehyde. E. SCHULEK (*Ber.*, 1925, **58**, [*B*], 732—736).—The formaldehyde solution is added to an excess of standard potassium cyanide solution in the presence of magnesium sulphate, which accelerates the hydrolysis of the primarily-formed potassium derivative of glycollonitrile, $2CH_2(OK)\cdot CN + MgSO_4 + 6H_2O = 2CH_2(OH)\cdot CO_2K + Mg(OH)_2 + (NH_4)_2SO_4$. After 1—2 mins. the precipitated magnesium hydroxide is dissolved by ammonium chloride, a little potassium iodide and not more than 2—3 drops of ammonia (10%) are added, and the excess of potassium cyanide is titrated rapidly with 0·05*N*-silver nitrate solution. The method is accurate in the presence of 10% of acetaldehyde, 50% of acetone, or 50% of ethyl alcohol.

For the determination of very small amounts of formaldehyde, the solution under investigation is added to a measured excess of standard potassium cyanide solution. After 2—3 mins. the mixture is acidified strongly with concentrated hydrochloric acid and treated with bromine water until permanently yellow; excess of bromine is removed by addition of phenol. Potassium iodide is added to the clear, colourless solution, and the liberated iodine is titrated after 30 mins. with sodium thiosulphate. The potassium cyanide solution must be standardised iodometrically. The process gives accurate results in the presence of 5% of acetaldehyde, 50% of acetone, ethyl alcohol, or methyl alcohol, or of 1% of dextrose or lactose. [Cf. *B.*, 1925, 423.] H. W.

Analysis of Xanthate. W. S. CALCOTT, F. L. ENGLISH, and F. B. DOWNING (*Eng. Min. J. Press.*, 1924, **118**, 980—981).—The xanthate is precipitated as the copper salt from a slightly alkaline solution by means of copper sulphate–sodium tartrate reagent, the precipitate is collected and decomposed with nitric acid, the copper being determined volumetrically. Sulphides or thiocarbonates, but not thiosulphates, sulphites, carbonates, xanthyl disulphide, or ethyl xanthate cause high results. A. A. E.

Qualitative Test for Weak [Organic] Bases. R. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 768—769).—A saturated solution of ferric chloride in concentrated hydrochloric acid when added to a solution of a weak base in light petroleum produces three layers, the middle one of which contains the base. This behaviour is due to the formation of ferrichlorides. Carboxylic acids, acid chlorides, thiophen, safrole, diphenyl ether, and methyl and ethyl

alcohols do not give the reaction, the two last named being too soluble in water. Other applications of the reaction are described.
S. K. T.

Toxicological Detection of Hydrocyanic Acid by Chelle's Reaction. G. MAGNIN (*J. Pharm. Chim.*, 1925, [viii], **1**, 336—339).—After keeping for periods up to 6 years, specimens of viscera suspected to contain hydrocyanic acid have been tested by the direct phosphoric acid method and by the method of Chelle. The former method gave negative results in all cases; the latter gave results identical with those originally obtained on the fresh specimens. C. P. S.

Determination of Cyanamide. L. A. PINCK (*Ind. Eng. Chem.*, 1925, **17**, 459—460).—The adverse effect of the presence of cyanamide derivatives on the determination of cyanamide by the usual methods may be overcome by extracting the crude material with water, precipitating the silver cyanamide in an aliquot portion of the extract by adding concentrated ammonia and ammoniacal silver nitrate solution, dissolving the precipitate in dilute nitric acid, and either titrating the silver cyanamide with thiocyanate or, if carbide is present, determining its nitrogen content. Re-dissolution and re-precipitation of the silver cyanamide is necessary if a very large proportion of dicyanodiamide is present.
D. G. H.

Determination of Picric Acid in the Presence of other Nitro-compounds. L. DESVERGNES (*Ann. Chim. Analyt.*, 1925, **7**, 97—100).—To an alcoholic solution of the dry, powdered material is added a solution of potassium iodide and iodate, and the mixture titrated with sodium thiosulphate solution. Extraction with carbon tetrachloride may be used to separate the picric acid when mixed with 1-nitronaphthalene. [Cf. *B.*, 1925, 429.]
D. G. H.

[Determination of] Uric Acid in Blood. W. G. LENNOX and M. F. O'CONNOR.—(See i, 711.)

Silicododecatungstic Acid. [Determination of Alkaloids.] E. O. NORTH and G. D. BEAL (*J. Amer. Pharm. Assoc.*, 1924, **13**, 889—898, 1001—1009).—When a solution containing sodium tungstate, sodium silicate, and hydrochloric acid is shaken with ethyl ether, and the ethereal solution evaporated, stable white *crystals*, $4H_2O,SiO_2{\cdot}12WO_3,5H_2O$, are obtained. The *potassium* and *ammonium* salts were prepared, as well as *salts* of organic bases, the alkaloidal salts being but slightly soluble. Alkaloids may be determined volumetrically by treating an extract, acidified with hydrochloric acid, with the silicotungstic acid solution until a drop of the supernatant liquid yields a green colour with a reddish- or brownish-orange coloured solution of malachite-green in hydrochloric acid. CHEMICAL ABSTRACTS.

Potentiometric Determination of Alkaloids with a Hydrogen Electrode. F. MÜLLER (*Z. Elektrochem.*, 1924, **30**, 587—600).—The results obtained by the electrometric titration of various

alkaloids are given, together with the corresponding p_H curves. In the case of atropine, by means of a back titration with sodium hydroxide free from carbonate after adding excess of hydrochloric acid, the break in the p_H curve corresponds with $k_{B\cdot OH}=1\times10^{-4}$ (16·5°). Cocaine gave $k_{B\cdot OH}=2\cdot5\times10^{-6}$ (24°) and narcotine $0\cdot73\times10^{-8}$ (24°). No values could be calculated for veratrine, narceine, and theobromine, the first-named being a mixture of several alkaloids, and the last two giving no sharp break in the curves. The titration of alkaloid salts with alkali hydroxide gives satisfactory results in the cases of pilocarpine and *iso*pilocarpine hydrochlorides ($k_{B\cdot OH}=1\cdot07\times10^{-7}$ and $0\cdot68\times10^{-7}$ at 18°) and of emetine and arecoline hydrobromides [$k_{B\cdot OH}=0\cdot81\times10^{-6}$ (16°) and $1\cdot45\times10^{-7}$ (17·5°), respectively]. With morphine hydrochloride, disturbing reduction reactions occur, which are partly eliminated by the use of a smooth platinum electrode, and with codeine phosphate, the breaks in the curve are not sharp enough for conclusions to be reached. The most suitable indicators for the different cases are indicated where possible from the potentiometric measurements. C. H. D. C.

Simple Determination of the Alkaloid-content of Nux Vomica and of *Strychnos* Preparations. T. SABALITSCHKA and C. JUNGERMANN (*Pharm. Zentr.*, 1925, **66**, 145—150).—That the official method of determination is faulty has already been pointed out (cf. *e.g.*, Herzog, "Chemishe und physikalische Prüfungsmethoden des Deutschen Arzneibuches," 1924). It is found that the convenient procedure adopted for the lupin alkaloids (A., 1924, ii, 635) is well adapted for this determination also, with the further improvement that the ether–chloroform extract is filtered (with precautions to avoid evaporation) before the aliquot part is pipetted off. [Cf. *B.*, 1925, 297.] W. A. S.

Microchemical Reactions for Tyramine and Histamine. L. VAN ITALLIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1925, **62**, 429—433).—The appearances under the microscope of the picrates, chloroplatinates, iodoplatinates, double bismuth iodides, phosphotungstates, and silicotungstates are described. S. I. L.

Identification of Vat Dyes on Cotton. J. I. M. JONES and W. KILBY (*J. Soc. Dyers and Col.*, 1925, **41**, 127—136).—Tables are given showing the reactions with various appropriate reagents of patterns of cloth dyed with commercial vat dyes, which are listed under trade names, with the "Colour Index" numbers when available. [Cf. *B.*, 1925, 437.] W. A. S.

Detection of Urobilin in Urine and Determination of Chlorides in Blood. RODILLON.—(See i, 722.)

Determination of Bile Acids. E. HERZFELD and A. HAEMMERLI.—(See i, 722.)

General, Physical, and Inorganic Chemistry.

Spectrum of Hydrogen. E. Gehrcke and E. Lau (*Ann. Physik*, 1925, [iv], **76**, 673—679; cf. A., 1923, ii, 197, 802).—A long, silvered discharge tube with a fluorite window has been used for the study of the continuous and many-lined spectra of hydrogen. In agreement with Schumann, a continuous spectrum is found to extend from 3300 to 1950 Å. When electrolytic hydrogen is used, a large number of lines are superposed on the continuous ground. These are shown to be due to carbon monoxide as an impurity. It is concluded that under the experimental conditions pure hydrogen shows a continuous spectrum free from lines. This view is not in harmony with the results of other observers, but the lines found nearly always agree with those traced to carbon monoxide. The same conditions of excitation cause both the continuous and many-lined spectra to be strongly developed. When the Balmer series appears strongly, these spectra are weak. Slow electrons therefore favour the appearance of both spectra. Stark has obtained a spatial separation of the continuous and many-lined spectra, and Horton and Davies give the excitation potentials as 12·6 and 15·9 volts. The authors have measured the intensities of the continuous and many-lined spectra under different conditions, and the results indicate a difference of 6 volts between the excitation potentials.

The parallelism between the effects of slow electrons and condenser discharges recorded earlier is confirmed and extended. Two groups of lines symmetrically distributed about 5881·87 and 5832·40 Å. are added to those already found. R. A. M.

Ultra-violet Spark-spectra of some Elements. R. J. Lang (*Phil. Trans.*, 1924, **A**, **224**, 371—419).—The spectrograph used is a modified form of that of McLennan (A., 1920, ii, 650) of greatly increased efficiency. The instrument was calibrated over the range 2000—200 Å., in which range the spectra of the following elements have been photographed: carbon, calcium, titanium, vanadium, chromium, manganese, cobalt, arsenic, molybdenum, cadmium, tin, antimony, tellurium, cerium, platinum, gold, lead, bismuth, thorium, and uranium. The wave-lengths recorded are given in tabular form, together with the corresponding data of other observers. R. W. L.

Spectra of Oxygen and Sulphur. E. Bungartz (*Ann. Physik*, 1925, [iv], **76**, 709—728).—According to Sommerfeld, odd multiplicity of spectral terms is to be expected in the oxygen–sulphur–selenium sub-group of the periodic table. Evidence is cited that the p and d terms of the "doublet" system of the oxygen spectrum are really triple terms. Experimental details are given whereby Wood's method of exciting the Balmer series of hydrogen (A., 1920, ii, 569) can be applied to oxygen. The series spectrum

is obtained in great purity against a perfectly even background. In the ultra-violet, however, the band spectrum is not entirely eliminated. The extension of the experiments to sulphur has been worked out with interesting results. The series spectrum of sulphur has been completed by the addition of two triplets belonging to the I and II diffuse series and located in the near infra-red. A large number of new lines have been measured extending from 6173·53 to 8694·296 Å., and four lines for oxygen are recorded in the same region. The sulphur lines are narrow and complicated in structure, but they have been provisionally classified into series. R. A. M.

Spectra of the Metals of the Aluminium Sub-group. K. R. Rao (*Proc. Physical Soc.*, 1925, **37**, 259—264).—The light from an aluminium spark under water was passed through the vapour of thallium and of indium heated in a steel tube provided with quartz windows to temperatures up to 1500°. Tables and photographs of the spectra as far as 2000 Å. are given. None of the lines of the principal series appears as an absorption line, even at the highest temperature. In both cases, at high temperatures there is a channelled space spectrum consisting of asymmetrical bands degraded towards the red. There is very marked absorption of the members of $1\pi_2-m\delta'$. E. B. L.

Series Spectra of Two-valency-electron Atoms of Phosphorus (P IV), Sulphur (S V), and Chlorine (Cl VI). I. S. Bowen and R. A. Millikan (*Physical Rev.*, 1925, [ii], **25**, 591—599).—The regular and irregular X-ray doublet laws, already shown to be applicable throughout the whole field of optics so long as a series of atoms of like electronic structure but varying effective nuclear charge is concerned, have been used to predict the positions of lines in the spectra of two-electron atoms, although in this case the spectra consist of triplets and singlets instead of doublets as in the case of stripped atoms. For P IV, 23 lines have been identified, for S V 17, and for Cl VI 6; 12 term values of P IV and 8 of S V were determined, and all known term values for two-electron atoms of magnesium, aluminium, silicon, phosphorus, and sulphur are tabulated. It is shown that when the frequency of a given spectral line progresses linearly with the atomic number (*i.e.*, to follow the irregular doublet law) the line is produced by a jump between orbits of the same total quantum number; the screening constants differ. A. A. E.

Series Spectra of Three-valency-electron Atoms of Phosphorus (P III), Sulphur (S IV), and Chlorine (Cl V). R. A. Millikan and I. S. Bowen (*Physical Rev.*, 1925, [ii], **25**, 600—605; cf. preceding abstract).—There have been identified 21 lines of P III, 20 lines of S IV, and 10 of Cl V; 10 term values of P III and 10 of S IV, including the x level, have been determined. Screening constants for one-, two-, and three-valency-electron systems increase regularly with the number of valency electrons, and decrease with increase in the atomic number. A. A. E.

Chlorine Spark Spectra. L. Bloch and E. Bloch (*Compt. rend.*, 1925, **180**, 1740—1742).—The oscillatory discharge in an electrodeless tube is capable of exciting first and second order spark spectra. Sodium chloride is introduced into a tube which is then evacuated. The salt decomposes, furnishing sufficient chlorine to maintain the discharge. If the discharge is interrupted the experiment must be started afresh. The spectrum contains lines due to chlorine, air, and alkali metal. The air lines are easily recognised, and only the lines which persist when another alkali chloride is substituted for sodium chloride are due to the halogen. The lines of the arc spectrum Cl I are absent. The first order spark spectrum, Cl II, contains the triplets 4819—4810—4794 and 4253—4241—4233 and the complex triplets 5457—5444—5423 and 3861—3851—3845 Å. Many new lines similar to the above have been found (but not recorded in this paper) and ascribed to Cl II. A large number of additional lines are ascribed to the second order spark spectrum Cl III. The Cl III spectrum extends far into the ultra-violet and includes the lines 3991·625, 3720·4, 3658·5, 3624·3, 3622·7, 3613·9, 3602·2. R. A. M.

Allocation of Terms to Some Multiplets in the Iron Spectrum. S. Goudsmit (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 572—583).—Terms have been allocated to the members of the multiplets discovered by Walters in the iron spectrum, using the rules of Sommerfeld and Landé. S. B.

Structure of Cobalt Spectrum. M. A. Catalán (*Z. Physik*, 1925, **32**, 336—369).—A classification of 517 lines is given and discussed; the energy levels show great similarity to those of iron; the terms show remarkable regularity. E. B. L.

Wave-length and Width of the *K*-Absorption Limit of Zinc. B. Walter (*Z. Physik*, 1925, **32**, 409—414).—This wave-length for zinc lies between the L_β line of tungsten, $1279{\cdot}17\times10^{-11}$ cm., and the L_γ line of tantalum, $1281{\cdot}0\times10^{-11}$ cm. The value calculated from Kossel's theory is $(1280\pm1{\cdot}0)\times10^{-11}$ cm. E. B. L.

Spectrum of Germanium. J. Lunt (*Month. Not. Roy. Astr. Soc.*, 1924, **85**, 38—46).—The spectrum of germanium has been re-examined in the visible region. The spark discharge between metallic electrodes and the vacuum discharge through germanium chloride were both used, and the lines have been classified according to their behaviour under various discharge conditions. Discrepancies up to 1·5 Å. were found between the wave-lengths of the spark and vacuum tube lines. S. B.

Large Line-displacements in the Spectra of Germanium and Chlorine under Different Conditions of Temperature. J. Lunt (*Month. Not. Roy. Astr. Soc.*, 1924, **85**, 148—156; cf. preceding abstract).—Displacements of certain lines in the spectra of germanium and chlorine, of the order of 1 Å., are occasioned by alteration of discharge conditions. The displacements in chlorine

have been tabulated from a comparison of the wave-lengths of the lines excited in germanium chloride vapour in vacuum tubes under widely differing types of discharge. The displacements are attributed to changes in "temperature" with the various conditions imposed, and a parallel is drawn with displacements observed in stellar spectra. S. B.

Quartet-system Multiplets in the Arc Spectrum of Yttrium. W. F. Meggers and B. E. Moore (*J. Washington Acad. Sci.*, 1925, **15**, 207—210).—Measurements of the magnetic resolutions of yttrium arc lines have revealed prominent quartet terms which have their analogues in the scandium arc spectrum (Meggers, this vol., ii, 77). The agreement between the observed interval ratios for the quartet terms F, F', and G_1 and those calculated by Landé's interval rule (*Z. Physik*, 1923, **15**, 189), is good, but poor for the quartet D term. M. S. B.

Regularity in the Fine Structure of Spectral Lines. G. Joos (*Physikal. Z.*, 1925, **26**, 380—382).—The spacings of the fine structure of the cadmium triplets, $2p-2s$, and of the bismuth line 4722 are multiples of 0·05. The introduction of a further quantum number, f, is necessary to explain fine structure (cf. Ruark, Mohler, and Chenault, A., 1924, ii, 797). J. S. C.

Pole-effect of Barium and Neodymium Rays in the Visible Region of the Spectrum. J. M. Mohr (*Compt. rend.*, 1925, **180**, 1397—1399).—With metal electrodes, the pole effect is greater at the positive than at the negative pole; when salts are used, the reverse is true. The displacement of spectral lines is of the same magnitude and sign at the negative pole, using carbon electrodes, as at the positive pole of metal electrodes. Barium and neodymium salts were placed in the crater of a carbon electrode and the light from the centre of the arc and the two poles was examined in one operation with an interference spectrograph. The barium lines show (*a*) displacements up to 0·003 Å. for the negative pole and negligibly small displacements for the positive pole, and (*b*) a few lines with larger displacements, *e.g.*, for 6141·75: negative +0·008, positive +0·002; and for 5777·77: negative −0·005, positive 0·000. The connexion between pole-effect and the lines in a series does not appear. The displacements are equally small with neodymium. Calcium lines were observed owing to impurity, and earlier measurements of the displacement are confirmed. This fact supports the view that the pole effect is not due to the density of the vapours. R. A. M.

New Lines between 3100 and 2200 Å. in the Arc Spectrum of Lanthanum at Normal Pressure. S. Pina de Rubies (*Compt. rend.*, 1925, **180**, 1478—1480).—The wave-lengths and intensities of more than 200 lines in the arc spectrum of lanthanum between the limits indicated are recorded. J. S. C.

***X*-Ray Spectra of Praseodymium, Neodymium, and Samarium.** E. Gleditsch and E. Botolfsen (*Compt. rend.*, 1925, **180**, 1653—1655).—The *X*-ray spectra of praseodymium,

neodymium, and samarium have been investigated by the method of Siegbahn, using a rotating crystal of rock salt. The following values, in Ångström units, have been found for the characteristic wavelengths of the different rays. Praseodymium: $\alpha=2\cdot4635$, $\beta_1=2\cdot2632$, $\beta_3=2\cdot2218$, $\beta_2=2\cdot1268$, $\gamma_1=1\cdot9794$, $\gamma_2=1\cdot8844$, $\gamma_3=1\cdot8255$. Neodymium: $\alpha=2\cdot3725$, $\beta_1=2\cdot1707$, $\beta_3=2\cdot1303$, $\beta_2=2\cdot0282$, $\gamma_1=1\cdot8708$, $\gamma_2=1\cdot7937$, $\gamma_3=1\cdot7390$. Samarium: $\alpha=2\cdot2059$, $\beta_1=2\cdot0014$, $\beta_3=1\cdot9610$, $\beta_2=1\cdot8708$, $\gamma_1=1\cdot7159$, $\gamma_2=1\cdot6475$, $\gamma_3=1\cdot5970$.

W. H.-R.

Absorption of a Line of the Principal Series of Singly Ionised Atomic Mercury. L. A. Turner and K. T. Compton (*Physical Rev.*, 1925, [ii], **25**, 613—617).—Carroll's conclusion that the line 1942 Å. is a member of the principal series and 2225 and 2848 Å. of the subordinate series of mercury is supported by the fact that only the first shows absorption when light from an electrodeless discharge in mercury vapour is passed through a region of a low-voltage arc in mercury vapour containing a high concentration of positive ions. Further, the lines appear respectively at 6·7, 12·3, and 10·7 volts.

A. A. E.

Spectrum of Mercury under Heavy Current Excitation. M. Fukuda (*Japan. J. Phys.*, 1924, **3**, 139—153).—The effect on the spectrum from a mercury arc of increasing the current density up to 5·3 amp./cm.^{2} has been examined in detail. The effect consists mainly in the broadening of certain lines and in the appearance of a large number of lines "forbidden" by the selection principle. Previously known series in the spectrum have been extended to higher members, and 40 forbidden lines newly arranged in series. The critical field intensities required for the excitation of the newly-observed forbidden lines have been estimated. In addition, a large number of new lines, both of the arc and the spark types, have been observed, which have not yet been arranged in series.

S. B.

Absorption and Emission Spectra of the Geissler Discharge in Mercury Vapour and in Mixtures of Mercury and Hydrogen. L. A. Turner and K. T. Compton (*Physical Rev.*, 1925, [ii], **25**, 606—612).—The positive column is a strong absorber for many lines of the sharp and diffuse subordinate series, the strength of the absorption decreasing in the order $2p-2s$, $2p-3s$, and $2p-3d$, $2p-4d$, $2p-5d$. The fact that the absorption by atoms in the $2p_1$ state is greatest, but of the same order of magnitude as that by atoms in the $2p_2$ and $2p_3$ states is difficult to reconcile with the short life of the $2p_2$ state. The bright region of the striated positive column (produced by addition of hydrogen) showed greater absorption of the $2p-2s$ lines than did the dark region. The negative glow emitted the arc spectrum and the spark line 2848 Å.; the continuous positive column emitted the arc spectrum, the striated column emitting also HgH bands.

A. A. E.

Vacuum Thermo-element. W. J. H. Moll and H. C. Burger (*Z. Physik*, 1925, **32**, 575—581).—A very neat and sensitive thermo-

couple for use in spectroscopy is described and a graph of the mercury spectrum, automatically registered, given. E. B. L.

Radiating Atoms in Magnetic Fields. P. ZEEMAN (*J. Franklin Inst.*, 1925, **199**, 585—596).—A lecture reviewing the historical and theoretical development of the Zeeman effect. F. G. T.

Intensities of Lines in Multiplets. H. N. RUSSELL (*Nature*, 1925, **115**, 835—836).

Anomalous Dispersion and Multiplet Lines in Spectra. C. V. RAMAN and S. K. DATTA (*Nature*, 1925, **115**, 946).—Attention is directed to observations parallel with those of Dorgelo (*Diss.*, Utrecht, 1924). A. A. E.

***K*-Absorption Levels of the Light Atoms.** H. ROBINSON (*Nature*, 1925, **115**, 945—946).—Revised ν/R values (*K* level) have been obtained as follows: calcium, 296·6; sulphur, 180·3; magnesium, 93·6; sodium, 76·6; oxygen, 36·7. Details of the work and improved apparatus will appear elsewhere. A. A. E.

Semi-optical Lines in the *X*-Ray Spectra. E. BÄCKLIN, M. SIEGBAHN, and R. THORÆUS (*Phil. Mag.*, 1925, [vi], **49**, 1320).—Polemical against Dauvillier and de Broglie (cf. this vol., ii, 458). R. A. M.

Continuous *X*-Ray Spectrum and Planck's Radiation Law. A. MARCH (*Ann. Physik*, 1924, [iv], **75**, 711—742).—Mathematical, with a discussion of experimental results. The continuous background is regarded as a heat radiation emitted by atoms of the anticathode which have been strongly heated by collision with electrons. A. S. R.

Coherence of Superposed *X*-Radiations. C. G. BARKLA and G. I. MACKENZIE (*Nature*, 1925, **115**, 942).

Broadening of Lines in Arc Spectra and the Stark Effect. H. LOWERY (*Phil. Mag.*, 1925, [vi], **49**, 1176—1183).—Lines produced in arc spectra by heavy currents (40 amps.) are affected similarly as in the Stark effect, *i.e.*, lines showing the Stark effect were broadened in the same sense (Kimura and Nakamura, A., 1924, ii, 799). Interrupted arc spectra (A., 1922, ii, 176, 410) of copper, silver, gold, nickel, and magnesium have been studied. The broadening of lines is similar to that observed in the heavy current arc spectra, and is such as would be expected from the observations on the Stark effect. Duffield (A., 1911, ii, 350) found certain broadening effects. He employed heavy currents and the arc had to be struck repeatedly. His results are therefore compatible with the present work. R. A. M.

Experimental Control of Electrically Broadened Spectral Lines. M. C. JOHNSON (*Proc. Physical Soc.*, 1925, **37**, 249—258).—The line H_α from a discharge in an ordinary type of Pflücker tube was selected for examination, viewed through a micrometer

eyepiece attached to a 20-plate echelon and a Hilger constant-deviation spectroscope. The effects of inductance, capacity, current-density, of rectified and unrectified currents, and of a magnetic field were studied. The width was also varied by supplying additional ions from a heated filament. It is concluded that the width of the line depends on the number of charges which surround the emitting particle. E. B. L.

Relative Mobility of Initial Positive Ions in Gas Mixtures at Low Pressures. H. B. WAHLIN (*Physical Rev.*, 1925, [ii], 25, 630—635).—The initial mobility of ions at low pressures appears to be determined chiefly by the mass of the ion rather than by its dimensions. Aged ions have lower mobilities and are probably clusters. A. A. E.

Ionisation of Salt Vapours. II. V. KONDRATÉEV (*Z. Physik*, 1925, **32**, 535—541; cf. A., 1924, ii, 291).—The vapours of zinc chloride and of sodium iodide were bombarded with slow electrons from a Wehnelt cathode, the nature of the ions being ascertained by determining the magnetic field required to deflect them through a certain arc. The chief process in zinc chloride vapour is decomposition into $ZnCl^+$ and Cl^-, which occurs at 12 ± 1 volts. There are also indications of the occurrence in very small quantity among the positive ions of $ZnCl_2^+$, Zn^+, and either Zn^{++} or Cl^+. Preliminary results indicate that ionisation of sodium iodide causes the formation of Na^+, I^-, and NaI^+. E. B. L.

Variation of the Energy absorbed by Ionisation in Air when Excited by *X*-Rays of varying Wave-length. L. GREBE (*Physikal. Z.*, 1924, **25**, 599—601).—Determinations have been made of the ratio of the energy of an *X*-ray beam, after having ionised a layer of air, to the intensity of ionisation produced over the range 0·397 to 0·166 Å. Relative values of the beam energy were obtained by observing the thermal effect produced in a lead target. The values so obtained are compared with the corresponding values derived from an equation due to Küstner (*Strahlentherapie*, 1924, **27**, 1) in which the total absorption is expressed as a function of the frequency and of the scattering effect. The values agree at the lower frequencies but diverge considerably at the higher ones. Appended is a discussion of the difficulties inherent in technique of this type and of the validity of Küstner's equation.
R. W. L.

Critical Potentials Associated with Excitation of Alkali Spark Spectra. F. L. MOHLER (*U.S. Bur. Standards, Sci. Paper* 505, 1925, **20**, 167—191).—Critical potentials for the production of radiation are found for rubidium vapour at 16 and 21·6 volts, and less defined potentials at 18, 25·2, and 68 volts. The ionisation curve shows a marked increase at 16 volts. Spark lines are excited at potentials between 17 and 25 volts. The intensity of these lines depends on the current density. The current density required to produce spark lines at 25 volts is estimated as 0·01—0·02 amp./cm.^{2} With cæsium, spark lines are excited with small

currents at 21·5 volts, and with large currents near 14 volts. Noticeable enhancement of all spark lines occurs at higher voltages, and a new spectrum appears above 40 volts. Critical potentials were found for potassium vapour at 19 and 23 volts (*U.S. Bur. Standards, Sci. Paper* 425) and increase of ionisation occurred at the higher potential. A similar increase is now found at 19 volts, and spark lines are excited at this point with high currents, and near 28 volts with low currents. Sodium vapour gives spark lines near 35 and 44 volts with large and small currents, respectively. Lithium vapour shows a critical potential at 54 volts and a single spark line occurs with large current densities at 2934·15 Å. (cf. A., 1924, ii, 365). Evidence is adduced for the view that the potentials Li 54, Na 35, K 19, Rb 16, and Cs 14 measure the work required to remove a single electron from the rare gas shell of the normal atom. Each of these values, except that of sodium, is equal within experimental error to the ionisation potential of the neighbouring rare gas ion. Direct comparison is impossible in the case of sodium, since the ionisation potential of neon is unknown. The critical potential for low-current spark excitation gives the work necessary to remove two electrons by a single collision. The critical potentials of potassium and rubidium at 23 and 21·6 volts, respectively, apparently measure the work required to remove a second electron from an ion, of which the valency electron is already removed. The relative intensities of the spectra of cæsium excited in the above thermionic discharge with different exciting potentials, in the high-voltage disruptive discharge (cf. this vol., ii, 4), and in the induction ring discharge (Dunoyer, A., 1922, ii, 729), are tabulated, and the fact that the two spark spectra of cæsium, which have widely different excitation potentials, appear in nearly the same relative intensity in the thermionic discharge at 80 volts and in the disruptive discharge, indicates that the effective discharge in the latter is about 80 volts. F. G. T.

Electron Emission of Metals. I. A. Becker (*Ann. Physik*, 1924, [iv], **75**, 781—800).—A general theoretical discussion of the subject. Richardson's work, δ-radiation, and the emission of electrons by the action of α-particles are specially dealt with.
A. S. R.

Behaviour of Hydrogen in the Discharge due to Alternating Electric Fields of High Frequency. R. W. Lunt (*Phil. Mag.*, 1925, [vi], **49**, 1238—1249).—The author's technique (this vol., ii, 579) for investigating the chemical effects in gases of alternating electric fields of the order of 10^7 cycles per sec. is applied to the study of the ionisation produced in hydrogen at the frequency $1{\cdot}5\times10^7$. The phenomena occurring in an ozoniser or ionisation vessel are analysed so that the voltage gradient and the current carried by the ions in the gas can be determined. An equation is given showing a connexion between impressed electric force, conduction current in the ionised gas, and the known motions of ions and electrons in hydrogen. From this it is possible to arrive at the mean intensity of ionisation of hydrogen under any given electrical conditions. This quantity

and also the impressed electric force are shown graphically over the pressure range 10—50 cm. The concept of equivalent temperature —that temperature at which the same density of ionisation would be produced by thermal dissociation as that observed in the ionisation vessel under any given conditions—is introduced. A series of values of this quantity at a series of voltages is expressed graphically against varying hydrogen pressure. R. A. M.

Electron Emission from Oxide-coated Filaments. L. R. KOLLER (*Physical Rev.*, 1925, [ii], **25**, 671—676).—Since the electron emission of platinum–iridium filaments coated with barium and strontium oxides is decreased by the presence of oxygen and increased by that of argon, hydrogen, carbon monoxide, and carbon dioxide, or by positive ion bombardment, the effect is probably due to a film of the metal. A. A. E.

Absorption Coefficient for Slow Electrons in Gases. R. B. BRODE (*Physical Rev.*, 1925, [ii], **25**, 636—644).—The absorption coefficients for electron accelerating voltages of 2—360 for argon, helium, methane, nitrogen, and carbon monoxide exhibit maxima at 12, 4, 7·5, 18, and 18 volts, respectively; the curve for hydrogen shows no maximum, the coefficient increasing steadily down to 2 volts. A. A. E.

Double Impacts by Electrons in Helium. G. GLOCKLER (*Nature*, 1925, **115**, 909—910).—Polemical against Dymond (this vol., ii, 253). A. A. E.

Double Impacts by Electrons in Helium. E. G. DYMOND (*Nature*, 1925, **115**, 910).—Polemical against Glockler (preceding abstract). A. A. E.

Constancy of Total Photo-current from Sodium with Temperature Change 20° to −190°. R. C. BURT (*Phil. Mag.*, 1925, [vi], **49**, 1168—1176).—An evacuated electric bulb of soda-glass is immersed in molten sodium nitrate and a potential of 100 volts is applied between the latter and the lighted filament. Sodium is driven through the walls; it evaporates and condenses at the top inside the bulb. In order to maintain the sodium surface clean, the lamp is attached to a mercury pump with two intermediate liquid air-traps. The sodium can be distilled back to the bottom of the bulb, so that light from the filament may be incident on the sodium surface. The photo-current is then measured at the ordinary temperature and at the temperature of liquid air. If the surface of sodium is clean, the total photo-current is practically constant over this range. If, however, the surface is faintly contaminated, the current may vary much more at a low temperature than at the ordinary temperature. On the other hand, a surface slightly more contaminated by some unknown vapour may be several times less sensitive at −190° than at 20°. Ives (A., 1924, ii, 444) found a temperature effect on photo-emission from sodium. The effects were reproduced by the author by allowing the sodium surface to be contaminated. R. A. M.

Direction of Emission of Photo-electrons. P. AUGER and F. PERRIN (*Compt. rend.*, 1925, **180**, 1742—1744).—The large dispersion of photo-electrons is explained on the basis of three assumptions, (*a*) that the process of emission occurs instantaneously, (*b*) that the electron leaves its orbit tangentially, its kinetic energy increasing suddenly by Nv, and (*c*) that the probability of emission for a given electron depends on the intensity of the incident radiation, or more precisely, on the square of the amplitude of the field acting on the electron. R. A. M.

Evaluation of the Magnetic Moment of Atoms. N. SEMENOV (*Z. Physik*, 1924, **30**, 151—152).—A criticism of the argument adopted by Stern and Gerlach, whose values are shown to be in error, in some cases by as much as 100%. R. W. L.

Paramagnetism of the Rare Earths. B. CABRERA (*Anal. Fís. Quím.*, 1925, **23**, 151—157; cf. A., 1924, ii, 142; this vol., ii, 173).—Data are given for the magneton numbers of the rare-earth metals, obtained from measurements, using the sulphates. Except for samarium, the values obtained approximate to whole numbers. Magneton numbers plotted against atomic numbers give a curve showing two maxima (cf. Meyer, this vol., ii, 173). This type of curve is not to be expected from the Bohr distribution of electrons but might be in agreement with the modified distribution suggested by Stoner (this vol., ii, 85). G. W. R.

Significance of Spectroscopic Magneton Numbers. E. C. STONER (*Phil. Mag.*, 1925, [vi], **49**, 1289—1309).—A theoretical discussion of the Landé-Sommerfeld schemes of co-ordinating multiplet structures and Zeeman effect. Electron orbits and cores are characterised by magnetic moments which are integral multiples of the Bohr unit. The azimuthal quantum number determines the magnetic moment of an electron orbit. The maximum term multiplicity is greater by two than the core moment the maximum value of which is equal to the number of electrons it contains in uncompleted groups. Magnetic balancing in pairs of core electrons gives rise to lower multiplicities, all odd or all even for odd or even numbers of core electrons. The magnetic moments deduced spectroscopically agree with those found by Gerlach and Stern. The core values are simply related with the ionic moments deduced from susceptibility measurements. The question of angular moments and the assignment of j values are discussed (cf. Pauli, this vol., ii, 339). R. A. M.

Mass-spectra of Chemical Elements. VI. Accelerated Anode Rays Continued. F. W. ASTON (*Phil. Mag.*, 1925, [vi], **49**, 1191—1201).—Indium is simple with mass number 115. Strontium is almost entirely 88, 86 occurring to the extent of only 3—4%; the principal constituent is decidedly less than a whole number, and the discrepancy between the atomic weight from mass spectra and chemical work (87·65) is no longer serious. Barium has a principal isotope of 138 slightly less than a whole number; there is no isotope below 136 but a minute amount of 136 or 137 may exist;

the chemical atomic weight is low. Lanthanum is simple, 139; praseodymium, simple, 141. Neodymium contains 142, 144, 146 not differing widely in relative amounts, with possibly a little 145. Cerium is 140, a whole number; a little 142 also exists. Zirconium has 90, 92, 94 (96 doubtful), the relative intensities of which are 10 : 2 : 4 : (1); the masses of zirconium isotopes are nearly integral with those of bromine, *i.e.*, less than whole numbers by about 0·1 unit. Cadmium has six isotopes 114, 112, 110, 113, 111, 116 in order of decreasing intensity; the masses appear to be integral with iodine (126·9). Cadmium resembles tin in respect of mass spectra. Tellurium has three isotopes 126, 128, 130, intensities 1 : 2 : 2; the mean atomic weight should therefore be greater than 128. Bismuth is a simple element of mass number 209. Silicon shows the 28 line strongly with faint lines corresponding with 29 and 30, so that the accepted atomic weight is probably low. Iron has two isotopes 56 and 54, intensities 20 : 1. Lead is complex, but the results are deferred. The elements remaining to be analysed are surveyed. Niobium, molybdenum, rhodium, ruthenium, and palladium will be very difficult to examine, but tantalum, tungsten, osmium, iridium, platinum, hafnium, and the rare earths should be less difficult. Gold and thallium will be difficult because of the difficulty of eliminating mercury completely. Thorium and uranium are the least hopeful because of their high atomic weights.

A complete list of all the non-radioactive isotopes so far discovered is given, as this paper marks the last of the series. Further work will be directed towards a more exact comparison of the masses of known isotopes rather than to the determination of the masses of the isotopes of the elements not yet studied. R. A. M.

Isotopes of Mercury. F. Stumpf (*Z. Physik*, 1924, **30**, 173—174).—A short theoretical criticism of Aston's theory of isotopes, with particular reference to the isotopes of mercury and their relation to gold. R. W. L.

Exact Determination of the Atomic Mass of the Lithium Isotope 6. J. L. Costa (*Compt. rend.*, 1925, **180**, 1661—1662).—By a modification of the method of Aston, the mass of the atom of the lithium isotope 6 has been compared with that of helium, 4·000. Two separate determinations gave the mass of the lithium atom 6, as 6·010 and 6·009, respectively, with a possible error of ± 0·002. W. H.-R.

Use of Fused Borax in the Determination of the Atomic Weight of Boron. H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson (*J. Chem. Soc.*, 1925, **127**, 150—162).—Following a review of previous determinations of the atomic weight of boron by methods which involve the use of fused borax, and give values appreciably higher than those obtained by methods involving the use of boron halides, a series of experiments is described in detail, in which the atomic weight of boron is determined from values obtained for the ratio borax glass : silver chloride. The evidence so obtained is held to condemn as unsatisfactory all methods involving the use of fused borax. R. W. L.

Revision of the Atomic Weight of Aluminium. III. Analysis of Aluminium Chloride. H. KREPELKA and N. NIKOLIĆ (*Chem. Listy*, 1925, **19**, 158—163; cf. A., 1924, ii, 763).—Pure aluminium chloride was obtained by the action of dry chlorine on an intimate mixture of carbon and alumina at a red heat. The mixture was prepared by precipitation of aluminium hydroxide from a solution of the chloride in which finely-divided carbon was suspended and subsequent ignition of the precipitate in dry nitrogen. The mean of five determinations of the ratio $AlCl_3 : 3Ag$ and of two determinations of the ratio $AlCl_3 : 3AgCl$ gave 26·971 as the atomic weight of aluminium, when 35·458 and 107·880 were taken as the atomic weights of chlorine and silver, respectively.

A. R. P.

Copper Oxide and the Atomic Weight of Copper. R. RUER and K. BODE (*Ber.*, 1925, **58**, [*B*], 852—859).—The recent determination of the atomic weight of copper by the authors (A., 1924, ii, 761) has been rejected by the German Commission on Atomic Weights on the ground that no evidence is adduced to prove that the final copper oxide is a well-defined chemical individual free from occluded gases. It is shown that copper oxide does not become constant in weight when ignited at any temperature between 750° and 1020°, losing not only occluded gases, but also a part of the chemically combined oxygen. At 750—900°, the oxide becomes sufficiently constant in weight in a current of oxygen, but its freedom from occluded gases cannot be guaranteed. The composition of copper oxide in contact with oxygen at the atmospheric pressure is constant at all temperatures below about 800°; above this temperature, traces of a lower oxide are produced which appear to remain dissolved in the cupric oxide, since otherwise the evolution of oxygen at a constant temperature would proceed until conversion into the lower oxide was complete. Homogeneous cupric oxide can therefore be produced by heating the oxide in a current of air and subsequently oxygen at 1000° and finally for a protracted period at 700° in oxygen. Repetition of this procedure with the same specimen of oxide shows that the loss in weight is considerable only after the first and second ignitions. Subsequently, the loss diminishes rapidly and becomes constant at 0·0008% after the sixth ignition; this loss appears to be due to slight volatility of the copper oxide. It is therefore considered that the conditions used by the authors are such that the final product was well-defined cupric oxide and that the value Cu=63·546 is trustworthy.

H. W.

Atomic Weight of Bromine. Inseparability of the Isotopes by Fractional Crystallisation. P. L. ROBINSON and H. V. A. BRISCOE (*J. Chem. Soc.*, 1925, **127**, 138—150).—Ammonium bromide was subjected to prolonged fractional crystallisation and the atomic weight of the bromine in the final head and tail fractions was determined by measurement of the ratio Ag : AgBr. The mean values of the atomic weight of bromine in these fractions were very approximately the same, showing that no concentration of one isotope in

the mixture had been effected. The mean value obtained was 79·914±0·003. A complete description is given of the elaborate experimental technique adopted. R. W. L.

Determination of the Radioactive Content of the Air by Streaming. H. BONGARDS (*Physikal. Z.*, 1924, **25**, 679—682).—Data are given indicating the variation of the conductivity of air. R. W. L.

Decay Constant of Radium Emanation. L. BASTINGS (*Proc. Camb. Phil. Soc.*, 1925, **22**, 562—566).—The decay constant, λ, of radium emanation has been determined to be 0·1808 day^{-1}, or the period of half-life to be 3·833 days, with a probable error of 0·2%. The method employed was the comparison of two emanation tubes of equal activities with a radium standard, the time being noted during which the combined activity of the two tubes fell to the original value of either taken separately. This gives a direct estimate of the half-life (cf. Curie and Chamié, this vol., ii, 8). S. B.

Behaviour of the α-Particles from Radium-*F* in a Longitudinal Electric Field. W. HAMMER and H. PYCHLAN (*Physikal. Z.*, 1924, **25**, 585—587).—Measurements have been made of the variation of the range of the α-particles when accelerated or retarded for a portion of their path by a field of the order of 40 kilovolts/cm. The results are found to agree very well with the formula proposed by Geiger (A., 1910, ii, 473). R. W. L.

Long-range Particles Emitted by Polonium. (MLLE.) I. CURIE and N. YAMADA (*Compt. rend.*, 1925, **180**, 1487—1489; cf. this vol., ii, 255).—Previous work is continued, layers of compressed air, oxygen, and carbon dioxide being substituted for metallic screens. The number of long-range particles is roughly proportional to the quantity of polonium and independent of the metal on which the polonium is deposited. The particles are not all of one type and their number decreases rapidly between 4 and 14 cm. of equivalent path. With oxygen and carbon dioxide, the number of long-range particles is roughly 10 per 10^7 α-particles. In air, they are about three times as numerous and their maximum range is about 16 cm. The possible nature of the particles is discussed. J. S. C.

Quantitative Optical Method for Differentiating between α- and H-Particles. E. KARA-MICHAILOVA (*Physikal. Z.*, 1924, **25**, 595—596).—The method is based on the variation of relative brightness of fluorescence produced by the rays on a zinc sulphide screen when examined several mm. from the end of the path. This characteristic serves to differentiate the two types of radiation. R. W. L.

Retrograde H-Particles from Disintegrating Atoms. G. KIRSCH (*Physikal. Z.*, 1925, **26**, 379—380).—The experiments of Rutherford and Chadwick (A., 1922, ii, 682) do not afford any conclusive proof of the existence of backward-moving H-particles. J. S. C.

Direct Determination of Distribution of Intensity in the Natural β-Ray Spectrum of Radium-*B* and -*C*. L. F. CURTISS (*Proc. Camb. Phil. Soc.*, 1925, **22**, 597—600).—A preliminary account of experiments on the intensity of the continuous background in the β-ray spectrum of radium-*B* and -*C*, designed to decide whether its appearance is due to secondary effects, or whether it originates within the disintegrating atoms. The spectrum was resolved magnetically, and the intensity of the rays of different velocities determined by direct measurement of their charge with a Compton electrometer. The results so far obtained indicate that bare sources have a weaker continuous spectrum than thin-walled emanation tubes. S. B.

Magnetic Spectrum of High-velocity β-Particles from Radium-*B*+*C*. J. D'ESPINE (*Compt. rend.*, 1925, **180**, 1403—1405; cf. A., 1913, ii, 270, 899; 1914, ii, 607; 1924, ii, 447; this vol., ii, 85).—The existence of swift β-particles from radium-*C* is confirmed. Two particles are found for which $H\rho$=9960 and 10,700, respectively. A band of high-velocity particles has also been observed between the values $H\rho$=15,000 and 27,000. Although feeble, this band has been measured with different magnetic fields, and it consists of several groups of particles which traverse thin screens of aluminium easily. A table is given showing several of the principal groups of β-particles from radium-*B* and -*C*. The values agree with those of Ellis and Skinner (A., 1924, ii, 85, 137). R. A. M.

Absorption of β-Rays by Matter. G. FOURNIER (*Compt. rend.*, 1925, **180**, 1490—1492; cf. this vol., ii, 176).—The coefficients of absorption of β-rays for elements of which the atomic numbers do not exceed 50 are represented in a satisfactory manner by the linear equation previously reported. Experiments with elements possessing higher atomic numbers show that the absorption is complicated by the production of a secondary radiation. On the assumption that the absorption coefficients of the primary radiation are calculable from the linear formula, the values of the absorption coefficients of the secondary radiation for platinum, gold, thallium, and lead are calculated. These latter coefficients are much smaller than the former and the secondary radiation is held to be electromagnetic in nature. J. S. C.

Characteristic γ-Ray Spectra and their Photo-electric Effect. J. THIBAUD (*J. Phys. Radium*, 1925, [vi], **6**, 82—98).—A *résumé* of previous papers (cf. A., 1924, ii, 515, 717; this vol., ii, 10, 85, 176, 257). F. G. T.

Heating Effect of γ-Rays from Radium-*B* and Radium-*C*. C. D. ELLIS and W. A. WOOSTER (*Proc. Camb. Phil. Soc.*, 1925, **22**, 595—596).—A method has been devised for the determination of the heating effect of γ-rays in presence of α-rays by measuring the difference in rise of temperature of aluminium and lead blocks exposed to the rays. The α-rays produce the same heating effect in each metal, being completely absorbed, whilst the γ-rays heat

the lead more than the aluminium, owing to the higher absorption coefficient of the former metal. The account is preliminary.
S. B.

Method of Analysis by Absorption of Radioactive Radiations. (MME.) J. S. LATTÈS (*Compt. rend.*, 1925, **180**, 1400—1402).—A general method of analysis is described applicable to all kinds of complex radiation. Details of technique are given and the analysis shows that with every group of primary γ-rays a definite group of secondary β-particles is found to correspond. This is held to justify certain theoretical calculations based on the intensity of the secondary radiation. R. A. M.

Disintegration of Atoms. H. PETTERSSON and G. KIRSCH (*Physikal. Z.*, 1924, **25**, 588—595).—A general review of present data with a discussion of the interpretations of the Cambridge and other schools. R. W. L.

Structure of Barium. H. COLLINS (*Chem. News*, 1925, **130**, 307—310).—From consideration of data based on the laws of relative volume and of heat of formation, the structure of the barium atom is deduced as $CaTi_2$. A. R. P.

Properties of Chemical Compounds and Atomic Structure. K. FAJANS (*Physikal. Z.*, 1924, **25**, 596—597).—The properties of chemical compounds are discussed in terms of polar and non-polar compounds of the Bohr atom. R. W. L.

Application of the Correspondence Principle to the Theory of Line-intensities in Band Spectra. R. H. FOWLER (*Phil. Mag.*, 1925, [vi], **49**, 1272—1288).—Theoretical. A general summary with considerable extensions. R. A. M.

Electrical Conductivity of an Element and its Place in the Periodic System. Z. A. EPSTEIN (*Z. Physik*, 1925, **32**, 620—638).—The electrical conductivities of metals are compared at temperatures which are the same fraction of their boiling points (absolute). These values multiplied by the cube root of the atomic volume, $\chi V^{1/3}$, when plotted against atomic numbers, show a regular decrease in each group from the maxima of the first members of the group. The point of view adopted is that of the mean interatomic conductivity, defined as the number of electrons transferred in unit time from atom to atom under a potential difference of 1 volt per atomic distance. An empirical relationship is shown to exist between the values for $\chi V^{1/3}$ and the distribution of electrons according to Bohr's theory. E. B. L.

Periodic Classification of the Elements and the Electrical Constitution of Atoms and of Valency. G. ODDO (*Gazzetta*, 1925, **55**, 149—174).—Various modifications are made in the table of the elements previously published (A., 1921, ii, 102), and conclusions are reached concerning the regions and structural conditions governing the ability of an element to combine with another. A ready electronic interpretation of the notion of valency is also derived. T. H. P.

Electron and Light-quantum from the Experimental Point of View. R. A. MILLIKAN (*Z. physikal. Chem.*, 1925, **116**, 65—80).—A translation of a Nobel Lecture, delivered at Stockholm on May 23rd, 1924. L. F. G.

Spectroscopy and Bohr's Theory of Atomic Structure. P. D. FOOTE (*J. Franklin Inst.*, 1924, **198**, 344—363; 517—540).—A concise account of recent developments of the Bohr theory. S. B.

Distribution of Transition Probabilities in the Atoms of Alkali Metals. H. BARTELS (*Z. Physik*, 1925, **32**, 415—438).—In the majority of cases the probability of transition from one energy state to another cannot be ascertained from measurements of the intensity of the lines, as these lie in the infra-red. They can be deduced mathematically from considerations based on the conception of a central electric field, and from them the mean life of the Bohr states can be calculated from the quantum numbers. The case for sodium is worked out and that of the other alkali metals will be similar. E. B. L.

World-Geometrical Properties Indicated by Quantised World-lines of the Electron in the Hydrogen Atom. E. REICHENBACHER (*Z. Physik*, 1925, **32**, 505—517).—From a consideration of the relativity geometry of the quantised electron orbits in the hydrogen atom, it is deduced that the electron is characterised by a fundamental "proper time," h/m_0c^2 (h=Planck's constant, m_0=mass of electron at rest, c=velocity of light); at the end of this time, or some multiple of it, the electron must return to its original condition or emit radiation. E. B. L.

Quantum Theory of the Ideal Gas. A. EINSTEIN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 18—25).—Mathematical (cf. *ibid.*, 1924, 261). From a consideration of the dimensions of the variables of a gaseous system, and of its behaviour under adiabatic compression, or in a conservative force field, the evaluation of the equation of state for an ideal gas is shown to reduce to the determination of a universal function of a single variable. F. G. T.

Quantum Radiation. A. LODGE (*Nature*, 1925, **115**, 838).

Calculation of Atomic Radii from Magnetic Susceptibility. B. CABRERA (*Anal. Fis. Quím.*, 1925, **23**, 172—180).—The mean radius of the electronic orbits of an atom may be calculated, using a well-known theorem of Larmor, from the magnetic susceptibility without making any assumptions as to the structure of the atom. If the Bohr structure of the atom be assumed, then the radii of the orbits of the superficial electrons may be deduced. The atomic radii of the elements of the helium group, thus calculated, are approximately half of those calculated from the kinetic theory, which was to be expected if the Bohr structure be assumed. The results obtained for sulphur, chlorine, argon, potassium, and calcium are in good agreement with those obtained by Grimm (A., 1922, ii, 127) from the theory of crystalline lattices. G. W. R.

Bands in the Secondary Spectrum of Hydrogen. G. H. DIECKE (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 490—500).—Extensions of the Fulcher bands in the secondary hydrogen spectrum are described. Three groups of bands, one in the red, one in the green, and one in the blue region, have been found. The zero and positive branches have been identified, and the negative branch may also be present. S. B.

Structure of the Second Positive Group in the Band Spectrum of Nitrogen. P. LINDAU (*Z. Physik*, 1924, **30**, 187—199).—By generalising an analysis of such bands advanced previously (A., 1924, ii, 711) to include an analysis due to Hulthén and Johansson (*Z. Physik*, 1924, **26**, 308), a new series formula is developed which leads to the conclusion that the differences between the wave-numbers of any two corresponding lines of the bands 3536, 3805 and 3755, 4059 are identical. Complete tables are given showing that the lines of the above bands may be arranged according to the above-mentioned series formula. R. W. L.

Emission Band Spectra of Aromatic Compounds. II. Their Origin. J. K. MARSH (*Phil. Mag.*, 1925, [vi], **49**, 1206—1216; cf. this vol., ii, 470).—Tesla luminescence spectra are capable of interpretation in terms of a theory which makes use of the conclusions of Baly (A., 1914, ii, 318; 1915, ii, 440, 499) and of Henri (A., 1922, ii, 331, 679). Tesla bands confirm the measurements of absorption and fluorescence bands, by which it has been proved that the frequency differences between successive bands are often equal to the absolute frequency of a band in the infra-red. The recurrence of overtones must be supplemented by an explanation of the appearance of more than one constant frequency difference in the spectra. The author considers in detail the results with benzene. The vapour absorption spectrum shows band intervals of 159 and 921·4 ($1/\lambda$). The emission spectrum exhibits intervals of 159 and 987. Henri has shown that the absorption spectrum of benzene vapour can be expressed by four equations of the type :

$$\nu=A-B+na-(pb+p^2b')+\alpha(m^2-q^2),$$

where $A-B$ is the contribution made by the quantification of an electronic energy change, $na-(pb+p^2b')$ results from the quantification of atomic vibrations and $\alpha(m^2-q^2)$ from quantified rotations, n and p are integers.

The author selects one of Henri's equations [the others have $(A-B)$ varying from the one chosen] : $\nu=37494+921\cdot4n-159(p+2p^2)$, and rewrites it $\nu=37494+6n\times159(1-0\cdot0358)-159\cdot2p(1+0\cdot01257p)$. All the fluorescence bands fit the equation : $\nu=37494-6n\times159(1+0\cdot0358)-159\cdot2p(1+0\cdot01257p)$. Thus the benzene bands are overtones of 159. The infra-red spectrum of ethylene consists of overtones of a band at $1/\lambda=476$ (three times 159) and of a band at 3049 (three times the great benzene band at 9·8μ or 1020). Accepting 159 and 1020 as the basic benzene frequencies, then $0\cdot5(1020\pm6\times159)=987$ or 33 and $6\times159-33=921$. Thus the main features of the benzene spectra depend on 1020 and 159. The smaller frequency is due to the C:C linking, and

the larger differs but slightly from ordinary vibration common to all compounds with CH groups. Since this band recurs in the aliphatic substituted benzenes and the ultra-violet interval is a fraction smaller than $\frac{1}{3}$, it is argued that the infra-red band is itself an overtone of a band in the far infra-red. It is shown that all the infra-red bands of benzene are integral multiples of 128·25. Meyer and Bronk have analysed the 3·25μ band (A., 1924, ii, 804) and the sub-groups are 42·7 and 84·9 apart. This suggests that 42·7, 84·9/2, 128·25/3 is a constant corresponding with rotation of CH groups. It is suggested that the blue Tesla luminescence is due to C:O groups, as is also the 5·8 μ band. R. A. M.

Anomalies of Intensity in Band Spectra. R. MECKE (*Physikal. Z.*, 1924, **25**, 597—599).—Theoretical. The subject is discussed from the point of view of the correspondence principle. Special reference is made to the cyanogen bands. R. W. L.

Intensities in Band Spectra. G. H. DIEKE (*Nature*, 1925, **115**, 875).—A summary is given of the application to the lines of a band of the rules of Burger and Dorgelo (*Z. Physik*, 1924, **23**, 258). A. A. E.

Structure and Distribution of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1925, **180**, 1454—1460; cf. A., 1919, ii, 486; 1920, ii, 69).—The frequencies of the bands in the infra-red absorption spectra of oxygen, carbon monoxide, hydrogen cyanide, ammonia, water vapour, and methane are represented by the expression $K=qd_1/rs$, where q and r are whole numbers, s is the number of atoms in the molecule, and d_1 the fundamental frequency 1062·5. J. S. C.

Band Spectra of Crystals and Complex Gases. H. KAHLER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 266—269).—The complete spectrum of uranyl salt crystals contains a high-frequency absorption branch and a low-frequency emission branch, the full spectrum being capable of expression by means of an equation of the band spectral type. The similarity to the absorption spectra of complex gases is shown by reference to Henri's data for the ultra-violet absorption of benzene. E. B. L.

Influence of Temperature on the Ultra-violet Absorption Bands of Oxygen. Short-wave Iodine Spectrum. C. FÜCHTBAUER and E. HOLM (*Physikal. Z.*, 1925, **26**, 345—349).—The absorption bands of oxygen have been examined, at temperatures from 400° to 1050°, in the region between the wave-lengths 2000 and 2200 Å. With increasing temperature, the bands become more intense, and extend towards the region of longer wave-length. This behaviour is attributed to the increase in oscillation energy of the atom, and is probably connected with the increase of specific heat of gases with rise of temperature. The sensitiveness to temperature does not appear to depend on impurities in the gas. The edges of the absorption bands at the ordinary temperature have also been measured up to 1830·6 Å. Comparison of the initial frequencies

with the final frequencies at different temperatures indicates that electron emission causes a considerable loosening of the bands between two oxygen atoms, and this results, not only in a large reduction of the fundamental frequency in the final state, but also in a large increase of the moment of inertia.

The line spectrum of iodine, produced under conditions practically equivalent to a spark discharge, has been examined between 2016·5 and 1830·5 Å. M. S. B.

Infra-red Absorption Spectra of Aldehydes and Ketones. J. LECOMTE (*Compt. rend.*, 1925, **180**, 1481—1482).—The infra-red absorption spectra of aldehydes are not identical with those of the isomeric ketones and the position of the band characteristic of the carbonyl group is not the same for aromatic as for aliphatic compounds. The positions of the absorption bands in the infra-red region of 8 aliphatic and 2 aromatic aldehydes and of 9 aliphatic and 6 aromatic ketones are recorded. J. S. C.

Absorption Spectra of Various Aldehydes and Ketones and Some of their Derived Compounds. J. E. PURVIS (*J. Chem. Soc.*, 1925, **127**, 9—14).—A method previously described (T., 1912, **101**, 1810) has been adopted in this work. The following substances show no selective absorption in solution: formaldehyde in water, paraldehyde, trithioformaldehyde, trithioacetaldehyde, β-trithiobenzaldehyde, methylal, and acetal in alcohol. α-Diphenylglyoxime shows a weak band at 2380 Å. Curves are given showing the relative absorptive powers of the following substances: benzylideneacetone, benzylideneacetoxime, benzylidenedeoxybenzoin, benzylideneacetophenone, and cinnamylidenecamphor. The results are construed to support a theory of the influence of aldehydic and ketonic groups on the colour of substances. R. W. L.

Absorptive Power of Liquids and their Vapours for Infra-red Radiation of Wave-length less than 3μ. T. DREISCH (*Z. Physik*, 1924, **30**, 200—216; cf. this vol., ii, 178).—Tables are given of the data obtained by the author and other workers for water, benzene, and chloroform over the range 0·85 to 3 μ.
R. W. L.

Explosion of Acetylene and Nitrogen. IV. Spectra of Explosions of Gases containing Hydrogen, Carbon, Nitrogen, and Oxygen. W. E. GARNER and S. W. SAUNDERS (*J. Chem. Soc.*, 1925, **127**, 77—82).—Complete details are given of the method adopted to determine the spectra emitted when mixtures of acetylene, nitrogen, and oxygen are exploded. The results from mixtures of oxygen and acetylene and from mixtures of oxygen, nitrogen, and acetylene are held to show that the cyanogen spectrum is due to both carbon and nitrogen. R. W. L.

Atmospheric Ozone as Absorbing Material for Radiations. C. FABRY (*J. Math. Physics*, 1925, **4**, 1—20).—The emission spectra of the sun and stars, as observed from the surface of the earth, cease abruptly at about 2900 Å. The uniformity of the wave-length

limit shows that it is determined by atmospheric absorption. Hartley first suggested that the absorbing agent is ozone. Using the photographic method for ultra-violet spectrophotometry, the author has determined the absorption coefficients of the atmosphere for different wave-lengths in the range 2922—3143 Å. To obtain such measurements, it is necessary to vary the thickness of the absorbing layer and this was achieved by making observations with the sun at varying heights above the horizon. A comparison of the results with the absorption coefficients of ozone confirmed the hypothesis that the limit of the solar spectrum is due to the absorption band of this gas. The greatest part of the atmospheric ozone probably lies in a very high and inaccessible region. As the absorption coefficient of ozone is small below 2200 Å., a reappearance of the solar spectrum at these wave-lengths would seem not impossible, but attempts to observe it with a system of spectrographs, designed to eliminate scattered light of longer wave-lengths, were unsuccessful. The absorption in this region may be due to ordinary oxygen. The absorption bands of ozone in the spectral region 3300 Å. can also be detected when the sun is very near the horizon. S. B.

Equilibrium of the Calcium Chromosphere. E. A. Milne (*Month. Not. Roy. Astr. Soc.*, 1924, **85**, 111—141).—A full solution is obtained of the problem of the equilibrium under radiation pressure of an atmosphere consisting of atoms supposed to possess only two stationary states—the normal and one excited state. This special case of the general problem of equilibrium corresponds fairly with an atmosphere absorbing spectral lines derived from the normal state of the atom, such as the principal series of Na, Ca, Ca^+, etc. The law of density deduced for an atmosphere fully supported by radiation pressure is that the density at any point is inversely proportional to the square of the height of the point above a certain fixed level. For an atmosphere only partly so supported, the law is quite different, and the density decreases exponentially with height.

The least departure from exact balance between radiation pressure and gravity at great heights should cause an overwhelming concentration of the atmosphere into the lowest levels. This is in agreement with the great variations observed in the height of the calcium chromosphere. It is concluded that the high level calcium chromosphere of the sun must be fully supported by radiation pressure. The investigation confirms the author's previous estimate of the life of an excited atom deduced from solar data. S. B.

Polarisation of Sodium Resonance Radiation in Magnetic Fields. A. Ellett (*J. Opt. Soc. Amer.*, 1925, **10**, 427—437).—The polarisation of *D*-line resonance radiation with various orientations of the impressed magnetic field has been determined under conditions which eliminate the depolarising action of high vapour pressure. The results are not in quantitative agreement with any current theory. It has also been shown that a magnetic field produces a rotation of the plane of polarisation in resonance radiation, and that this rotation is due to the Larmor precession of the excited

atoms. The value of τ for the $2p_1$ orbit of sodium, calculated from the rotation, is $1{\cdot}35 \times 10^{-8}$ sec. S. B.

Polarisation of Resonance Radiation in Weak Magnetic Fields. G. Breit (*J. Opt. Soc. Amer.*, 1925, **10**, 439—452; cf. A., 1924, ii, 441).—A theoretical discussion of the recent experimental results on this subject (cf. preceding abstract). S. B.

Extinction of Resonance Fluorescence of Mercury. H. A. Stuart (*Z. Physik*, 1925, **32**, 262—272).—Light from a quartz mercury-vapour lamp was concentrated on a bulb containing mercury vapour. The resonance light produced was focussed on a second bulb containing mercury vapour and the light emitted from this second bulb was photographed, and the decrease in its intensity measured when gases were present at various pressures. The results are regarded as indicating that the radius of the mercury atom in the excited state is about three times as great as that of the normal atom. Collision with molecules of oxygen, hydrogen, and carbon monoxide transform the energy of the excited mercury atom into heat; with carbon dioxide, only 20% of the collisions, and with helium only 0·03%, are of this type. E. B. L.

Polarised Fluorescence and Phosphorescence of Solutions of Dyes. IV. W. L. Lewschin (*Z. Physik*, 1925, **32**, 307—326).—Fluorescent light excited by polarised light is itself partly polarised, the extent up to a limit depending on the viscosity of the solvent. Increase of concentration or of temperature decreases the polarisation. An explanation of these facts is sought by regarding the source of the radiation as a di-pole the axis of which is rotated during the life period of the excited state. The angle of rotation corresponding with the degree of polarisation is calculated from the theory of the Brownian movement. E. B. L.

Fluorescence and Chemical Change. D. N. Chakravarti and N. R. Dhar (*Z. anorg. Chem.*, 1925, **142**, 299—328).—Eosin and other fluorescing substances are oxidised by air or reduced by suitable substances (sucrose etc.), both reactions being highly catalysed by light and yielding products which do not fluoresce. Thus, in general, experiments on fluorescence cause destruction of the eosin, but the chemical change is not directly connected with the phenomenon of fluorescence as assumed by Perrin (cf. Weigert, A., 1922, ii, 681). L. J. H.

Influence of Magnetic Fields on the Polarisation of Resonance Fluorescence. W. Hanle (*Z. Physik*, 1924, **30**, 93—105). —An investigation of the effects of magnetic fields of the order of 1 to 100 gauss on the resonance fluorescence of mercury vapour indicates that not merely does the field tend to depolarise the resonance fluorescence excited by plane polarised light, but it also rotates the plane of polarisation; the results also lead to values for the life of an excited atom in good agreement with those of other workers. It is shown that the effect observed is other than the Faraday effect. The phenomena are discussed at length with reference to the quantum theory. R. W. L.

Chemiluminescence and Heteropolar Combination. A. PETRIKALN (*Z. Physik*, 1925, **32**, 569—574).—The decomposition of the iodide of Millon's base is shown to be an endothermic reaction; above 350°, the decomposition is accompanied by the emission of light, the spectrum exhibiting the bands of mercuric iodide and the mercury lines 4047, 4359, 5461 Å.; with a specially made spectrograph the line 2537 was obtained. It is concluded that the electron holding the mercury and nitrogen atoms together belongs to the 2*s* orbit. E. B. L.

Tesla-luminescence Spectra. V. Polynuclear Hydrocarbons. W. H. MCVICKER, J. K. MARSH, and A. W. STEWART (*J. Chem. Soc.*, 1925, **127**, 999—1006; cf. A., 1924, ii, 712; this vol., ii, 12).—The emission spectra of seventeen polynuclear substances are described and the following conclusions are reached: the attachment of a phenyl group directly to one point of the benzene ring decreases the intensity of emission, *i.e.*, it decreases the amplitude of vibrations; when methylene groups are inserted between the nuclei, the amplitude of vibration is less affected and there is an increase in the length of the spectrum, mainly towards the red end; the spectrum is faint when the nuclei are separate and becomes more intense as the rings are fused into a connected structure; there is a simultaneous shift of the spectrum towards the red and an increase in the number of bands; introduction of the phenyl nucleus and of alkyl radicals into fused ring compounds appears to shorten the spectrum; Tesla-luminescence does not appear to be related to the length of the conjugated chain. F. G. S.

Luminescence of Solid Nitrogen and the Auroral Spectrum. L. VEGARD (*Nature*, 1925, **115**, 837—838; cf. McLennan, this vol., ii, 88).—Polemical, and a claim for priority in the observation of the three maxima of the band N_1. A. A. E.

Ultra-violet Radiations and Antirachitic Substances. J. C. DRUMMOND and T. A. WEBSTER (*Nature*, 1925, **115**, 837).—Kugelmass and McQuarrie's observation (*Science*, 1924, **60**, 274) of the production of ultra-violet light when antirachitic substances undergo autoxidation could not be confirmed. The photographic fogging obtained by these authors was probably due to the known phosphorescence of fused silica. A. A. E.

Kinetic Theory of Metallic Conduction. E. L. DAVIES and G. H. LIVENS (*Proc. Camb. Phil. Soc.*, 1925, **22**, 555—561).—It is shown that the kinetic theory of metallic conduction leads to formulæ for conductivity coefficients which are consistent with experimental data. S. B.

Dielectric Constants of Liquid and Solid Hydrogen. M. WOLFKE and H. K. ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 627—630).—The dielectric constant of liquid hydrogen at its boiling point under atmospheric pressure has the value 1·225±

0·001. The constant increases with falling temperature to the neighbourhood of the melting point, where it reaches its highest value, after which it decreases in solid hydrogen on further decrease of temperature. S. B.

Dielectric Constants of Liquid Hydrogen and Liquid Oxygen. G. Breit and H. K. Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 617—620).—The dielectric constants of liquefied hydrogen and oxygen have been determined by the high-frequency oscillation method. The value for liquid hydrogen at 20° Abs. is given as 1·21, and for liquid oxygen at 70° Abs. as 1·50. The measurements, although of a preliminary character, indicate that the temperature variation of the dielectric constant is satisfactorily given by the Clausius–Mosotti expression. S. B.

Dielectric Constant of Liquid Helium. M. Wolfke and H. K. Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 621—626).—The dielectric constant of liquid helium has been determined at its b. p. under 765 mm. pressure. The high-frequency oscillation method was used. The value determined is 1·048±0·001, the temperature being 4·2° Abs. S. B.

Measurement of the Dielectric Constants of Liquids. H. Harris (*J. Chem. Soc.*, 1925, **127**, 1049—1069).—The determination of dielectric constants of liquids by alternating current bridge methods is discussed. The method employed by Nernst (A., 1894, ii, 437) and by Turner (A., 1901, ii, 53) is criticised. In the present determinations, a Schering and Semm's bridge is employed, a valve generator replaces the Nernst interrupter, and two non-reactive 1000-ohm coils the liquid resistances used by Nernst for the ratio arms. Details of the experimental and of the standard condensers are given and the method of correction for the earth capacities of the bridge and leads, the parallel resistance, and of the fibre end pieces of the experimental condenser, is outlined. The true dielectric constants of the following carefully purified liquids have been accurately measured at 25°±0·01°: benzene 2·2482±0·0003 and 2·2488±0·0005; carbon tetrachloride 2·219±0·002; chloroform 4·6417±0·001; ethylene dichloride 10·131±0·001; *o*-nitrotoluene 26·066±0·005; nitrobenzene 34·093±0·007. F. G. S.

Dielectric Constants of Good Conductors. R. Fürth (*Physikal. Z.*, 1924, **25**, 676—679).—The method employed is to determine the torque on an ellipsoid, containing the fluid conductor, when suspended in an alternating electrical field of frequency 50. From the value obtained for this torque, classical electromagnetic theory leads to values of the dielectric constant if the conductivity be known. The values obtained for aqueous sucrose solutions over the range of concentration 20—60% are in agreement with those obtained by Drude when using a frequency corresponding with a wave-length of 70 cm. Results are also given for aqueous solutions of sodium chloride over the concentration range 0·0—0·1%. The

values obtained are not independent of the field strength, but diminish as the field diminishes. R. W. L.

Calculation of Refractive Indices by the Logarithmic Rule of Mixtures. K. LICHTENECKER (*Physikal. Z.*, 1925, **26**, 297—302).—In previous papers (*ibid.*, 1924, **25**, 169, 666) it has been shown that the resistance of alloys and the dielectric constants of non-conducting binary mixtures are linear functions of their volume composition. The same rule has now been found to govern accurately the refractive indices of binary mixtures of liquids, in the absence of volume changes on mixing. The refractive indices of carbon disulphide–methylal mixtures are cited as an example, and the rule also holds for pyridine–water mixtures, when allowance is made for the volume contraction. The deviations from the rule may be used for the indirect measurement of volume changes on mixing liquids. S. B.

Rotatory Dispersive Power of Organic Compounds. XIV. Simple Dispersion in 1-Methyl*cyclo*hexylidene-4-acetic Acid. E. M. RICHARDS and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 238—240).—Data are given for the dispersion-ratios α/α_{5461} over the range 6708 to 4072 Å. It has been found that the values obtained can be calculated by neglecting all terms in Drude's equation but the first and by assuming an absorption maximum at 2364. Despite the evidence, which indicates that the acid has no such characteristic frequency, the authors think that the dispersion of the acid is as simple in essence as their abbreviated form of Drude's equation would indicate. R. W. L.

Dynamic Isomerism. XVII. Mutarotation of Aluminium Benzoylcamphor. I. J. FAULKNER and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 1080—1085; cf. Burgess and Lowry, this vol., i, 46).—*Aluminium benzoylcamphor*, $(C_{17}H_{19}O_2)_3Al$, m. p. 227—228°, has been prepared by the method used for the preparation of beryllium benzoylcamphor (Burgess and Lowry, *loc. cit.*), and, like the beryllium compound, it shows mutarotation although containing no mobile hydrogen atom. The mutarotation is reversible and has been observed in benzene, ethylene bromide, acetone, and chloroform. In ethylene bromide, the change extends over about a week, and in acetone and in chloroform it takes place in a few minutes. The fact that the mutarotation in chloroform is in the opposite direction to that in the other solvents used suggests the formation of a compound with the chloroform of higher rotatory power. The velocity of mutarotation in benzene, unlike that of the beryllium compound in this solvent when pyridine is present as catalyst, does not obey the unimolecular law, but is approximately proportional to the cube of the concentration, although the termolecular coefficients vary appreciably during the change. The course of the reaction in ethylene bromide after the first half-hour also conforms roughly to the termolecular law. It is suggested that the result may perhaps be associated with the necessity for inverting the points of attachment of three chelate groups in order to reverse the optical activity of the aluminium. F. G. S.

Optical Rotation and Atomic Dimension. IV. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1925, **47**, 1281—1284; cf. A., 1924, i, 837).—The specific rotations of chloro-, bromo-, and iodo-tetra-acetylglucose and of chloro- and bromo-triacetylxylose have been redetermined. The new values show a much closer agreement between the ratio of the difference in specific rotation, Cl–F, Br–Cl, and I–Br, and the ratio of the differences of atomic diameter as recorded by Bragg. J. S. C.

Optical Rotation and Atomic Dimension. V. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1925, **47**, 1285—1298; cf. preceding abstract).—Two classes of asymmetric compounds containing substituted halogen atoms are recognised: (*a*) compounds in which the halogens are directly attached to the asymmetric carbon atom, (*b*) compounds in which the halogens modify an asymmetric group attached to the asymmetric carbon atom. In the latter case, the molecular rotation differences are proportional to the differences in atomic diameter recorded by Bragg. The specific rotations of halogen derivatives of salicin and their penta-acetates have been measured and the methods of preparation and properties of α-fluoro-, chloro-, and bromo-acetyltetra-acetylglucose are given. J. S. C.

Thermochemical Investigations on the Constitution of Acids in Solution. D. D. KARVE (*J. Indian Chem. Soc.*, 1925, **1**, 247—262).—Further data in support of the Hantzsch theory of pseudo acids and ionogenic condition (cf. A., 1918, ii, 4; 1923, ii, 475) are obtained by an investigation of the heats of solution of hydrogen halides, sulphuric, nitric, formic, acetic, and trichloroacetic acids in aqueous and non-aqueous solvents. In the dissolution of an acid, purely physical phenomena all result in the absorption of heat, and the positive heats of solution are therefore due to combination between the acids and the solvents to form solvates which are either true or pseudo-oxonium hydrates of types (1) $R{\cdot}CO_2H,H_2O$ or (2) $R{\cdot}CO_2H\ldots OR_2$. The heats of solution of the above-mentioned acids in a large number of organic solvents are determined and discussed in relation to the Hantzsch theory, the main conclusions being as follows: with sulphuric acid, solvate formation of true oxonium salts of the type H_2SO_4,HOR_2 (R=H or alkyl) occurs with much evolution of heat, whilst the relatively small heat of solution in ethyl sulphate and nitrobenzene denotes a very small tendency towards salt formation; hydrogen halides form oxonium salts and etherates of which only the hydrogen chloride compound can be isolated (cf. Steele, McIntosh, and Archibald, *Z. physikal. Chem.*, 1909, **55**, 152); the heat of solution of nitric acid in alcohol or ether is a measure of the heat of formation of the pseudo salt, whilst the smaller heats of solution in water, where the true hydroxonium salt is present, denote that transformation from the pseudo acid to the true acid is endothermic; with formic acid, the heat of solution in water is too small to be measured and therefore the dissociation of the acid absorbs very nearly the same amount of heat as is evolved by salt formation, whilst in acetone, alcohol, or ether the heat of solution is the heat of formation of the pseudo salt; with acetic acid, in water

the heat of solution is negative in concentrated solution and positive in more dilute solutions where sufficient of the hydroxonium salt is formed to overbalance the heat absorbed by dissociation; the heat of solution of trichloroacetic acid in water is small and is negative in solvents which do not contain oxygen, whilst the heat of solution is greatest in acetone, which, therefore, forms a true salt, $CCl_3 \cdot CO_2 \cdot H \ldots OCMe_2$. The numbers of molecules of solvents required to produce inactivation of the various acids towards ethyl diazoacetate are also determined. J. W. B.

Magneto-chemical Researches on the Formation of Open Chains and Nuclear Groupings in Organic Compounds. P. PASCAL (*Compt. rend.*, 1925, **180**, 1596—1597).—The magnetic susceptibilities of a series of compounds containing a group $-C_{6-n}N_n$, where n is 0, 1, 2, 3, or 4, have been measured. The group was the skeleton of a nuclear grouping or of an open or closed chain. Increase in the number of ethylenic linkings and the formation of closed chains, like polymerisation, cause a marked decrease in diamagnetism. These factors thus increase the resultant magnetic moment of the molecule and correspond with increasing dissymmetry of electronic structure. On the other hand, an increased diamagnetism is observed in the cases of nuclei with three symmetrical double bonds. This effect is also found in open-chain compounds containing tertiary carbon or nitrogen atoms. The value $-55{\cdot}5 \times 10^{-7}$ has been used for the magnetic susceptibility of combined nitrogen. Direct measurements give -59×10^{-7} (Hector) and -50×10^{-7} (Také Soné). The author's earlier work on the additivity of diamagnetism (A., 1909, ii, 487, 788, 859; 1910, ii, 100, 179, 483, 580) is confirmed and extended. R. A. M.

Colour and Molecular Geometry. III. Graphical Presentation of the Theory. J. MOIR (*J. Chem. Soc.*, 1925, **127**, 967—972).—A simplification of the general theory (A., 1924, ii, 641) is possible since it appears that in most cases the active part of the hapton (T., 1923, **123**, 2801) is the oxygen or nitrogen it contains. Since these atoms have the same atomic diameter and occur at both ends of the molecule when the auxochrome is $-OH$ or $-NH_2$, the wave-length of the absorption band is given by the simplified formula $\lambda = 51{\cdot}4(c+1{\cdot}77)\sqrt{c+0{\cdot}65}$, in which c is half the distance between the terminal oxygen or nitrogen atoms round which the electron moves. The equation is approximately linear over the range of the visible spectrum, rendering the calculation of colour easy. The calculated positions of the absorption bands of a number of monocyclic and dicyclic compounds considered are in good agreement with the experimental values. F. G. S.

Constitution of Nitric Acid and the Nitronium Salts formed from it by Perchloric and Sulphuric Acids. A. HANTZSCH [with L. WOLF] (*Ber.*, 1925, 58, [*B*], 941—961).—The absorption curve of solutions of nitric acid in water may be calculated with great accuracy from those of ethereal solutions of nitric acid and aqueous solutions of alkali nitrates. It is therefore justifiable to

conclude that such solutions contain equilibrium mixtures of the pseudo acid, $O_2N{\cdot}OH$ and true acid (present as the hydroxonium salt, $(NO_3)[H{\cdot}OH_2]$). Homogeneous nitric acid closely resembles its esters but its absorption is noticeably more feeble than might be expected from the slight constitutive difference between pseudo acid and ester, so that the presence of a third type of molecule must be assumed (cf. von Halban, A., 1923, ii, 835; Schaefer, A., 1917, ii, 61, 186). In addition, the pronounced electrical conductivity of nearly homogeneous nitric acid indicates the presence of some form other than the pseudo acid. Indications of the nature of the feebly-absorbent electrolyte are found in the observation that solutions of nitric acid in absolute sulphuric acid contain a largely dissociated electrolyte which is very much more transparent than an equally concentrated ethereal or aqueous solution of nitric acid. The analogous behaviour of acetic acid dissolved in absolute sulphuric acid, whereby the acetylium cation is produced, suggests the production of a nitronium cation and therefore the possible presence of the two salts, $[NO(OH)_2][SO_4H]$ and $[N(OH)_2][SO_4H]_2$. It is remarkable that a nitronium salt of pyrosulphuric acid, $HS_2O_7[(HO)_2NO]$ or $S_2O_7[(HO)_3N]$, was isolated by Weber in 1871. The conception of a nitronium cation is strengthened further by the isolation from almost anhydrous nitric and perchloric acids of *nitronium diperchlorate*, $[ClO_4]_2[(HO)_3N]$, m. p. 130° (decomp.) after softening at 55°, and *nitronium monoperchlorate*, $ClO_4[(HO)_2NO]$, decomp. above 130°; these are stable salts which can be crystallised from perchloric acid and nitric acid, respectively. It is therefore considered that, contrary to the views of Saposchnikov (A., 1915, i, 393), "nitrating" acid does not contain nitrogen pentoxide, but nitronium hydrogen sulphate, $[N(OH)_3](SO_4H)_2$; this conception is confirmed by the observation that the absorption spectrum of nitrogen pentoxide dissolved in sulphuric acid differs from that of "nitrating acid." In homogeneous nitric acid, it is thus reasonable to conclude that analogous wandering of the hydrogen atom occurs to a more limited extent with the production of the nitronium ion and hence of the salt-like electrolyte, nitronium nitrate, $(NO_3)_2[(HO)_3N]$. Almost anhydrous nitric acid is to be regarded as a solution of conducting nitronium nitrate in non-conducting pseudo nitric acid. On certain assumptions, it is calculated that the equilibrium mixture for the 98·6% acid at 0° contains 80% of pseudo nitric acid and 20% of nitronium nitrate (contrary to previous observations, the 100% acid is too unstable to permit observations at 0°).

Optical analysis shows that the nitronium nitrate is completely hydrolysed by the addition of one molecular proportion of water, since from this point the absorption curves can be additively constructed from those of the pseudo acid in ether and the true acid in water. The conversion of the pseudo acid into the true acid (or its hydroxonium salt) is practically complete after the addition of 8 mols. of water, whereas the dissociation at this point does not amount to 40%. The last traces of the pseudo acid have disappeared after addition of 50 mols. of water, and the solution then contains only hydroxonium salt which is not completely ionised, in

the sense of the classical dissociation theory, in $N/100$-solution. In the most dilute solutions, the sole absorbent material is the nitrate ion; orthonitric acid and nitrogen pentahydrate do not exist (the so-called diacetylorthonitric acid, $N(OH)_3(OAc)_2$, is a molecular compound of the pseudo acid, $[(CH_3\cdot CO_2H)_2HO\cdot NO_2]$).

The reactions between the three strongest oxyacids, perchloric, sulphuric, and nitric, give particularly strong evidence in favour of the chemical theory of acids according to which the strength (acidity) can only be measured chemically in accordance with Berzelius' principles by their tendency towards salt formation and not physically by their ability to furnish hydrogen ions. According to the dissociation theory, perchloric acid is the strongest acid, followed by nitric and then by sulphuric acids. Actually, homogeneous perchloric acid is incomparably stronger than nitric acid, and sulphuric acid, which is more feebly ionised in aqueous solution, is in the homogeneous condition stronger than nitric acid, since it causes the production of nitronium sulphate. In aqueous solution, the great differences towards salt formation of the three acids are almost annihilated, since water as a basic anhydride, particularly in excess, and hence in dilute solution, converts them almost completely into hydroxonium salts.

Absolute nitric acid, m. p. −42·3°, appears to be stable at −40°. The 99·5% acid is somewhat unstable at 0°, whereas the 98·4% acid can be preserved for a few days at a moderate temperature. The minimum value observed for the electrical conductivity of 99·5% acid is $\chi=89\times10^{-4}$ at 0°, whereas an almost absolute acid gave the value $\chi=94\times10^{-5}$ at −40°. The liquid acid, of the composition HNO_3,H_2O, is not a uniform material. Veley and Manley's observation that solutions of nitric acid exhibit a minimum conductivity is not confirmed. H. W.

Induction of Alternate Polarities, especially in Relation to the Extent and Intensity of Transmission. A. Lapworth (*Chem. and Ind.*, 1925, **44**, 397—398).—The author's views on induced alternate polarities are limited to cases of induction through one saturated carbon atom (T., 1922, **121**, 426; A., 1921, ii, 543); transmission through two saturated carbon atoms in immediate or delayed succession can be explained on different lines, and it is not necessary to assume that a true inductive effect passes from one end of the reacting system through its full length. Complications not yet discussed arise from the polar effects produced by groups of atoms, such as the ethylene and acetylene groups, these effects being manifested in reactions depending on the development of active negative polarity on carbon atoms, *e.g.*, nuclear hydrogen-substitution in the aromatic series. R. B.

Electronic Conception of Valency and Heats of Combustion of Organic Compounds. M. S. Kharasch and B. Sher (*J. Physical Chem.*, 1925, **29**, 625—658).—It is assumed that the heat of combustion is due to a liberation of energy when the valency electrons are shifted from the orbits occupied in methane and similar substances to those occupied in carbon dioxide, the latter orbits being

further from the carbon atom. The heat of combustion is then proportional to the number of electrons so displaced and for saturated hydrocarbons is equal to $26{\cdot}05N$ kg.-cal. per mol, where N is the number of electrons in the molecule that have the same position round the carbon atoms as in methane. This formula also applies to unsaturated hydrocarbons having the same arrangement of electrons round the carbon atoms as have saturated compounds, *i.e.*, to benzenoid and conjugated hydrocarbons, but in ethylene derivatives one pair of electrons is displaced and there is an additional liberation of energy of 13 kg.-cal., the heat of combustion being, therefore, $26{\cdot}05N+13$. When carbon is united to atoms other than hydrogen the energy liberated by the electrons concerned is less than 26·05 kg.-cal. and the heats of combustion of various classes of compounds are as follows: primary alcohols, ethers, esters, amines, and nitro compounds, $26{\cdot}05N+13$; secondary alcohols and ketones, $26{\cdot}05N+6{\cdot}5$; tertiary alcohols, phenols, acids, amides, anilides, and amino-acids, $26{\cdot}05N$. The calculated and experimental values of the heats of combustion of 278 compounds are given; in only 37 cases is the difference more than 1% and in 152 it is less than 0·5%.

A. G.

Contraction Constants and Affinity of Solid Compounds. A. BALANDIN (*Z. physikal. Chem.*, 1925, **116**, 123—134).—The contraction constants of 76 solid compounds as calculated by the formula $C=V/\Sigma V_0$ (cf. Schilov, A., 1922, ii, 350) are in close agreement, in most cases, with those calculated from a new formula $C=R-U/U_0$, where R and U_0 are constants depending on the nature of the anion and U is the heat of formation. The significance of the latter formula with reference to the oscillations of the component atoms of the salts is discussed (cf. A., 1924, ii, 719).

L. F. G.

Form of Ultramicrons. H. SIEDENTOPF (*Kolloid-Z.*, 1925, **36** [*Zsigmondy-Festschr.*], 1—14).—The scintillation phenomenon is described, and the possibility of increasing the sensitiveness of this effect for the detection of ultramicrons is discussed. The necessary conditions for obtaining a sufficient uniform illumination between cover-glass and slide, using a narrow aperture, are indicated, but it is shown that such a method would give no information as to the actual magnitude of the observed particles. By the application of Nichelson's interferometric measurements of the diameters of fixed stars to ultramicroscopy, positive results could, however, be obtained. The apparatus, which can be used for measuring microscopic as well as ultramicroscopic lengths, is described in detail, and the mathematics of the simpler cases are discussed. L. L. B.

Effect of Allotropic Change on the Grain Growth in Thallium. G. ASAHARA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 273—276).—A series of X-ray photographs of thallium near its transformation point shows that a crystal when once formed does not disintegrate into smaller ones when undergoing allotropic change. The crystal lattice thus glides easily from one type to another without fracture of the crystal. In most metals, grain

growth is accelerated by annealing, but in thallium the crystals appear to attain their maximum size very readily on heating. Subsequent heating and cooling does not destroy the crystallites.
R. A. M.

Crystal Structure of the High Temperature Form of Cristobalite [SiO_2]. R. W. G. WYCKOFF (*Amer. J. Sci.*, 1925, [v], **9**, 448—459).—*X*-Ray diffraction measurements lead to a length for the edge of the unit cube, at temperatures between 290° and 430°, of 7·12±0·01 Å. The unit cube contains 8 mols. of SiO_2. The atomic arrangement is such that the silicon atoms have the same grouping as in crystalline silicon with oxygen atoms located midway between each pair of nearest silicon atoms. Each silicon atom is surrounded by four equally distant oxygen atoms. The closest distance between oxygen and silicon is 1·54 Å.
J. S. C.

Crystal Structure of Lithium Potassium Sulphate. A. J. BRADLEY (*Phil. Mag.*, 1925, [vi], **49**, 1225—1237).—The salt is a simple hexagonal sulphate. The crystal lattice was measured by means of a powder photograph. The unit cell consists of a prism of base 5·13 Å. and height 8·60 Å. containing 2 mols. of lithium potassium sulphate. The crystal is made up of a system of sulphate ions in hexagonal close packing, alternating with metallic ions. The lithium ions and the sulphate ions are arranged similarly. The potassium ions form a simple hexagonal lattice. The sulphate ion is a tetrahedron of oxygen atoms surrounding a central sulphur atom, the distance S—O being 1·5—1·6 Å. Intensity measurements on the *X*-ray spectrometer were used to determine the parameters fixing the relative positions of all the different kinds of atoms with the exception of lithium atoms. The positions of the latter were determined by spatial considerations. R. A. M.

Electrical Measurements on Metals of Great Purity (Tungsten, Molybdenum, and Nickel). W. GEISS and J. A. M. VAN LIEMPT (*Z. Metallk.*, 1925, **17**, 194—197).—Large single crystals of tungsten and of molybdenum were made by growing minute crystals of the former in the vapour of tungsten hexachloride and of the latter in molybdenum pentachloride, respectively, and the resulting crystals were drawn into wire. The tungsten wire so produced had an electrical resistance at 0° of 0·0491 ohm per metre length of 1 mm. cross-section, and the molybdenum wire 0·0503 ohm; the temperature coefficients were 481×10^{-5} and 473×10^{-5}, respectively. After annealing until recrystallisation had set in, the resistance of the tungsten wire decreased to 0·0482 ohm. Pure nickel was deposited on a small bullet of the metal heated electrically at 150° in an evacuated tube filled with nickel carbonyl; the metal was deposited on the bullet in a series of concentric shells which were quite free from iron, although the carbonyl contained appreciable amounts. The temperature coefficient of resistance of this metal was 667×10^{-5}; after annealing at 1000° to effect recrystallisation, this increased to 706×10^{-5}. A. R. P.

Electrical Conductivity of Rock Salt and Calcite at High Temperatures. F. VON RAUTENFELD (*Physikal. Z.*, 1924, 25, 602—604).—The electrical conductivities of rock salt over the range 600—800° and of calcite over the range 200—600° have been determined for direct current (D.C.) fields and for alternating current (A.C.) fields of frequency 1000, the fields being of the order of 200 volts/cm. For rock salt the conductivity varies logarithmically with the temperature, the A.C. values being slightly higher than the D.C. values. The conductivities parallel and perpendicular to the major axis and perpendicular to the cleavage plane of calcite bear an approximately constant ratio to each other; they vary approximately logarithmically with the reciprocal of the temperature. A description is given of the experimental technique. R. W. L.

New Alloy of Iron and Nickel of High Permeability. E. M. DELORAINE (*J. Phys. Radium*, 1925, [vi], **6**, 20—28).—Largely a *résumé* of the work of Arnold and Elmen (*J. Franklin Inst.*, 1923, **195**, 621). The physical properties of "permalloy," a nickel–iron alloy containing about 80% Ni, are described. The maximum permeability is obtained by heating the material at 900° for an hour, allowing it to cool slowly, reheating at 600°, and allowing it to cool more rapidly. Its magnetic properties are affected by heat treatment, by mechanical strain, and by the presence of impurities, of which carbon is chief. The initial permeability at the ordinary temperature of this alloy may be more than thirty times that of soft iron. Possible uses of the alloy are discussed. It is specially good for submarine telegraphy, transmitting four times more rapidly than an ordinary cable. A. S. R.

Magnetic Ferric Oxide. R. CHEVALLIER (*Compt. rend.*, 1925, **180**, 1473—1475).—Conversion of a commercial oxide having a composition closely approximating to Fe_3O_4 into ferric oxide results in a change in the permanent magnetic characteristics. Experiments in which the magnetic properties were determined after heating for a fixed time at various temperatures show that between 600° and 700° the magnetic properties of ferric oxide decrease very rapidly but do not entirely disappear, since at temperatures in the region of 900° the strongly magnetic oxide, magnetite, is produced. The decrease in magnetic properties is of a permanent character and the original activity is not restored after heating for some hours at a lower temperature. J. S. C.

Artificial Magnetic Anisotropy of Nickel. Realisation of a State with a particularly Simple Cycle. R. FORRER (*Compt. rend.*, 1925, **180**, 1394—1397; cf. this vol., ii, 486).—The discontinuities in the magnetisation cycle of nickel have been simplified. When the wire (l=50 mm., d=1 mm.) is wound tightly round a 5 mm. cylinder only the S_2 break is found, when it is wound loosely only the S_1 discontinuity appears in the cycle. When a finer stretched wire is wound round a smaller cylinder, the reversible sides of the cycle are straight and parallel, whilst the break is now

97% of the height of the cycle. The term "critical field" is applied to that field which sharply reverses the oriented magnetisation, and the expression "coercive field" to that tending to annul the magnetisation. Systematic work shows that mere flexion round smaller and smaller cylinders first straightens the reversible part of the cycle. The reversible part increases until the coercive field reaches an upper limit near $9g$. The same treatment applied to the stretched nickel wire (with a high coercive field) causes the appearance of jumps, diminishes the inclination of the reversible part, and causes the coercive field to decrease to the same limiting value of $9g$. Finally, a perfectly definite state is reached, in which the reversible part of the cycle has a minimum inclination and a well-defined value of $9g$ for the critical field. R. A. M.

Evaluation of the Grating Energy of Crystals. W. WESSEL (*Z. Physik*, 1924, **30**, 217—224).—Analysis after the classical fashion of the thermal equilibrium between the vapour of a salt and its ionised radicals shows that the grating energy of the salt can be determined from known data and partial pressures of the ions present. The chemical constants involved are calculated by the method of Born and Heisenberg (A., 1924, ii, 434). Direct measurements of the partial pressures of ions are wanting; they are projected by the author. R. W. L.

Migratory Constituents in the Crystal Lattice. G. F. HÜTTIG (*Fortschr. Chem., Phys., Phys.-Chem.*, 1924, **18**, 5—32; from *Chem. Zentr.*, 1924, ii, 2225—2226).—From a consideration of the equilibria of heterogeneous systems, it is concluded that systems of two components can exist in which the molecules of one component can move freely through the rigid lattice of the other component. Such systems are divided into three classes according to the form of their decomposition curves at constant pressure or constant temperature. A theory is deduced for the osmotic pressure of the mobile component. The decomposition curves are described by the equation $\log p_0/p = k/n$, where p_0 is the vapour pressure of the solvent, p the vapour pressure of the solution, n the molecular weight of the solvent, and k a constant. A number of systems, *e.g.*, uranosouranic oxide–uranous oxide–oxygen, are mentioned and the corresponding values of k given. This constant has the same significance as the reciprocal of the Raoult constant i in liquid solutions. G. W. R.

Physical Interpretation of *X*-Ray Spectra of Fatty Acids. L. DE BROGLIE and J.-J. TRILLAT (*Compt. rend.*, 1925, **180**, 1485—1487).—Fatty acids consist of chains of CH_2 groups cut by $-CO_2H$ planes of considerable electronic density and by planes of feeble or zero density which separate the $-CH_3$ groups of neighbouring molecules. The planes of feeble density may be considered as planes of strong density provided a phase difference π is introduced. Under these conditions, the distribution of intensities in the *X*-ray spectra of fatty acids is readily explained. J. S. C.

Physical Chemistry of Proteins. V. Molecular Weights of Proteins. I. Minimal Molecular Weights of certain Proteins. E. J. COHN, J. L. HENDRY, and A. M. PRENTISS (*J. Biol. Chem.*, 1925, **63**, 721—766).—Figures are given for the minimal molecular weights of the following proteins: gelatin, zein, gliadin, glutenin, edestin, caseinogen, hæmoglobin, hæmocyanin (*Limulus* and *Octopus*), serum-albumin and globulin, fibrin, egg-albumin, and Bence-Jones protein. The values have been calculated from a simultaneous consideration of the minimal molecular weights derived from the content of an individual element (*e.g.*, iron in hæmoglobin) or from that of an individual amino-acid, and of the equivalent weights as represented by combination with acids and bases, together with osmotic pressure determinations. C. R. H.

Electrical Properties of Neon, Hydrogen, and Nitrogen. S. P. MCCALLUM and C. M. FOCKEN (*Phil. Mag.*, 1925, [vi], **49**, 1309—1320).—A short filament was supported at a fixed distance from an earthed silvered plate, A, and another plate B was arranged parallel to A so that its distance from the filament could be adjusted. When a is the fixed distance, x the variable distance, and V the negative potential of the filament, the upper plate B is maintained at a negative potential Vx/a, thus establishing a uniform field $X=V/a$ between the plates. The negative current to the fixed plate A is plotted against voltage and for two different distances of x, using neon at 20 mm. pressure, the curves are superposable up to 45 volts, after which the currents obtained with the larger distance are greater than those with the smaller distance. The same is true for the positive current to the adjustable plate. The divergence indicates some process of ionisation in addition to ionisation by collision of electrons with the molecules of the gas. With hydrogen at 4 mm., no divergence was found under the experimental conditions ($V=85$ volts, $X/p=30{\cdot}4$). At 1 mm. pressure, a divergence occurred at $V=72$ ($X/p=103$). With nitrogen, no divergence appeared at 1·2 mm., but at 0·15 mm. it occurred at 46 volts ($X/p=438$).

The rate of increase of ionisation with increase in electric force ($X=V/a$) is very much greater in neon than in the two diatomic gases. Pressure produces much larger changes in conductivity in the diatomic gases than in neon. The results are compatible with ionisation by collision. The additional ionisation cannot be attributed to radiation, and is probably due to positive ions.

R. A. M.

Magnetic Properties of Atoms and Molecules. B. H. WILSDON (*Phil. Mag.*, 1925, [vi], **49**, 1145—1164; cf. this vol., ii, 481).—Theoretical. In the earlier papers it was assumed that precessional or nutational movements of the orbits which form the chemical bond synchronise the frequencies of the naturally untuned orbits in a manner whereby the total moment of momentum in opposite directions of the bond is equalised. This postulate with the principle of spatial quantising enables the author to arrive

mathematically at quantitative conclusions concerning magnetic properties which fit the data reasonably well. R. A. M.

Electrical Birefringence of Limonene. R. DE MALLEMAN (*Compt. rend.*, 1925, **180**, 1483—1485).—The Kerr constant for limonene has been determined, employing the author's method of measuring electrical birefringence (*ibid.*, 1923, **176**, 380). The rotatory power remains constant within the limits of experimental error in the electrical fields employed. The birefringence is small and positive in sign. The value of the Kerr constant in absolute units, $6{\cdot}5\times10^{-8}$ (15°, $0{\cdot}546\mu$), is intermediate between the values of benzene and of toluene and about four times that of pinene. The significance of this number from the point of view of structural formulæ is discussed. J. S. C.

Influence of Occluded Gas on the Electrical Resistance of a Wire. T. SEXL (*Z. Physik*, 1925, **32**, 333—335).—The change in resistance depends on the quantity of gas occluded, not on its chemical nature, and is expressed by the formula $R=R_0(1+\alpha k)$, where k is the ratio of the volume of the wire containing gas to that of the wire itself.

Applying Lorentz's theory of electrical conductivity and assuming that the increase in resistance is solely caused by the collisions of the electrons with the molecules of the gas, an equation for the conductivity is obtained which is in satisfactory agreement with experiment. E. B. L.

Radio Technique in Metallurgy. J. CZOCHRALSKI (*Z. anorg. Chem.*, 1925, **144**, 263—266).—It would be expected that if a needle rested on a particle of silicon in an aluminium–silicon alloy this combination would act as a radio detector. This, however, is not the case, the silicon having lost its activity in this direction, and it is suggested that detector action may be due to an impurity in ordinary silicon. Such a test for detector action may be useful in the examination of some alloys. A. G.

New Property of Diamagnetic Gases at Low Pressures. A. GLASER (*Sitzungsber. Akad. München*, 1924, 79—85).—The variation in the diamagnetic susceptibility of hydrogen, nitrogen, and carbon dioxide, at pressures below atmospheric, has been studied at 15° by a comparative method. The curves obtained, relating susceptibility with the pressure of the gas, are not simply linear, as required by the classical theory, but deviate from the straight line at pressures below 630 mm., 400 mm., and 360 mm. for hydrogen, nitrogen, and carbon dioxide, respectively, the values of susceptibility approaching three times the expected values at low pressures. This effect is regarded as due to the orientation of the molecules in the line of the magnetic field when the pressure is low enough to reduce the interference by collision of other molecules. The susceptibility is $-0{\cdot}000327\times10^{-6}$ and $-0{\cdot}000178\times10^{-6}$ unit for nitrogen and hydrogen, respectively, at 760 mm. and 15°. G. M. B.

Polarisation of Light scattered by Organic Vapours. A. S. GANESAN (*Phil. Mag.*, 1925, [vi], **49**, 1216—1222).—Imperfect polarisation of light scattered by gases and vapours (observed in a direction perpendicular to the incident beam) depends on the nature of the scattering substance. In argon and mercury vapour, the light is almost perfectly polarised; in hydrogen, the imperfection ρ (weak component/strong component) is 3·8%; in carbon dioxide, it is 11%. It is not, however, generally true that the imperfection of polarisation increases with the number of atoms in the molecule, because for ethyl ether and pentane (15 and 17 atoms, respectively) it is 3% and for triatomic carbon disulphide it is 16·7%. Accordingly, the author has studied series of related compounds: paraffins, some monohydric alcohols, chlorine substitution products of methane, benzene and its homologues, ketones, and some formic and acetic esters. In the paraffins the molecules increase in length from pentane to octane, but anisotropy of shape is not associated with increased depolarisation (optical anisotropy). A double bond increases depolarisation, *e.g.*, amylene shows a greater value for ρ than the normal value for the paraffin series. In *iso*-compounds ρ is less than the normal value. Benzene, toluene, and xylene have ρ=6·5%. Methyl esters show greater values of ρ than ethyl esters. The symmetrical carbon tetrachloride has a smaller value of ρ than has chloroform. R. A. M.

Metallic Reflexions. I and II. I. EBELING (*Z. Physik*, 1925, **32**, 489—501).—The sharply-marked minimum in the reflective power of silver at 3160 Å. becomes less pronounced with increasing temperature and is displaced towards the red. The spectrum reflected from massive copper, the absorption spectrum of precipitated copper, and the suspension of colloidal copper in ruby glass, investigated by means of a photo-electric cell, show indications of a band structure; one of the reflexion minima, between 5800 and 3850, becomes slightly more accentuated at low temperatures. Some relations between the optical properties of metals in the solid, colloidal, and gaseous states are pointed out. E. B. L.

Specific Heat of Incandescent Tungsten. L. J. BOCKSTAHLER (*Physical Rev.*, 1925, [ii], **25**, 677—685).—Measurements of thermionic current changes lead to a value of 0·045 for the specific heat of tungsten between 2375° and 2475° Abs. A. A. E.

Specific Heat of Superheated Ammonia Vapour. N. S. OSBORNE, H. F. STIMSON, T. S. SLIGH, and C. S. CRAGOE (*U.S. Bur. Standards, Sci. Paper* 501, 1925, **20**, 65—110).—The specific heat at constant pressure of superheated ammonia vapour has been determined at temperatures from −15° to +150°, and pressures from 0·5 to 20 atm. The method adopted was to measure the rise in temperature produced by a measured electric power added as heat to a steady stream of vapour flowing through a vacuum-jacketed instrument. Elaborate precautions were taken and numerous corrections made for which the original must be consulted. The results may be expressed accurately by the empirical equation

$C_p=1{\cdot}1255+0{\cdot}00238\theta+76{\cdot}8/\theta+5{\cdot}45p10^8/\theta^4+p(6{\cdot}5+3{\cdot}8p)10^{27}/\theta^{12}+2{\cdot}37p^6 10^{42}/\theta^{20}$, where C_p is expressed in joules per g. per 1°, p in metres of mercury at 0° and standard gravity, and θ in degrees absolute. The values of C_p thus calculated agree with the experimental values within 0·3% in all cases. A few determinations of the Joule–Thomson coefficient have also been made. W. H.-R.

Heat of Formation of Nitrogen Trichloride. W. A. Noyes and W. F. Tuley (*J. Amer. Chem. Soc.*, 1925, **47**, 1336—1341).—The following are recorded: heat of solution of 1 mole of gaseous chlorine in carbon tetrachloride, 4539 cal.; heat of solution of 1 mole of gaseous hydrogen chloride in carbon tetrachloride, 3680 cal.; heat of interaction of 1 mole of nitrogen trichloride in solution with 3 moles of gaseous hydrogen chloride giving 3 moles of gaseous chlorine and solid ammonium chloride, 41,800 cal.; heat of formation of nitrogen trichloride in solution in carbon tetrachloride from gaseous nitrogen and gaseous chlorine, −54,700 cal. J. S. C.

Heat of Formation of Acetaldol. T. P. G. Shaw (*J. Soc. Chem. Ind.*, 1925, **44**, 195—196T).—The heat of formation of acetaldol [β-hydroxybutaldehyde] has been found to be 17,222 cal. (within 1—2%) by means of an adiabatic copper calorimeter, which is described. The chief source of error lies in the analysis of the mixture of acetaldehyde and aldol. R. B.

Velocity of Sound in Liquids and its Relation to the Heat of Vaporisation. T. V. Ionescu (*J. Phys. Radium*, 1924, [vi], **5**, 377—383).—The velocity of sound in a number of liquids was measured by a method which involved the manipulation of small quantities of liquid. Except for toluene the measured velocities agreed fairly well with Newton's formula, where $V=\sqrt{E/\rho}$. Comparison of the experimental values with those obtained from the formulæ $V=\sqrt{L}$ (Boydan) and $V=\sqrt{L/\alpha T}$ (Lewis) in which L represents the heat of vaporisation, α the coefficient of dilatation, and T the absolute temperature, indicates that Boydan's formula leads to low values and Lewis' to high values. R. W. L.

Freezing Points of Hydrofluoric Acid. J. D. C. Anthony and L. J. Hudleston (*J. Chem. Soc.*, 1925, **127**, 1122—1128).—The freezing points of hydrofluoric acid have been determined for 0·025—4·140N-solutions, and the activities calculated. The freezing-point depression is found to be an almost linear function of the molarity. This is in accordance with the general theory (Davies and Hudleston, A., 1924, ii, 167), the increase of molecular conductivity in concentrated solutions (Deussen, A., 1905, ii, 311) not affecting the apparent molecular weight, $2HF=H^{\cdot}+HF_2'$. Assuming that no appreciable quantity of double molecules, H_2F_2, exists in solution and applying the law of mass action to the ionic equilibria of HF_2' and HF (Davies and Hudleston, *loc. cit.*), the total molarity of ions and molecules in solution is found and the freezing point calculated for a series of concentrations. It is found that

there is no appreciable difference between the calculated and the observed values of the freezing point up to 0·5N-solution.

F. G. S.

Relation between the Temperature and Velocity of Transformation of Metastable Non-variant Systems. N. I. STEPANOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 500—502).—Cases are considered in which the velocity of a transformation diminishes when the temperature is raised, use being made of the following equation for the absolute velocity of the transformation of metastable non-variant systems:

$$V=Ka^T(T_0-T)^n,$$

where T_0 is the absolute temperature of the equilibrated system, T the temperature at which the transformation occurs, n a positive number, a a number greater than 1, and K a positive coefficient depending on the units in which V is measured. The significance of each term in this equation is discussed and also the different types possible for the curves representing the velocity. The considerations advanced are in agreement with the results of Cohen's work on the mutual transformations of grey and white tin. T. H. P.

Transformation Temperature of Thallium. G. ASAHARA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 253—276).—The value of the transformation temperature of thallium is $232·5\pm<0·5°$ when very pure electrolytic thallium is investigated by thermal analysis. This value is preferred to the rather lower value 231·3° recently obtained by X-ray analysis (this vol., ii, 483). The experimental curves (heating) showed a small second maximum, which has been traced to the physical conditions under which the work was carried out. It is not chemical in origin. Certain modifications in technique are detailed, and a summary of the existing data on the transformation point is added. R. A. M.

Extension of Trouton's Law to the Fusion of Metals. A. JOUNIAUX (*Bull. Soc. chim.*, 1925, [iv], **37**, 513—518).—Trouton's law is extended to the fusion of metals, and existing data are used to calculate the constant $K=ML/T$ for a number of metals, where T is m. p. Abs., L latent heat of fusion, and M molecular weight. On the assumption that metals are monatomic, the value of K generally diminishes with rise of melting point, but may be expressed by the empirical relation $\log K=0·8058/T-0·28506\log T+1·20096$. The values of K thus calculated agree well with the experimental values of ML/T, except for the alkali metals. The calculated values suggest diatomic molecules for these metals in contradiction to accepted views. W. H.-R.

Chemical Constant of Chlorine. R. R. S. COX (*Proc. Camb. Phil. Soc.*, 1925, **22**, 491—492).—Recent experimental data are used to correct the value of the chemical constant of chlorine given in a previous paper (*ibid.*, 1923, **21**, 541). The new value of the constant, deduced from the dissociation of chlorine, is 0·64. There is still an unexplained discrepancy with the theoretical value of 0·9. S. B.

Density of Bromoform. Application to the Testing of Aluminium. P. PASCAL (*Bull. Soc. chim.*, 1925, [iv], **37**, 502—503).—The density of pure bromoform is determined as 2·9315, 2·8827, 2·8779, 2·7934, 2·7364, 2·6823, at 0°, 17·5°, 19°, 50°, 70°, and 90°, respectively. The density of aluminium lies within these values, and specimens may be tested by immersion in bromoform, the latter being gradually heated and stirred, and the temperature noted at which the specimen sinks. The specimen should be protected by a thin film of collodion, albumin, or 50% aqueous glycerol. W. H.-R.

Density of Rock Salt and Calcite. O. K. DEFOE and A. H. COMPTON (*Physical Rev.*, 1925, [ii], **25**, 618—620).—Rock salt has d 2·1632±0·0004 g./c.c., and calcite has d 2·7102±0·0004 g./c.c. at 20°. A. A. E.

Isotopy of Lead. (MLLE.) B. PERRETTE (*Compt. rend.*, 1925, **180**, 1589—1591).—The densities and the wave-lengths of certain arc lines of ordinary lead and of a uranium-lead from a Congo pitchblende have been compared and the following results obtained: Ordinary lead d^0 $11{\cdot}336_3$±0·0004, atomic weight 207·20, atomic volume 18·2776; uranium-lead $11{\cdot}278_4$±0·0004, 206·14, 18·2774, respectively. The constancy of atomic volume for isotopic elements is thus confirmed. The atomic weights are those obtained by Brennen (this vol., ii, 174). For the spectroscopic work, a vacuum arc was used in conjunction with a Fabry-Perot interferometer. Great precautions were taken to ensure an identical experimental arrangement for both isotopes. All the lines measured gave slightly higher values for uranium-lead than for ordinary lead. The results all refer to arc lines emitted by the neutral lead atom: wave-length 4058, difference in wave-length found 0·0076±0·0008; 3740, 0·0070±0·0008; 3684, 0·0073±0·0008; 3640, 0·0072±0·0010; 3573, 0·0068±0·0010. No significance is attached to the apparent decrease in the difference. R. A. M.

Relation between the Critical Temperature and the Expansion of Liquids. N. DE KOLOSSOWSKY (*J. Phys. Radium*, 1925, [vi], **6**, 99—104).—The relation between the critical temperature and the expansion of a liquid for a given reduced temperature is expressed by the formula $k_m(BT_c-273)=1$, where k_m is the expansion modulus of the liquid at the reduced temperature, and B a numerical constant dependent on that temperature. For the reduced temperature $T=0{\cdot}6T_c$, the value of B is 2. It is shown that the expression in that case applies satisfactorily to a number of substances with critical temperatures between 127° and 1072° Abs. For the above reduced temperature van der Waals' formula $\alpha_m T_c$=constant, where α_m is the coefficient of expansion of the liquid at the reduced temperature, has the form $\alpha_m T_c=0{\cdot}75$. F. G. T.

Surface of State of *cyclo*Hexane. N. N. NAGORNOV and L. A. ROTINJANC (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 371—404).—The results are given of physical measurements of

carefully purified *cyclo*hexane, b. p. 80·75°/760 mm., m. p. 6·54°, *d* 0·79063 at 7°, 0·78221 at 16·12°, 0·77384 at 25·08°, 0·75942 at 40·21°, 0·74416 at 50·95°, and 0·72215 at 78·05°. The value of the specific volume at $t°$ is given by $1·26482/\{1—0·0011599(t—7)—0·0000008356(t—7)^2\}$. At 25°, the value of pv diminishes from 1 when p=760 mm. to 0·9855 when p=50,000 mm. to 55,000 mm. and then gradually increases to 1·0736 when p=200,000 mm. The value 554·02° Abs. is found for the critical temperature (T_c) and 30,835 mm. for the critical pressure (p_c). For a number of temperatures ranging from 275·95° to —4·51°, calculations have been made of the values of the constant f of van der Waals' equation, $\log(p_c/p)=f(T_c—T)/T$. Comparison of these numbers with those for *n*-hexane and benzene show that f has not the same value for all substances. Moreover, in each case, as the temperature falls the value of f at first diminishes to a minimum when log (p_c/p) is about 0·7 and then increases. The paper contains a number of curves and tables of results, and reference is made particularly to the work of Young and Fortey (T., 1899, **75**, 873), Ramsay and Young (T., 1885, **47**, 82; A., 1887, 763), and Young and Thomas (T., 1895, **67**, 107).

T. H. P.

Van der Waals' Equation of State. J. J. Van Laar (*Z. physikal. Chem.*, 1925, **116**, 119—122).—Polemical, with reference to Berger's work (A., 1924, ii, 654; this vol., ii, 376). L. F. G.

Apparatus for the Rapid Measurement of Surface Tension at the Interface of Two Liquids. Influence of Temperature. P. L. du Noüy (*Compt. rend.*, 1925, **180**, 1579—1580).—The force necessary to drag a ring of thin platinum wire from the interface of two liquids is measured directly in dynes. An accuracy of 0·05 dyne can be attained in measuring the static interfacial tension between two liquids or solutions. The surface tension at a liquid/air interface decreases with rise in temperature; the interfacial tension increases with increasing temperature. R. A. M.

Surface Tension of Solutions of the Sodium Salts of α- and β-Diphenylsuccinic Acids and of Fumaric and Maleic Acids. I. Ribas (*Anal. Fís. Quím.*, 1925, **23**, 148—150).—The surface tensions of solutions of the sodium salts corresponding with 5% solutions of the free acids were measured by the drop method. The values obtained, relative to water as unity, were α-diphenylsuccinic acid 0·87, β-diphenylsuccinic acid 0·97, fumaric acid 0·99, maleic acid 0·96. G. W. R.

Capillary Rise of Water in Tubes of Various Metals. E. K. Carver and F. Hovorka (*J. Amer. Chem. Soc.*, 1925, **47**, 1325—1328).—A convenient method for the accurate determination of surface tension is described. Water and benzene rise to the same height in tubes of glass as in tubes of various metals. These observations cannot be reconciled with those of Bigelow and Hunter (A., 1911, ii, 471), who found that these two liquids rose to greater heights in capillary tubes of metal than in tubes of glass. J. S. C.

Influence of Pressure on Velocity of Diffusion of Metals in Mercury. E. COHEN and H. R. BRUINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 555—564).—The velocity of diffusion of cadmium in mercury at 20° and 1500 atm. pressure has been determined. The increase of pressure from 1 atm. to this high value depresses the velocity of diffusion by about 5%. S. B.

Potentiometric Measurement of Velocities of Diffusion of Metals in Mercury. E. COHEN and H. R. BRUINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 535—554).—A potentiometric method has been described for the determination of the coefficient of diffusion of metals in mercury, which, within certain limits, can be applied at any desired temperature and pressure. This method has been used to determine the coefficient of diffusion of cadmium in mercury at 20° and 1 atm. pressure. S. B.

Calculation of the *P*-*x* Curves of Binary Liquid Mixtures. L. FRANK (*Ber.*, 1925, **58**, [*B*], 962—964; cf. this vol., ii, 188).—Relationships are deduced from the partial pressure formulæ and the Duhem equation which permit the calculation of the total and partial pressure curves of liquid mixtures particularly when they are not greatly deflected. The composition of the gaseous phase can also be calculated. H. W.

Molecular Compounds of Phenols. III. Behaviour of Binary Systems with Hydrogenated Phenols. G. WEISSENBERGER and F. SCHUSTER (*Monatsh.*, 1924, **45**, 413—424; cf. Weissenberger and Piatti, this vol., i, 538, 539).—Determinations have been made at 20° of the vapour pressure (by a streaming method), of the viscosity, and of the surface tension (by the capillary rise method) of mixtures in eight successive proportions of each of the following pairs of substances: *cyclo*hexanol–benzene, *cyclo*hexanol–acetone, *cyclo*hexanol–ethyl acetate, *cyclo*hexanol–methyl alcohol, *cyclo*hexanol–chloroform, 2-methyl*cyclo*hexanol–benzene, 3-methyl*cyclo*hexanol–benzene, and 4-methyl*cyclo*hexanol–benzene. In each of these systems the observed vapour pressures are higher than those calculated from the molecular concentration by the Raoult–van't Hoff relation. The hydrogenation of the benzene nucleus has therefore completely suppressed the residual affinity made evident by similar experiments with phenols. The vapour pressure deviation reaches a maximum for mixtures which are in most cases equimolecular. These results are confirmed by the viscosity data, the viscosities of the mixtures being in all cases less than those calculated by the simple mixture law indicating a diminution of the intermolecular attraction. The surface tension values, again, are in all cases much smaller than the calculated values. The following surface tension values at 20° are recorded: *cyclo*hexanol 34·5, 2-methyl*cyclo*hexanol 31·3, 3-methyl*cyclo*hexanol 29·6, 4-methyl*cyclo*hexanol 30·5, methyl alcohol 22·7, acetone 22·8, ethyl acetate 23·3, benzene 28·8, chloroform 26·5 dynes/cm.

G. M. B.

Molecular Compounds of Phenols. IV. Binary Systems with Phenol and its Ethers. G. WEISSENBERGER, F. SCHUSTER, and K. SCHULER (*Monatsh.*, 1924, **45**, 425—435).—Determinations have been made of the vapour pressures at 15° of a series of mixtures of phenol with methyl alcohol, ethyl alcohol, acetone, and ethyl ether, respectively. The values observed are in all cases lower than those calculated from the mixture rule, and the divergence is a maximum in the system phenol–acetone for a concentration which corresponds with the compound $2Ph\cdot OH,Me_2CO$ found by Schmidlin and Lang (A., 1910, i, 836) by thermal analysis of these mixtures. From similar maximum deviations, the existence is inferred of analogous compounds formed by phenol and the three cresols with alcohols, ketones, and ethers of the form 2Ar·OH,M, where M is a molecule of the second constituent. Corresponding measurements for mixtures of phenol with benzene, toluene, chloroform, carbon tetrachloride, and carbon disulphide show vapour pressures which are higher than the calculated. For the systems anisole and acetone, ethyl ether, carbon tetrachloride, and carbon disulphide, respectively, the vapour pressure values are again higher than those calculated. The methylation of the hydroxyl group of phenol thus completely suppresses compound formation with these substances, a result which lends support to the opinion of Pfeiffer and others that compound formation occurs in such cases by co-ordination with the hydrogen atom of the hydroxyl group. In the single system anisole–chloroform, however, the evidence points to formation of the compound $2Ph\cdot OMe,CHCl_3$. The oxygen atom is probably involved in this case.

Measurements of surface tension and viscosity at 15° are recorded for each of the above systems of phenol or anisole with volatile substances. The only clear indication obtained from the surface tension figures is a sharp maximum in the phenol–methyl alcohol system corresponding with the compound formation indicated by the vapour pressure measurements. The remaining surface tension data and the viscosity values lead to no precise conclusions.

G. M. B.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XLV. Binary Systems of Benzhydrol with Phenols and Amines. R. KREMANN and H. DRAZIL (*Monatsh.*, 1924, **45**, 345—354; cf. A., 1919, ii, 457).—Fusion curves have been constructed for the binary systems given by benzhydrol with phenol, α-naphthol, β-naphthol, quinol, resorcinol, pyrogallol, *o*-, *m*-, and *p*-nitrophenols, 2 : 4-dinitrophenol, picric acid, α- and β-naphthylamine, *o*- and *p*-phenylenediamine, respectively. In the system benzhydrol and phenol a single compound is formed of the composition 1 mol. benzhydrol : 2 mols. phenol, m. p. 47·3°, no confirmation being obtained of the equimolecular compound (cf. Schmidlin and Lang, *Ber.*, 1912, **45**, 899). With β-naphthol, benzhydrol forms a compound (2 mols. β-naphthol : 3 mols. benzhydrol), m. p. 62°, and with picric acid a compound (2 mols. picric acid : 1 mol. benzhydrol), m. p. 131°. With the

remaining substances in the above list benzhydrol forms no compound, but yields in each case a simple eutectic. G. M. B.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XLVI. Binary Systems of Azobenzene with Phenols. R. KREMANN, K. ZECHNER, and G. WEBER (*Monatsh.*, 1924, **45**, 305—310).—Fusion curves for the binary systems of azobenzene with various phenols show no compound formation. The eutectic temperatures and percentages of azobenzene in the eutectic mixtures with various phenols are as follow: *p*-nitrophenol 49°, 90%, β-naphthol 51°, 82%, quinol 55°, 1%, resorcinol 57·2°, 80%, *o*-nitrophenol 29°, 40%, *m*-nitrophenol 58°, 76%, α-naphthol 48°, 66·5%, pyrocatechol 60°, 87·5%, pyrogallol 65°, 100%, 2 : 4-dinitrophenol, 54°, 72%, and picric acid, 56°, 67·5% of azobenzene respectively. G. M. B.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XLVII. Binary Systems of Acids or Esters with Phenols. R. KREMANN, E. ZECHNER, and H. DRAZIL (*Monatsh.*, 1924, **45**, 355—378; cf. preceding abstract).—Fusion curves have been constructed for the binary systems formed by succinic and cinnamic acids respectively with each of the following: phenol, α-naphthol, β-naphthol, resorcinol, quinol, pyrocatechol, pyrogallol, *m*-nitrophenol, *p*-nitrophenol, 2 : 4-dinitrophenol, and picric acid, and for the system cinnamic acid and *o*-nitrophenol. No compound is formed between succinic acid and any of the phenols named, a simple eutectic being found in each case. Cinnamic acid, on the other hand, forms an equimolecular compound with picric acid, m. p. 106·5°, which is largely dissociated in the liquid phase at its melting point, whilst the melting-point curves of cinnamic acid with *m*-nitrophenol and 2 : 4-dinitrophenol show a practically horizontal portion between two eutectics in each case (at 77·5° and 29—36% of cinnamic acid with *m*-nitrophenol and at 91° and 30—41% of cinnamic acid with 2 : 4-dinitrophenol), indicating easily dissociated compounds which are probably, by analogy, equimolecular in composition. Cinnamic acid forms no other compounds, but gives a simple eutectic in each of the other systems examined. From these results, it is inferred that compound formation is due to the double bond rather than to the carboxyl group of cinnamic acid and to the nitro groups rather than to the hydroxyl group of the nitrophenols.

Complete fusion curves have been constructed for the binary systems of methyl oxalate with phenol, α-naphthol, β-naphthol, pyrocatechol, quinol, resorcinol, pyrogallol, *o*-, *m*-, and *p*-nitrophenols, 2 : 4-dinitrophenol, picric acid, and *p*-toluidine, respectively. Methyl oxalate forms a compound with phenol, m. p. 47·5°, of the composition 4 mols. phenol to 1 mol. ester, and with quinol a compound, m. p. 94°, of the composition 1 mol. quinol to 4 mols. ester. Compound formation was not indicated in any other case, simple eutectics being found. Fusion curves have also been constructed for the binary systems ethyl oxalate with resorcinol, β-naphthol, and quinol over the ranges 0—62%, 0—75%, and 0—97% of ester,

respectively. There was no indication of compound formation, although Baeyer and Villiger have described an equimolecular compound of ethyl oxalate with quinol. G. M. B.

Study of the Ternary Mixture: Water–Ethyl Alcohol–*n*-Butyl Alcohol. F. DROUILLON (*J. Chim. phys.*, 1925, **22**, 149—168).—The system was studied by the synthetic method. Mixtures rich in water are totally miscible at ordinary temperatures, but separate into two layers on warming; on increasing the temperature still further, another critical solution temperature is reached. Mixtures poor in water form two layers at the ordinary temperature, but they are totally miscible at higher temperatures. The critical solution temperature for water–*n*-butyl alcohol is 129·5°, and the solution contains 28% of the alcohol. The results are tabulated and given in the form of curves. The position of conjugate points on the diagram was determined by analysis of the two liquid layers in equilibrium. Details of the method employed are given. W. T.

Compound AuCu in Gold Alloys. L. STERNER-RAINER (*Z. Metallk.*, 1925, **17**, 162—165).—The compound AuCu separates in long, light-yellow needles from slowly cooled alloys of copper and gold containing 56·5% to 93·0% Au, and from copper–silver–gold alloys the composition of which falls within the region bounded by lines joining the silver corner of the ternary diagram to the points on the copper–gold side corresponding with alloys of the above composition. Rapid cooling of the alloy through the range 500° to 20° suppresses the separation of the compound, reduces the hardness and tensile strength of the alloy, and increases the ductility. [Cf. *B.*, July 24th.] A. R. P.

Equilibrium Diagram of the Copper–Zinc System. D. ITSUKA (*Mem. Coll. Sci. Kyoto*, 1925, **8**, 179—212).—A reinvestigation of the equilibria in the copper–zinc system has confirmed for the most part the results of earlier workers. Minor differences were, however, observed, especially in the positions of the boundary lines between the different constituents. In general, these were found to lie more towards the copper side than had previously been stated. The peritectic at 695° in alloys containing 20—30% Cu has only one saturation point, and that in alloys containing 0—12% Cu lies at 425°, which is much higher than previously found. The transformation in the β phase at 450—475° takes place in two stages, the maximum temperature of 475° occurring with 53% Cu. The δ solid solution decomposes below 550° into eutectoidal $\epsilon+\gamma$ and between 560° and 590° there is a small field of $\delta+\gamma$ in alloys containing 26—30% Cu. Zinc begins to volatilise from the surface layers of brass at about 470°. [Cf. *B.*, July 24th.] A. R. P.

Magnetisation of Ferro-Nickel [Alloys] (Thermomagnetic Properties). M. PESCHARD (*Compt. rend.*, 1925, **180**, 1475—1478).—Alloys containing more than 34·4% of nickel (Fe_2Ni) are reversible in the sense that their magnetic properties disappear and reappear at the Curie point, whilst alloys containing less than this

amount of nickel are irreversible. If sufficiently cooled the latter acquire a strong magnetisation which is connected with the change of the iron from the γ to the β modification. Under certain conditions, alloys in the "β" state exhibit reversibility. The various cases possible are discussed and the experimental results expressed diagrammatically. J. S. C.

Solubilities in Water of Rubidium and Cæsium Chloroplatinates. E. H. ARCHIBALD and L. T. HALLETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1314—1318).—The solubility has been determined between 0° and 100° at 10° intervals. The solubilities in g./100 g. of water at 0° and 100° are respectively: rubidium salt 0·0137 and 0·334, cæsium salt 0·0047 and 0·0915. J. S. C.

Equilibrium in the System Zinc Sulphate–Water. E. COHEN and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1925, **115**, 433—439).—Further experiments have been undertaken which show that the earlier work of one of the authors (Cohen, *ibid.*, 1900, **34**, 179) was partly in error. The existence of the metastable monoclinic heptahydrate between 7° and 35° (Bury, this vol., ii, 119) is confirmed. N. H. H.

Solubility Curves of Zinc Sulphate. E. COHEN and C. W. G. HETTERSCHIJ (*Z. physikal. Chem.*, 1925, **115**, 440—443).—A redetermination of the solubility curves of $ZnSO_4,6H_2O$ and $ZnSO_4,7H_2O$ (rhombic) has been made since the method of analysis used by one of the authors in previous work (Cohen, *ibid.*, 1900, **34**, 179) was subsequently shown to give results 0·4% too high. The transition point now found is 37·9°. N. H. H.

Solubility of Calcium Fluoride in Acetic Acid. L. DUPARC, P. WENGER, and G. GRAZ (*Helv. Chim. Acta*, 1925, **8**, 280—284).—Calcium fluoride (fluorite) is not, as hitherto supposed, insoluble in dilute acetic acid. Acetic acid (0·5*N*) dissolves at 40° 0·153 g., at 60° 0·178 g., at 80° 0·206 g., at 100° 0·229 g. per litre. The corresponding figures for *N*-acid are 0·175, 0·203, 0·237, 0·264, and for 2*N*-acid 0·192, 0·229, 0·267, 0·300. W. A. S.

Solubility of Magnesium Hydroxide. I. Existence of different Modifications of Magnesium Hydroxide. J. K. GJALDBAEK (*Z. anorg. Chem.*, 1925, **144**, 145—168).—The differences in the recorded values of the solubility of magnesium hydroxide in water are ascribed chiefly to the existence of two forms of the hydroxide, a labile and a stable form. Errors may also have arisen on account of the readiness with which the dissolved hydroxide attacks glass with the formation of magnesium silicate. Determinations, by the *E.M.F.* method, of the hydrogen-ion activity of solutions of magnesium chloride, saturated with the hydroxide by the addition of suitable quantities of sodium hydroxide, were made in paraffined vessels and showed that values of $p\alpha_H$ (the negative logarithm of the hydrogen-ion activity) fell to a constant value, corresponding with the stable form of the hydroxide. This was also observed when the hydroxide was replaced by magnesium

oxide or metal and the final $p\alpha_H$ values were in close agreement; the same values were obtained without an initial fall when the hydroxide was converted into the stable form before use. The initial hydrogen-ion activities, corresponding with the labile form of hydroxide, were less concordant. A. G.

Solubility of Magnesium Hydroxide. II. Solubility Products and Dissociation Constants of the Magnesium Hydroxides. J. K. GJALDBAEK (*Z. anorg. Chem.*, 1925, **144**, 269—288).—The hydroxyl-ion activities of saturated solutions of magnesium hydroxide in aqueous magnesium chloride were calculated from the hydrogen-ion activities, determined as already described (cf. preceding abstract). The magnesium-ion concentration was equal to the known concentration of the chloride plus that of the hydroxide and carbonate, determined by electrometric titration with acid; the activity coefficient of the latter ion was calculated from Bjerrum's formula, $-\log f = nk\sqrt[3]{C_{ion}}$, in which f is the activity coefficient, n the valency of the ions, and C_{ion} the ionic concentration. The solubility products at 18° of the stable and labile forms of the hydroxide were thus calculated to be $10^{-10\cdot93}$ and $10^{-9\cdot2}$, respectively; the second dissociation constant was found to be approximately $10^{-2\cdot1}$ and, when allowance was made for incomplete dissociation, the calculated solubilities at 18° of the two forms were $1\cdot61\times10^{-4}$ and $7\cdot0\times10^{-4}$, respectively; nearly all previously recorded values lie between these two figures. The molar heat of solution of the stable form is −2200 calories and that of the labile form approximately zero. A. G.

Influence of the Variation of the Coefficient of Viscosity with Temperature on the Specific Heat of Solutions. N. DE KOLOSSOWSKY (*Bull. Soc. chim.*, 1925, [iv], **37**, 605—608).—The specific heats of dilute aqueous solutions of organic substances such as carbamide, acetamide, dextrose, formic, oxalic, and citric acids are given accurately by $(18\mu+2n+3)/(18\mu+M)$, where M is the molecular weight of the substance, n the number of atoms in its molecule, and μ the number of molecules of water per molecule of solute. For some substances, such as the saturated alcohols, there is a considerable deviation from the values calculated from this formula, but the deviation is given by the additional term $350d(\eta_0-\eta)/dT$, where η_0 and η are the coefficients of viscosity of the solvent and the solute respectively. The observed deviation agrees with the value calculated from this expression in the case of ethyl and propyl alcohols, acetic acid, and sucrose, but in the case of methyl alcohol there is a further discrepancy. G. M. B.

Salt-formation between Creatine and Sodium Hydroxide. A. HAHN and H. FASOLD (*Z. Biol.*, 1925, **82**, 473—484).—A saturated aqueous solution of creatine at 10° contains 10·9 g. of creatine per litre; at 12°, the amount lies between 14·4 and 14·9 g. The amount dissolved in sodium hydroxide increases from 12·72 g. per litre in 0·2N-solution to 23·20 g. in N-solution. K_a for creatine is $5\cdot2\times10^{-15}$. Since K_b is 5×10^{-12} (A., 1921, i, 515), creatine is about

a thousand times stronger as a base than it is as an acid. The hydrolysis of the sodium salt of creatine increases with dilution, being almost complete in 0·05*N*- to 0·025*N*-solution. The velocity of the conversion of creatine into creatinine by sodium hydroxide increases slowly with the concentration of the alkali. O. O.

Salt Solutions. P. Mondain-Monval (*Ann. Chim.*, 1925, [x], **3**, 72—190).—The formula, $502LdT/T^2+idc/c=0$ is shown to represent the solubility of sodium and ammonium nitrates, the factor i being given by the relation $dp/p=i\,.\,dc/c$, where p is the vapour pressure. Heats of solution are recorded (at 0° and about 18°) for potassium, sodium, and ammonium nitrates, potassium and ammonium chlorides, and potassium sulphate. The calculated and observed values of L agree except in the case of the last-named salt. Similar data are recorded for certain mixed salt solutions with a common ion. The general rule that the ratio of L above and below a transition point is equal to the ratio of the gradients of the respective solubility curves is confirmed for ammonium nitrate. For two curves meeting at a eutectic the relation: $(dc_2/dT)/(dc_1/dT)=c_2L_2/c_1L_1$, is verified for the above six salts; the suffixes 1 and 2 refer to the two curves. The same rule holds for solutions containing mixtures of salts with a common ion provided the left-hand side is multiplied by i_2/i_1. The relation $d\log L/dc=-d\log i/dT$ is confirmed experimentally.
S. K. T.

Ammoniation of Ions in Aqueous Solutions. J. Lošan (*Rec. trav. chim.*, 1925, **44**, 459—465).—Cryoscopic measurements of aqueous ammoniacal solutions of the chlorides of lithium, sodium, potassium, magnesium, and ammonium have been made in order to determine to what degree the metal ions are capable of binding ammonia molecules. Lithium and, still more, magnesium ions show this effect to a marked degree. In the other cases an increased depression of freezing point is observed, but this is attributed to the masking of the ammoniation effect by the hydration of ions and molecules by the solvent with a consequent decrease in its activity. This is demonstrated by comparison with analogous experiments in which ammonia is replaced by dextrose, which does not combine with the ions: here a still greater increase of depression is observed (potassium excepted). The ammoniation effect is taken as proportional to the differences between corresponding depressions in the two sets of experiments. This gives decreasing ammoniation in the order lithium, sodium, ammonium, potassium. The effect thus decreases with increase in ionic volume. N. H. H.

Displacement of Acids by Diffusion. E. Demoussy (*Compt. rend.*, 1925, **180**, 1498—1500; cf. A., 1924, ii, 147).—Previous work is extended to include various mixtures of alkali and alkaline-earth chlorides with organic acids. The alkaline-earth chlorides yield numbers for the displacement of hydrochloric acid which are sensibly identical. The displacement is much smaller in the case of the alkali chlorides. Displacement of hydrochloric acid also varies with the degree of ionisation of the organic acid, and under comparable

conditions the order of the acids starting with the least efficient is : acetic, citric, formic, oxalic. Replacement of the chloride ion by the less mobile sulphate ion results in a reduced displacement. Analogous results were obtained with mixed solutions of potassium chloride and barium hydroxide. J. S. C.

Absorption of Hydrogen Chloride in Concentrated Sulphuric Acid. V. Čupr (*Rec. trav. chim.*, 1925, **44**, 476—479).—The absorption of hydrogen chloride in sulphuric acid over a range of concentration of 76·43 to 100·00% H_2SO_4 has been measured at 25° and atmospheric pressure. The absorption shows a minimum at about 89% H_2SO_4, *i.e.*, at a higher concentration than that corresponding with the hydrate H_2SO_4,H_2O which contains 84·48% H_2SO_4. N. H. H.

Adsorption from Viscous Media by Charcoal. G. Weissenberger and H. Waldmann (*Monatsh.*, 1924, **45**, 393—412).—The adsorption of iodine by five different varieties of charcoal from solution in glycerol, *cyclo*hexanol, and *n*-butyl phthalate (d^{18} 1·49, viscosity 13·5 times that of water) is found to reach a true equilibrium which obeys the Freundlich adsorption equation. The time required to reach equilibrium at 18° is 1·5 hrs. for glycerol, 1 hr. for *cyclo*hexanol, and 3 hrs. for butyl phthalate solutions. Figures are recorded showing the variation of the adsorption from equivalent solutions of iodine as the composition of the solvent is varied by diluting the glycerol with water, the *cyclo*hexanol and the butyl phthalate with benzene, whereby the viscosity of the liquids is much reduced. The amounts adsorbed at equilibrium are found to vary inversely as the viscosity of the medium for each set of mixtures, the values agreeing with an equation $x/m=\beta/\eta^{1/\gamma}$, where x is the amount adsorbed, m the weight of adsorbent, η the viscosity of the medium, and β and γ are constants peculiar to the substances involved, the values obtained for β and $1/\gamma$ being : glycerol 5·19 and 0·447, *cyclo*hexanol 1·11 and 0·515, butyl phthalate 1·060 and 0·0453. This effect is explained by the correlation of high viscosity with a high degree of polymerisation in the liquid and at the same time with a ready adsorption of the complex liquid molecules, which by competing with the iodine for the surface of the carbon lower the apparent adsorption. The addition of the less viscous liquid causes dissociation of the complexes, less adsorption of the liquid, and therefore more adsorption of iodine. By means of Freundlich's formula, the final concentration and amount adsorbed for a series of initial concentrations are calculated and found to agree with the values observed experimentally.

The results are found to be of the same type for the different varieties of charcoal used. G. M. B.

"Activated" Graphite as a Sorbent of Oxygen. D. H. Bangham and J. Stafford (*J. Chem. Soc.*, 1925, **127**, 1085—1094).—Graphite which has absorbed large quantities of hydrogen shows greatly increased activity as a sorbent of oxygen. A study of the kinetics of the sorption of oxygen showed that it took place at

constant pressure according to the equation $s=kt^b$, where s is the quantity of oxygen sorbed at time t after its introduction to the graphite, k and b being constants. The experiments were performed with graphite surrounding a platinum electrode in a small glass bulb, connected to the gas measuring system. By heating the graphite in a vacuum to 350°, and submitting it to the electric discharge in hydrogen, large quantities of the gas were taken up, and the graphite was then found to be very active towards oxygen. The activity towards carbon dioxide was scarcely changed. The equations for the sorption of oxygen all involved a common power of t, viz., $t^{0\cdot190}$. Experiment showed that the "induced" activity of the graphite towards oxygen was directly proportional to the hydrogen introduced electrically, and was independent of the amount of graphite used. Objections are raised to the view that hydrogen is maintained in an active state by the graphite and is removed by combination with oxygen, and a mechanism of the phenomenon based on the crystal structure of graphite is discussed. L. L. B.

Adsorption by Activated Sugar Charcoal. II. Adsorbability of Hydrogen and Hydroxyl Ions. E. J. Miller (*J. Amer. Chem. Soc.*, 1925, **47**, 1270—1280).—The view that hydrogen and hydroxyl ions are equally adsorbed by charcoal is based on erroneous evidence, the hydroxyl ion being last instead of first in the series which expresses the adsorbability of anions by pure charcoal. Experiments have been carried out using pure, ash- and nitrogen-free charcoal (A., 1924, ii, 664). The adsorption of hydrochloric acid from its aqueous solutions is increased in presence of sodium chloride. Addition of sodium and potassium chlorides to solutions of the corresponding hydroxides results in an increase in the concentration of the alkali; this is attributed to hydrolytic adsorption, hydrochloric acid being adsorbed and an equivalent amount of alkali liberated. The strong inorganic bases are "negatively" adsorbed, *i.e.*, the charcoal adsorbs water, leaving the alkali concentrated in a smaller volume. Adsorption from solutions of salts is either exclusively hydrolytic or partly hydrolytic and partly molecular. Certain theoretical points are discussed. J. S. C.

Negative Adsorption and Oxidising Action of Suspended Charcoal. T. Oryng (*Kolloid-Z.*, 1925, **36**, 287—288; cf. A., 1913, 761).—Polemical, against Feigl (A., 1922, ii, 51). E. M. C.

Adsorption of Vapours by Silica Gel by a Dynamic Method. W. A. Patrick and L. H. Opdycke (*J. Physical Chem.*, 1925, **29**, 601—609).—The adsorption of water, ethyl alcohol, carbon tetrachloride, and benzene vapour on silica gel containing 3·57% of water at 30° has been investigated by a dynamic method. The vapours were admixed with dry air in definite proportions and passed over the gel until equilibrium was attained. A hysteresis effect was observed with water vapour. The remaining liquids gave results which agreed with the authors' theory of capillary condensation. The time taken for water vapour to reach equilibrium was very long.

Since water undergoes an increase in viscosity with reduced pressure it must be highly viscous in the capillary pores of the silica gel.
M. B. D.

Adsorption of Water Vapour and some other Vapours by the Surface of Glass. D'HUART (*Compt. rend.*, 1925, **180**, 1594—1596).—The weight of water adsorbed by the internal surface of the apparatus described varies little with temperature between 14° and 24°; it is proportional to the surface area and to the vapour pressure. This direct variation with vapour pressure holds between 5 mm. and the saturation point, but even in the highest vacua obtainable in the presence of phosphorus pentoxide a certain amount of water (0·009 mg./dm.^{2}) adheres to the glass after several hours. With vapours other than water the adsorption is much feebler and often cannot be measured, as in the cases of ethyl alcohol, chloroform, benzene, and toluene. The apparatus described may be used for the rapid determination of the humidity of gases or of hydrogen in organic compounds, and for the determination of the vapour densities of very volatile liquids. The results in the vapour-density measurements are more accurate than those obtained by the method of Victor Meyer. R. A. M.

Sorption of Nitrous Oxide and Sulphur Dioxide by Glass. D. H. BANGHAM and F. P. BURT (*J. Physical Chem.*, 1925, **29**, 540—550; cf. this vol., ii, 284).—The sorption of nitrous oxide and sulphur dioxide by glass has the same time characteristics as were previously found with carbon dioxide. It was found impossible to remove completely the sulphur dioxide from the glass wool. M. B. D.

S-Shaped Adsorption Curve. K. W. FLÖROV (*Kolloid-Z.*, 1925, **36**, 215—217).—For reactions yielding a new solid phase of higher solubility product than that of the adsorbent, the initial portion of the adsorption curve is convex to the concentration axis (Pavlov, A., 1924, ii, 594). The complete adsorption curve, however, should be S-shaped. To prove this, the system barium sulphate–potassium chromate has been investigated, with barium sulphate as adsorbent. Three series of measurements, using the reactants in different proportions, gave three curves, all convex in their initial portions. The curve for 0·5 g. of barium sulphate to 100 c.c. of solution has a well-defined maximum. From the results, it is obvious that the reaction is complex, and for strong solutions, the equation $2BaSO_4+K_2CrO_4=BaSO_4,BaCrO_4+K_2SO_4$ is suggested.
L. L. B.

S-Shaped Adsorption Curves and their Calculation. Wo. OSTWALD and H. SCHULZE (*Kolloid-Z.*, 1925, **36**, 289—300).—The adsorption of acetic acid by charcoal from mixtures of acetic acid and water was positive in all cases studied, with a maximum for 15% of acetic acid. Acetic acid was negatively adsorbed from mixtures with ten organic solvents, the effect being most marked for mixtures with ethylene bromide. The adsorption curve throughout the whole range of mixtures of dry acetic acid and ethylene bromide is S-shaped. Up to 15·8% of acetic acid, the

adsorption is positive, and above this point negative. The S-shaped curve is not fitted satisfactorily by any of the equations put forward by Ostwald and de Izaguirre (A., 1922, ii, 480; 1923, ii, 128), but the two separate portions of the curve fitted are accurately reproduced by the simplest of their equations. It is assumed that acetic acid and ethylene bromide form a compound containing 15·8% of acetic acid and that this compound alone is adsorbed, the component in excess behaving only as a solvent. There is some evidence of a eutectic point and of minima in the surface tension and viscosity curves in the neighbourhood of this composition. It is suggested that the point of zero adsorption from binary mixtures may be used to detect compound formation. E. M. C.

Basic Exchange with Salts of Organic Nitrogen Compounds. E. UNGERER (*Kolloid-Z.*, 1925, **36**, 228—235).—The adsorption of salts of organic bases by calcium-permutite has been investigated, and the mechanism of the reaction has been found to depend upon base exchange, which follows the well-known adsorption isotherm. The salts used included the hydrochlorides of guanidine, betaine, methylamine, and aniline, tetramethylammonium iodide, arginine nitrate, and the alkaloids quinine, cinchonine, and strychnine, the alkaloids being dissolved in 94% alcohol to eliminate side-reactions on account of hydrolysis. Natural clay shows a similar behaviour towards the alkaloids. L. L. B.

Evaporation of Water from Clean and Contaminated Surfaces. N. K. ADAM (*J. Physical Chem.*, 1925, **29**, 610—611).—The deductions of Hedestrand (this vol., ii, 102) on the influence of colloidal films on the rate of evaporation of water vapour from water surfaces are inconclusive, since the experiments only measure the rate of escape of water vapour as controlled by the air film existing on the water surface. The results only show that the rate of evaporation in the presence of a colloidal film did not diminish by more than 0·2%. M. B. D.

Metallic Lustre. II. W. D. BANCROFT and R. P. ALLEN (*J. Physical Chem.*, 1925, **29**, 564—586).—When light of sufficient intensity seems to come from a single surface and there are suitable variations of intensity in space or time, metallic lustre is obtained. Substances such as solid dyes, potassium permanganate, etc. which show selective surface reflexion are so opaque for the rays thus reflected that the light comes practically from a single surface. M. B. D.

Unimolecular Films on Water. Oriented Adsorption of Derivatives of Benzene. W. D. HARKINS and E. H. GRAFTON (*J. Amer. Chem. Soc.*, 1925, **47**, 1329—1335).—The areas occupied by the molecules of various hydroxyl derivatives of benzene have been derived from measurements of the surface tensions of aqueous solutions of these substances. The orientation of the molecules on the surface of water is discussed and the various molecular magnitudes are compared with the dimensions obtained for molecules of benzene, naphthalene, and anthracene in the crystalline form. The

molecules of phenol are oriented with the hydroxyl group in the liquid and the phenyl group on edge above it. In the case of quinol both hydroxyl groups are within the liquid whilst the phenylene group remains on the surface. J. S. C.

Effect of Vapours of Some Organic Liquids on the Surface Tension of Water. V. Kořán (*Rec. trav. chim.*, 1925, **44**, 466—475).—The changes in the surface tension of water dropping into the saturated vapours of carbon tetrachloride, light petroleum, toluene, benzene, chloroform, triethylamine, and ethyl ether have been measured and the temperature influences in each case exactly determined. It is found that the surface activity of these vapours is parallel to the interfacial activity of the corresponding organic liquids on water. The results are discussed with reference to the views of Harkins. N. H. H.

Surface Tension of Gelatin Solutions. J. H. S. Johnston and G. H. Peard (*Biochem. J.*, 1925, **19**, 281—289).—There is no quantitative relationship between the surface tension of a colloidal solution and the potential difference between the particles and the medium. The surface tension of gelatin solutions is at a maximum at the isoelectric point p_H 4·7 and again at p_H 2·8—3·0, after which it decreases steadily. The minima are at p_H 3·8—4·0 on the acid side and in the neighbourhood of p_H 9 on the alkaline side. Increase of temperature or addition of electrolytes causes a lowering of surface tension of gelatin solutions. The surface tension of gelatin solutions is little affected by time after equilibrium is attained; this occurs in a few hours at 25°, except in the case of isoelectric gelatin. For such gelatin solutions the surface tension rises to the value for water as flocculation proceeds. S. S. Z.

Sign of the Electrical Layer Furthest away from the Surface of a Solution in Contact with Air or Metal. R. D. Kleeman and C. R. Pitts (*J. Physical Chem.*, 1925, **29**, 508—516).—Small bubbles of air rising up a tube containing a solution of a salt, acid, or alkali produce a fall of potential in the liquid in the tube. The fall of potential is attributed to the peeling off of charges from the electrical double layers associated with the surfaces of the bubbles. A tangential motion given to the liquid near one of the electrodes would tend to peel off the outermost layer of electricity and set up a difference in potential between the electrodes. No simple relations are disclosed. M. B. D.

Influence of Colloidal Solutions on the Electrocapillarity of Mercury. K. Šandera (*Rec. trav. chim.*, 1925, **44**, 480—487).—The influence of various colloids, notably gelatin, glycogen, gum arabic, ferrous hydroxide, starch, arsenious sulphide, mastic, silica, aluminium hydroxide, and fatty acids, on the electrocapillarity of mercury has been investigated by the dropping mercury electrode method of Kučera (*Ann. Physik*, 1903, **11**, 529, 698). The minimum concentration which will affect the electrocapillarity appreciably varies considerably with different colloids. Thus for gelatin it is

0·001%; glycogen, 0·01%; gum arabic, 0·05%; ferrous hydroxide, 0·1%; starch, 0·03%; arsenious sulphide, 0·5%. The effect of change of concentration is demonstrated by the behaviour of gelatin in 0·0862*N*- and 0·137*N*-sulphuric acid. Here the first additions of colloid cause the greatest lowering of interfacial tension and similar results are given with colloidal silica in sodium chloride, but here the maximum of the capillarity curve is raised. The so-called anomalous adsorption was never observed. The influence of the electric charge of the colloids is expressed by the rule that, in general, positive colloids shift the maximum to the more negatively polarising potential and *vice versa*. The displacement of the maximum is influenced by the nature of the electrolyte. This may be due to a change of the electric charge of the colloids by the ions present. With colloidal silica, the order of mixing the solution affects the displacement. Experiments are described which show that the most effective degree of dispersion is intermediate between that of a suspension and molecular dispersion. The influence of positive and negative colloids as contrasted with positive and negative ions is explained by the assumption that the colloid particles have an apparent charge due to the selective adsorption of positive or negative ions which will then surround them by a double layer (of potential ζ). Thus "positive" particles adsorb with preference negative ions. From this it is deduced that the shift of the potentials corresponding with the maxima of the capillarity curves serves as a measure of the adsorption potential (ζ) surrounding the charged particles. N. H. H.

General Structure of Matter in the Colloidal State. I. Form and Chemical Composition of Disperse Particles in Suspensoids and Precipitates. P. P. von Weimarn (*Kolloid-Z.*, 1925, **36**, 237—240).—A *résumé* of the author's views. L. L. B.

Alteration in the Fibre *X*-Ray Spectrogram of Cellulose on Swelling in Concentrated Aqueous Solutions. J. R. Katz and H. Mark (*Z. physikal. Chem.*, 1925, **115**, 385—404).—The swelling of cellulose (ramie) in concentrated solutions of acids, bases, and salts, which is much greater than in pure water (cf. A., 1924, ii, 652), has been studied by means of *X*-ray spectrograms. Swelling in solutions of zinc chloride, calcium thiocyanate, potassium iodide, and potassium iodide with mercuric iodide produced no change in the cellulose lattice. With the two latter solutions, however, the cellulose spectrogram disappeared if the preparations were not washed, but returned on washing. Swelling in nitric and sulphuric acids could not be studied fully owing to the ready solubility of the cellulose. In sufficiently strong solutions of sodium, potassium, and lithium hydroxides, the cellulose diagram gives place to that of a new substance the crystallites of which lie parallel to the fibres. After washing the preparations, both diagrams are observed. Ammoniacal copper oxide solution gives similar results. Concentrated solutions of this and of the alkalis cause an enlargement of the cellulose lattice up to 4%. N. H. H.

Cholesterol and its Esters. II. E. KEESER (*Biochem. Z.*, 1925, **157**, 166—171).—The sols of cholesterol and of its esters confer their stabilising power on the colloid by which they are adsorbed. The nature of the cation in the salts derived from cholesteryl esters (*e.g.*, sodium or potassium salt of cholesteryl sulphuric acid) has a marked influence on the stabilising power of the latter. Methyl, ethyl, propyl, and butyl alcohols all raise the electrical conductivity of the sols of cholesterol and its esters, but as the concentration of the alcohol increases this rise becomes progressively less; in high concentrations of alcohol the conductivity and the dissociation are diminished. The stability of these sols is increased by the addition of alcohol. Addition of carbamide or glycine increases the stability of an arsenic trisulphide or a sulphur sol. H. D. K.

Silicate Solutions and Some Silicious Gels. J. G. VAIL (*J. Soc. Chem. Ind.*, 1925, **44**, 214—219T).—A discussion and correlation of the properties and the uses of silicious gels and sols. The theory that colloidal silica particles always tend to coalesce into larger aggregates and finally to gel, and that whether sols or gels they adsorb positively charged ions on their surface, receives considerable support from observed facts. L. A. C.

Formation of Colloidal Manganese Dioxide in the Reduction of Permanganate by Arsenious Acid. Influence of its Adsorptive Power on the Extent of the Reaction. M. GELOSO (*Bull. Soc. chim.*, 1925, [iv], **37**, 641—656).—The titration of potassium permanganate with sodium arsenite in 0·1*N*-solutions to a green colour gives consistent results within a certain range of concentration of sulphuric acid, the manganese being reduced to a state of oxidation corresponding with Mn_3O_5. In neutral solution or with insufficient acid, a brown turbidity or a yellow coloration is obtained, whilst an excess of acid gives a pink solution, the corresponding states of oxidation of the manganese ranging continuously from MnO_2 through Mn_6O_{11} and Mn_3O_5 to Mn_2O_3. The end-point is similar with certain concentrations of nitric acid but never in presence of tartaric or phosphoric acids. The degree of oxidation of the manganese at the end-point is affected considerably by $Ag^{\cdot}$ ions, less by AsO_4' ions, whilst in presence of $Mn^{\cdot\cdot}$ ions the reduction proceeds quantitatively to MnO_2. The variation in composition of the reduction product with various conditions proves that the formulæ Mn_3O_5 and Mn_6O_{11} do not represent definite compounds, the green liquid being a colloidal solution of MnO_2 with other substances adsorbed. This sol has a wide absorption band extending to 4900 Å., and it polarises the light it scatters. A similar sol is obtainable by adding sulphuric acid to a solution containing permanganate and arsenite and diluting the product. The state of oxidation of the manganese in this solution is found to correspond with MnO_2, and the same is true of the black solid which it deposits on keeping. The latter contains arsenic but not as a definite compound. The composition of the colloid obtained in titration is probably

$n MnO_2MnO$, where n is larger than 2, and the influence of some of the added salts is explained on this assumption. G. M. B.

Is the Solution of Cellulose in Ammoniacal Copper Oxide a Peptisation? E. Baur (*Kolloid-Z.*, 1925, **36**, 257—259).—It is shown from the data of Hess and others (A., 1924, i, 143—148) that the distribution of copper between cellulose and a solution of cellulose in Schweitzer's reagent may be represented by an adsorption equation. E. M. C.

Composition of Solutions of Cellulose in Ammoniacal Copper Oxide. K. Hess and E. Messmer (*Kolloid-Z.*, 1925, **36**, 260—264).—Baur's conclusion (see preceding abstract) that the combination of cellulose with "cuprammonium" is an adsorption process is controverted. No other metal behaves exactly like copper. The reaction is independent of the dispersion of the cellulose over wide ranges. Similar complexes are formed by other carbohydrates, of suitable constitution, which give true solutions. It is shown than an equation based on the mass-action law is more satisfactory for purposes of interpolation than is the one based on the hypothesis of adsorption. E. M. C.

Plasticity of Cellulose in "Cuprammonium Hydroxide." E. K. Carver and H. Folts (*J. Amer. Chem. Soc.*, 1925, **47**, 1430—1434).—An improved form of Bingham and Green's plastometer (*Proc. Am. Soc. Test. Mat.*, 1909, **19**, ii, 640) is described. With this measurements have been made of the plasticity of 0·5—2% solutions of standard cellulose (cf. Gray and Cory, *Ind. Eng. Chem.*, 1924, **16**, 853, 1130), in "cuprammonium hydroxide" solution containing 1·5% of copper and 20·5% of ammonia, by weight, to which 2% of sucrose was added to reduce oxidation. The results obtained confirm those of Joyner (T., 1922, **121**, 1511, 2395). F. G. W.

Cause of Conductivity of Casein Solutions. M. Fischenich and M. Pólányi (*Kolloid-Z.*, 1925, **36**, 275—281; cf. A., 1920, i, 684; Plattner, A., 1923, i, 963).—The diffusion through a membrane of conducting substances from a neutral solution of casein is due neither to bacterial decomposition nor to membrane hydrolysis. On dialysis in collodion membranes the conductivity may fall to one-half without any precipitation of casein. Variations in the conductivity of the outer solutions after dialysis are ascribed to differences in permeability to impurities in the casein. The conductivity is reduced by 20% on dialysis through parchment and the outer liquid contains organic substances which are not casein. Since the addition of gelatin has substantially the same effect on the conductivity of neutral casein solutions when in solution at 25° and as a jelly at 0°, it is concluded that casein ions play no part in the conductivity of neutral casein solutions. E. M. C.

Protein and Potassium Ions. W. E. Ringer (*Z. physiol. Chem.*, 1925, **144**, 85—96).—Electrometric determinations have shown that nucleoprotein prepared from horse-serum combines,

in neutral solution, with potassium ions to a small extent. Euglobulin in potassium chloride solution depresses the activity of the chloride ions but not of the potassium ions; in alkaline solution, it depresses the activity of the potassium ions very slightly. Reduced and oxygenated hæmoglobin in neutral and acid solution exerts no influence on the potassium or chloride ions. It is concluded that, at neutral reaction, water-soluble proteins do not form complex ions, whereas water-insoluble proteins may combine with a small quantity of cations or a larger amount of anions. C. R. H.

Relationship between Ostwald's Viscosity Equation and Poiseuille's Law. K. Matthäus (*Kolloid-Z.*, 1925, **36**, 281—282).—An expression for the viscosity in the turbulent state is derived from Ostwald's equation for colloidal solutions, which do not obey Poiseuille's law. E. M. C.

Influence of Rate of Shear on the Measurement of the Viscosity of Disperse Systems. IV. W. Ostwald (*Kolloid-Z.*, 1925, **36**, 248—250).—The work of a number of investigators in this direction is reviewed. The simple logarithmic relation $Vt^{-1}=kP^n$, formerly applied by de Waele (*J. Oil and Colour Chem. Assoc.*, 1923, **6**, 33) and by Farrow and Lowe (*J. Textile Inst.*, 1923, **14**, 414) to capillary viscosimeter measurements with vaseline and starch paste, has been found by the author and his colleagues to hold for 25 sols when using capillary viscosimeters of varied types, and also when using the Hess or Couette apparatus. L. L. B.

Viscosity and Elasticity of Soap Solutions. H. Freundlich and H. J. Kores (*Kolloid-Z.*, 1925, **36**, 241—243).—Viscosity measurements with the Couette apparatus show that solutions of sodium oleate and dilute solutions of sodium stearate possess no elasticity at the ordinary temperature. On the other hand, a marked elastic effect is shown by a solution of a mixture of the two soaps, in which both are present in about the same concentration as in the measurements with the pure soaps. L. L. B.

Influence of Alcohol on the Viscosity of Blood-serum. K. Hayashi (*Kolloid-Z.*, 1925, **36**, 227).—A repetition of Fürth and Blüh's measurements of the viscosity of blood-serum containing alcohol (*ibid.*, 1924, **34**, 129). Three series of experiments are recorded, using an Ostwald viscosimeter in a water-bath at 20°, and in each case the viscosity rose practically linearly with the alcohol content. The minimum recorded by Fürth and Blüh was not confirmed. L. L. B.

Emulsions. W. Seifriz (*J. Physical Chem.*, 1925, **29**, 587—600).—Emulsions of various paraffin hydrocarbons in water with casein as an emulsifying agent are of the oil-in-water type up to d 0·828 and of the water-in-oil type above 0·860. The intermediate range gives rise to only very unstable emulsions which may be of either type. These results cannot be explained on the oriented molecular wedge hypothesis. The following electrolytes stabilise the oil-in-water emulsions: sodium hydroxide > barium hydroxide >

thorium nitrate > aluminium sulphate > barium chloride > sodium chloride. With the exception of the last two electrolytes, certain of the water-in-oil emulsions can be reversed by them. This effect cannot be ascribed to a lowering of the interfacial surface tension.

M. B. D.

Effect of Added Substances on the Stability of Dispersoids. II. P. P. VON WEIMARN and S. UTZINO (*Kolloid-Z.*, 1925, **36**, 265—274).—The stability of dispersoid sulphur solutions, prepared by grinding sulphur with dextrose, generally increases with the addition of increasing amounts of salts up to a concentration of the order of 0·01 millimol. per litre and decreases for higher concentrations. For chlorides the concentration needed to give maximum stability decreases with the valency of the cation, and the relative increase in stability at the maximum increases with the valency. No increase in stability was found with potassium nitrate. A second region of maximum stability in more concentrated solutions is shown by certain sulphur compounds. This second maximum stability is well marked with potassium thiocyanate (at 10 millimols. per litre) and is also found with calcium thiocyanate and potassium sulphate, but not with sulphuric acid. Attention is directed to a general analogy between the behaviour of sulphur and cellulose.

E. M. C.

Colloid Chemistry of the Vitamin Problem. F.-V. VON HAHN (*Kolloid-Z.*, 1925, **36**, 271—274).—Some 50 foodstuffs of widely different types showed a close agreement between the surface activities of the aqueous extracts or juices and the contents of water-soluble vitamins. With onions, bananas, milk, and egg yolk the surface activities were too high, but much lower values were obtained after ultrafiltration; the majority of the extracts underwent no change on ultrafiltration. The percentage reductions of the surface tension of water for extracts grouped according to their vitamin contents were: nil 0—1·4, low 1·8—9·2, medium 10—17, high 15—26. Marked reductions in surface activity resulted from heating or drying apples and potatoes. In a separation by Funk's method, the fractions rich in vitamin reduced the surface tension by about 25%, whilst the vitamin-free fractions reduced it by 2—4%. It is suggested that the characteristic action of foodstuffs containing vitamins is to be ascribed to an increase in the permeability of the walls of the intestine to colloids and substances of high molecular weight owing to the high surface activity of substances in the vitaminoid state.

E. M. C.

Stability of Colloidal Solutions. III. Coagulation of Copper Ferrocyanide Sol. K. C. SEN (*J. Physical Chem.*, 1925, **29**, 516—539; cf. A., 1924, ii, 830).—A solution of a negatively charged copper ferrocyanide sol prepared from potassium ferrocyanide and copper chloride and subsequent dialysis was found to be normal so far as the Schultze–Hardy law is concerned. When a univalent electrolyte was used for coagulating the sol, the anion was found to exert a considerable effect. Thus, nine times the number

of equivalents of salt were required for coagulation when potassium ferrocyanide was substituted for potassium bromide. The effect of the anion is not so marked with bi- and ter-valent cations. The effect of dilution is to stabilise the sol towards uni- and bi-valent coagulating ions and to make it more sensitive to ter- and quadri-valent ions. The behaviour of potassium chloride was anomalous in that dilution apparently had no effect. This behaviour was found to be due to the presence of a considerable amount of potassium ferrocyanide. Sucrose is without effect when potassium chloride is used as a coagulant, but makes the sol unstable towards barium chloride. Ethyl and propyl alcohols sensitise it towards all coagulating ions. The sol becomes more stable to all electrolytes on keeping, which is probably due to the release of some free ferrocyanide ion by the slow hydrolysis of the colloid, and this stabilises the remaining sol. Potassium ferrocyanide increases the stability of the sol towards potassium chloride and barium chloride to a maximum after which the stability decreases. The antagonistic effect between pairs of salts is due to the stabilising effect of the ions which carry a charge opposite in sign to that of the precipitating ion.

M. B. D.

Stability of Colloidal Solutions. II. Stability of Colloidal Solutions of Chromium Hydroxide and Copper Ferrocyanide in Presence of Stabilising Ions and Coagulation of the Colloids by Mixtures of Electrolytes. K. C. Sen and M. R. Mehrotra (*Z. anorg. Chem.*, 1925, **142**, 345—366).—The stability of chromium hydroxide sols towards potassium sulphate or oxalate is increased by successive additions of hydrochloric acid up to a maximum and is then reduced by further quantities. Mixtures of the two salts, on the other hand, have additive coagulating powers. Similar results are obtained with copper ferrocyanide, with ferrocyanide or alkali as stabiliser and potassium or barium chloride as coagulant. The theory is fully discussed and the conception of antagonistic effects between cations is rejected for the majority of such cases. The ion bearing the same charge as the colloid exerts the preponderating influence. Stabilisation by dilution, or by one of a mixture of electrolytes, and the phenomenon of acclimatisation are related and explicable on the same theory.

L. J. H.

Influence of Wave-length on the Coagulation of a Colloidal Solution by *X*-Rays. A. Dognon (*Compt. rend. Soc. Biol.*, 1924, **91**, 197—199; from *Chem. Zentr.*, 1925, ii, 1447—1448).—The coagulation of a mastic sol, sensitised by sodium chloride, is promoted by exposure to Röntgen rays, the longer waves appearing to effect the coagulation somewhat faster than shorter waves. The energy absorbed by the solution was the same in both cases.

R. B.

Velocity of Coagulation of Antimony Trisulphide. C. K. Jabłczyński and A. Przezdziecka-Jedrzejowska (*Bull. Soc. chim.*, 1925, [iv], **37**, 608—612; cf. this vol., ii, 35).—By the optical method previously described it has been found that the velocity of

coagulation of antimony trisulphide sols, in the presence of small amounts of potassium chloride, is in accordance with Smoluchowski's equation. The stability of the sol is much diminished when the free hydrogen sulphide has been removed by means of a stream of hydrogen. G. M. B.

Velocity of Coagulation of Colloidal Mixtures. C. K. JABŁCZYŃSKI and H. LORENTZ-ZIENKOWSKA (*Bull. Soc. chim.*, 1925, [iv], **37**, 612—615; cf. preceding abstract).—Since the coagulation of mixed sols containing arsenious and antimonious sulphides in various proportions is found to proceed according to the same law found to hold for sols of these two substances separately, the process of coagulation must be a purely physical one. Any selective chemical action would have produced a deviation from the observed relation. G. M. B.

Theory of Peptisation and Protective Effect of Colloids and Non-electrolytes. K. C. SEN (*Kolloid-Z.*, 1925, **36**, 193—202).—The peptisation of hydroxides with acids shows that an adsorption of the acid always precedes colloid formation. In the peptisation of metallic salt solutions and the formation of basic salts, the hydrogen ion is probably the actual peptising agent, the action of the metal ion being of less importance. A consideration of Langmuir's adsorption theory shows that in general an adsorption should occur wherever there is a possibility of chemical action. Experiments are described in support of this theory. The view that only ions and charged colloids can act as peptising agents is emphasised. Neutral molecules and proteins effect the stabilisation of a sol by an adsorption and covering of the colloid particles, such stabilisation being only effective in the presence of electrolytes. Protected colloids in general owe their stability to the Helmholtz double layer, and the protective action of such different substances as glycerol, sucrose, egg-albumin, etc. is probably the same. The behaviour of non-electrolytes and proteins varies slightly, in that the adsorption complex of the former can be easily destroyed, whilst the protein forms a solid surface coating.

The conclusions drawn by Loeb from his work on the protective action of gelatin for collodion particles (cf. A., 1923, ii, 301) are criticised, and the theory of Liesegang's rings is discussed. L. L. B.

Nature of Swelling in Substances giving a Debye–Scherrer Diagram. J. R. KATZ and H. MARK (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 520—528).—The changes taking place in certain colloids during imbibition have been studied by the *X*-ray method. Whereas cellulose, fibroin, and chitin show no change in the lattice during swelling, this is not always the case. With inulin the lattice volume increases by 8—11% when the total volume of the colloid increases by 11½%. Soluble starch probably exhibits similar behaviour. It would therefore seem that imbibition may be either an intermicellar or an intermolecular process according to the nature of the substance. The lattice will only change with the latter type of imbibition. S. B.

Cause of the Characteristic Extensibility of Caoutchouc. Alteration of X-Ray Spectrum of Caoutchouc on Extension. J. R. KATZ (*Kolloid-Z.*, 1925, **36**, 300—307).—Unstretched *Hevea* caoutchouc gives an amorphous *X*-ray spectrogram. Stretched caoutchouc gives in addition a line spectrogram, corresponding with an assemblage of "crystals" arranged with their axes in the direction of the stretching. The relative intensity of the line photogram increases with the stretching and finally the whole of the caoutchouc appears to be in the "crystalline" form. The interferences are confined to a small diffraction angle. The size of the lattice is about 8 Å. in the direction of stretching. The elementary cell is probably smaller in one or more directions than the caoutchouc molecule and possibly corresponds with simple units, such as tri-isoprene. Caoutchouc consists of a crystalline and an amorphous substance, but, since the crystalline interference lines occur only with more than 100% stretching, the early stages in the extensibility must be ascribed to some cause other than the formation of "crystalline" material. E. M. C.

Effect of Drying on Permanently Deformed Gels. E. HATSCHEK (*Kolloid-Z.*, 1925, **36**, 202—206; cf. *ibid.*, 1924, **35**, 67).—Gels in the form of quadratic prisms, made by pouring the sol into paraffined paper moulds and cooling, were subjected to bending or twisting forces, so that they received a permanent deformation. In the case of both bent and twisted prisms, the deformation increased considerably on drying, *e.g.*, in one case the torsion before drying was 62°, and after drying 433°. The question is discussed as to whether the change on drying is a consequence of the preceding deformation, or the characteristic form of the gel. Special moulds for giving an initial bend or twist to gels were prepared, and with these, no increase of deformation occurred on drying. The conclusion is reached that deformation causes some radical change to take place in the gelatin. L. L. B.

Periodic Stratification of Magnesium Hydroxide. K. POPP (*Kolloid-Z.*, 1925, **36**, 208—215).—In order to investigate more thoroughly the nature of Liesegang's layers, the ring-system formed by the interaction of magnesium chloride and ammonia has been qualitatively and quantitatively studied. Which of the two reagents is contained in the gelatin has no essential influence on the banding; in both cases a "clearing" ring appears, and the rings disappear on diffusion of ammonium chloride into the gel. When ammonia diffuses into gelatin containing magnesium chloride, it is found that with decreasing magnesium chloride concentration, the rings increase in number and thickness, whilst the space between them decreases; with decreasing ammonia concentration, the rings decrease in number and thickness, whilst the space between them increases; with decreasing ammonium chloride concentration, the rings increase in number and thickness, whilst the space between them decreases; with decreasing gelatin concentration, both the rings and the space between them increase in thickness, whilst their number remains the same; with falling temperature, both the rings

and the space between them increase in thickness. The rhythmic precipitation occurs in coarsely dispersed colloid and molecular media, such as clay, 0·6% agar, silicic acid, fine sand, and glass beads in water. L. L. B.

Electro-ultrafiltration of Gelatin and Glue. H. Bechhold and A. Rosenberg (*Biochem. Z.*, 1925, **157**, 85—97).—A new method for the purification of colloids by a combination of ultrafiltration and electrodialysis is described in detail. In a relatively short time colloids may be freed almost completely both from electrolytes and dialysable decomposition products. A method of double ultrafiltration combined with electrodialysis, by which liquid is ultrafiltered at both the cathode and the anode of the electrodialyser, permits of the complete removal of salts from gelatin and from glue. By this means a globulin has been separated from glue. H. D. K.

Cataphoresis of Metal Sols in Organic Dispersion Media. F. Evers (*Kolloid-Z.*, 1925, **36**, 206—207).—Phenomena similar to those observed by Hatschek and Thorne (this vol., ii, 197) with nickel sols in benzene, in presence of caoutchouc, were also observed by the author and Harries (*Ber.*, 1923, **56**, 1048) in the case of platinum sols stabilised by caoutchouc. Cataphoresis showed that both positively and negatively charged particles were present in the sol. From the fact that the disperse platinum always separates at the electrode with perhydrocaoutchouc, it is inferred that the platinum in the solution is aggregated with the caoutchouc.
L. L. B.

Theory of Membrane Equilibria. E. Hückel (*Kolloid-Z.*, 1925, **36**, 319—320).—A correction (cf. this vol., ii, 528).
E. M. C.

Direct Measurement of Mean Free Path of Uncharged Silver Atoms in Nitrogen. F. Bielz (*Z. Physik*, 1925, **32**, 81—102).—Silver was heated in a silica tube to a temperature of 1100° and its vapour allowed to pass through an orifice and impinge on glass plates. The thickness of the deposit was measured by an optical method after converting the metal into the iodide. The product of the mean free path in cm. and the pressure of the nitrogen in mm. of mercury was approximately constant = 0·0098. The radius of the silver atom was found to be $1{\cdot}0\times10^{-8}$ cm., an inexplicably small value. E. B. L.

Dissociation of Chlorine. H. von Wartenberg and D. Weigel (*Z. anorg. Chem.*, 1925, **142**, 337—344).—In part polemical against Trautz and Geissler (this vol., ii, 294). The dissociation of chlorine at 1205°, determined by Meyer's method, agrees, within the limits of error, with the values of Henglein (A., 1922, ii, 823) and of Wohl (A., 1924, ii, 600). L. J. H.

Dissociation of Auric Chloride. M. Petit (*Bull. Soc. chim.*, 1925, [iv], **37**, 615—623; cf. Rose, T., 1895, **67**, 881).—The total pressures produced when auric chloride is heated to temperatures

from 100° to 251° have been measured by a static method and the results compared with those of Rose and of Meyer (*Diss.*, Paris, 1912). The dissociation of the trichloride is practically irreversible, but the pressure observations are satisfactory if taken at progressively rising temperatures. An estimate of the vapour pressure of the trichloride is obtained from separate experiments in which the weight of auric chloride volatilised in a known volume is determined. By subtraction of these values of vapour pressure from the total pressures observed the dissociation pressures of auric chloride are obtained. By means of Clapeyron's equation the heat of formation of the trichloride from aurous chloride and chlorine is found at various temperatures: it rises from 16·8 to a maximum of 20·6 between 181° and 202° and then falls to 15·6 large calories between 229° and 251°. The temperature at which the dissociation pressure =760 mm. is calculated to be 249°. G. M. B.

Deduction of the Type of a Two-component System by Means of the Addition of a Third Component. F. A. Freeth (*J. Physical Chem.*, 1925, **29**, 497—507).—The principle of Schreinemakers, that any two solid substances will always yield a characteristic solubility diagram, which is the same in type for every possible liquid used as solvent, provided that the liquid in question does not form compounds with either of them, can be used to differentiate between types of binary systems about which thermal analysis cannot give final evidence. It is suggested that an isothermal of the system water–potassium nitrate–sodium nitrate at about 140° would decide the correct interpretation of the results of Madgin and Briscoe (T., 1923, **123**, 1608, 2914) and those of Hissink (A., 1900, ii, 339). It is improbable that ammonium nitrate and ammonium sulphate form mixed crystals (cf. Perman and Howells, T., 1923, **123**, 2130). An isothermal at 170° with water as a third component would provide the necessary evidence as to the correctness of the assumption. The case of *d*-camphor oxime–*l*-camphor oxime is also discussed. M. B. D.

Properties of Physical Systems in the Neighbourhood of the Critical State. L. Gay and N. Perrakis (*J. Chim. phys.*, 1925, **22**, 169—185).—The authors discuss the critical state for two phases in a system of any degree of complexity. Application of the phase rule shows that if n is the number of degrees of freedom of the system, and if $(n-1)$ independent variables are fixed, then any two properties of the two phases considered can be represented as a function of the nth variable by a single curve. When one of the phases disappears the properties are represented by a surface. The authors show that by suitable numerical representation it is always possible to define this equilibrium curve. When variations imposed on a physical system cause it to pass through the critical state, a decrease in the number of phases is not indicated unless the properties studied concern one of these two phases. The authors investigate the modes of numerical representation so that the critical curve around the critical point

is fairly straight and of appreciable length. The conditions for this desideratum are given. W. T.

System Chloride–Sulphate–Sodium–Water. A. J. PELLING (*J. S. Afr. Chem. Inst.*, 1925, **8**, 3—6).—The 94·5° isotherm, and extra data for the 0° isotherm of this system are given, and the invariant solution at 94·5° is determined. B. F.

Free Energy and Heat Content of Tellurium Dioxide and of Amorphous and Metallic Tellurium. Reduction Potential of Tellurium. R. SCHUMANN (*J. Amer. Chem. Soc.*, 1925, **47**, 356—362).—Cells of the type $Te(s)+TeO_2(s)|HClO_4(0{\cdot}10—0{\cdot}74N)|H_2$ (1 atm.) have an *E.M.F.* of −0·5286 at 25° and −0·5213 at 45°. The free energy of formation of tellurium dioxide is −64,320 cal. and its heat of formation is 77,700 cal. at 25°. The amorphous and metallic forms of tellurium have identical electrometric properties. The amount of tellurium dissolved is proportional to the activity of the hydrogen ion in solution so it must be present as a univalent positive ion, perhaps $Te(OH)_3^{\cdot}$ or $TeO(OH)^{\cdot}$. The molal reduction potential of tellurium corresponding with $Te(s)+2H_2O=TeO(OH)^{\cdot}+3H^{\cdot}+4\ominus$ is −0·5590 volt. L. J. H.

Law of Volatility. C. MATIGNON (*Bull. Soc. chim.*, 1925 [iv], **37**, 503—513; cf. Matignon, A., 1908, ii, 465).—The superiority of carbon as a reducing agent, compared with silicon, is attributed to the volatility of carbon monoxide and dioxide. If the reduction of a metallic oxide is written in the form $MO+C=CO+M-Q$ cal., the free energy of the reduction process is given by the relation $A=8T(\log T+2{\cdot}05)-Q$, and reduction will occur as soon as the temperature is sufficiently high to give a positive value to A. In cases in which both initial and final systems contain volatile substances, the same considerations apply, each volatile molecule in the initial system being counterbalanced by a gaseous molecule in the final system, and the volatility being measured by the difference in the number of gaseous molecules in the initial and final systems. W. H.-R.

Reactivity in the Solid State between Acidic and Basic Metal Oxides. F. DE CARLI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 533—537; cf. A., 1924, ii, 758).—Heating curves were determined for equimolecular mixtures of basic and acidic oxides. For the mixture MoO_3–BaO reaction began at 290°, the temperature rising to 1200° in 25 sec., and a white friable mass resulting. The thermal effects in the following cases were much weaker and occurred at the temperatures indicated. MoO_3–CaO 650°; MoO_3–PbO 650°; MoO_3–SnO 400°; MoO_3–CdO about 500°; MoO_3–NiO about 495°; MoO_3–CoO 410°; MoO_3–ZnO 270°, and a weaker effect at 720°; MoO_3–MgO no reaction. WO_3–BaO 190°; WO_3–CaO 245°; WO_3–PbO 210°; WO_3–SnO 265°; WO_3–CdO 250°; WO_3–NiO 260°; WO_3–CoO 255°; V_2O_5–BaO 270°; V_2O_5–CaO 630°; V_2O_5–PbO about 560°; V_2O_5–CdO 480°; V_2O_5–SnO 250°; V_2O_5–ZnO 260°; V_2O_5–MgO 455°; Cr_2O_3–BaO 220°; Cr_2O_3–

CaO about 550°. Tin dioxide, bismuth trioxide, lead dioxide, and alumina react only with barium oxide. F. G. T.

Behaviour of Clays, Bauxites, etc. on Heating. III. H. S. HOULDSWORTH and J. W. COBB (*Trans. Ceram. Soc.*, 1923—1924, **23**, 279—292).—The shrinkage of clays is not a continuous process but takes place in a number of stages, each stage being completed at a definite temperature. The shrinkages of considerable magnitude occur at almost the same temperatures with the different clays, *i.e.*, 530°, 880°, 950°, and 1030—1060°. Changes in density and in refractive index of kaolinite also occur at these temperatures. The temperatures of appreciable dehydration of kaolin and fireclays (420—450°) and other minerals were determined on heating slowly. These temperatures were raised considerably (80° or more) when reached rapidly. The shrinkage of kaolin at 530° is associated with its dehydration. Kaolin and fireclays show a distinct heat absorption at 500—530° and a heat evolution at 950°. Pure alumina, prepared by calcining the nitrate, gives an exothermic reaction at 1060° and red bauxite at 1000°. Thermal changes are shown by many of the other substances examined. Except in the case of cyanite and biotite, all the endothermic reactions occur at the same temperatures as those at which a loss in weight begins when the materials are heated under similar conditions. None of the indications of exothermic and endothermic reactions with clays can be attributed to the presence of small quantities of impurities. The change responsible for the exothermic effect at 950° with clays could be completed on continued heating at 900°, and that causing the evolution of heat at 1060° with alumina could be completed by a similar heating at 950°. No evolution of heat at 950° was detected when mixtures of alumina and silica of composition $Al_2O_3+2SiO_2$ were heated, or when mixtures of the composition Al_2O_3,SiO_2+SiO_2, prepared from sillimanite, cyanite, andalusite, or allophane, and silica, were heated. The changes observed on heating clays may be due both to changes in the chemical constitution of the molecules of the clay and to a rearrangement of those groups of molecules which form the unit of crystal structure of the clay. [Cf. *B.*, 1925, 500.] H. S. H.

Measurement of Very High Electrolyte Resistances by Kohlrausch's Method. H. ULICH (*Z. physikal. Chem.*, 1925 **115**, 377—384).—An improved form of the Kohlrausch apparatus is described, in which a thermionic valve is used as a source of alternating current. The arrangement permits of the measurement of resistances of the order 10^5 ohms as easily and accurately as those of 100 to 1000 ohms. N. H. H.

Trustworthiness of the Quinhydrone Electrode for the Measurement of Hydrogen-ion Concentration in Various Solutions. I. M. KOLTHOFF (*Z. physiol. Chem.*, 1925, **144**, 259—271).—Comparison of the results of p_H determinations of a large number of solutions by means of the quinhydrone and hydrogen

electrodes indicates that, in protein-free solutions, the former gives excellent results if the liquid is well buffered and has $p_H < 9$. In weakly buffered solutions the limiting p_H is displaced towards the acid side. In all cases, good results are obtained at 18° with $p_H < 8$. In acid and in weakly buffered solutions, good results are obtained by application of Biilmann's equation. Error due to the presence of proteins is dependent on the kind and concentration of the protein and on the p_H; the more alkaline the solution, the greater the disturbance and the less constant the results. In agreement with Lester (*J. Agric. Sci.*, 1924, **14**, 634), the author finds that the electrode can be used for the determination of the p_H of milk, cream, and whey. The p_H of saliva can be obtained providing it is not distinctly alkaline; the error for blood-serum at $p_H > 6$ is large but for diluted blood-serum it is much smaller. P. W. C.

Solvation of Ions and the Electrode Potential. J. Heyrovský (*Rec. trav. chim.*, 1925, **44**, 447—450).—Some consequences of the author's solvation formula for electrode potential (cf. this vol., ii, 544) are worked out. It is shown that for a concentration cell with electrodes of a univalent metal in N- and $3N$-aqueous solutions of its binary salt the *E.M.F.* should be 10—12 millivolts greater than that calculated from the Nernst formula. In this and similar deductions it is assumed that the ions do not form complex anions which would lower their "activity" considerably. From the formula the abnormal "activity" should increase proportionally with the molecular weight of the solvent. N. H. H.

Abnormal Ionic Activities in Concentrated Alkoxide Solutions. Z. Kontníková and M. Shikata (*Rec. trav. chim.*, 1925, **44**, 451—458).—In order to test the deductions of Heyrovský from his formula for electrode potential (see preceding abstract) the authors have measured the *E.M.F.* of concentration cells having sodium or potassium amalgam electrodes in solutions of the corresponding alkoxides in ethyl and in *iso*amyl alcohols. With dilute solutions the cells give values corresponding with the Nernst logarithmic formula, but with concentrations greater than about $1{\cdot}8N$ with ethyl alcohol and $0{\cdot}8N$ with *iso*amyl alcohol they show abnormal ionic activity (greater in the latter case) in agreement with Heyrovský's formula. Concentrated sodium *iso*amyloxide solutions exhibit a peculiar slow decrease of activity.
N. H. H.

Conditions Affecting the Reproducibility and Constancy of Weston Standard Cells. W. C. Vosburgh (*J. Amer. Chem. Soc.*, 1925, **47**, 1255—1267).—The presence of small amounts of acid in the electrolytes does not appreciably affect the *E.M.F.* and tends to make the cells more reproducible and less liable to vary. All mercuric salts must be completely removed from the mercurous sulphate, which should not be exposed to air after purification. Abnormalities result from the presence of basic mercurous sulphate. J. S. C.

Thermodynamic Potential Difference at the Boundary of Two Liquid Phases. S. WOSNESSENSKY (*Z. physikal. Chem.*, 1925, **115**, 405—423).—Measurements have been made with cells of the types *N*-calomel electrode|aqueous solution *A*|non-aqueous solution|aqueous solution *B*|*N*-calomel electrode, and *N*-calomel electrode|aqueous solution|non-aqueous solution|*N*-calomel electrode. Solutions of the following electrolytes at different concentrations were used: potassium chloride, lithium chloride, picric acid, potassium thiocyanate, ammonium thiocyanate, potassium iodide, salicylic acid, calcium chloride, nitric acid, hydrochloric acid, acetic acid, succinic acid, sodium sulphate, phosphoric acid, citric acid, sulphuric acid. The non-aqueous solvent was usually *iso*amyl alcohol, but in a few cases this was replaced by phenol. The values for the *E.M.F.* can be calculated from the distribution formula $C_1/C_2^n=k$. When $n=1$ the *E.M.F.* should become zero. The experimental results support this assumption. N. H. H.

Formation of Mixed Electrodes at Phase Boundaries. K. HOROVITZ (*Z. physikal. Chem.*, 1925, **115**, 424—432).—The results obtained by the author and his co-workers for the boundary potential between glass and aqueous solutions are given in brief and a reply is made to the criticism of Gross and Halpern (this vol., ii, 405). N. H. H.

Polarisation Capacity and Electrical Double Layers. A. L. CLARK (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 275—292).—Experiments have been carried out to determine whether the Helmholtz double layer actually exists and to ascertain the cause of the variations in capacity of polarised surfaces when charged to varying potential differences. Cells were made by immersing a large electrode of mercury, platinum, platinum-black, gold, tungsten, lead, or carbon in an electrolyte solution and then inserting a small electrode of the same substance. Capacities were determined by the direct and oscillation period methods, the values determined by the latter method being usually much smaller than those determined directly. Neither the concentration of the electrolyte (except in very dilute solutions, when the capacity appears to increase) nor the distance between the electrodes over a range extending down to 0·01 mm. has much effect. The capacity is practically unchanged when potassium hydroxide is substituted for sulphuric acid as dissolved electrolyte. The results are discussed and are shown to afford support for the reality of the Helmholtz double layer. J. S. C.

Recent Studies on Reversible Oxidation-Reduction in Organic Systems. M. CLARK (*Chem. Reviews*, 1925, **2**, 127—178).

Dropping Mercury Cathode. I. J. HEYROVSKÝ (*Rec. trav. chim.*, 1925, **44**, 488—495).—An introduction to and review of experimental work by the author and his collaborators (cf.

following abstracts). The process at the dropping mercury cathode may consist (1) in the deposition of cations or (2) in the reduction of any substance capable of being chemically reduced. In (1), the dropping mercury cathode "deposition potential" series differs from the reversible "electrolytic potential" series owing to differences in the affinities of the metals for mercury, but in (2), the "reduction potential" series of reducible ions must run strictly parallel to the series of "reduction electrode-potentials" as measured under similar conditions by a platinum electrode, since the electrode material does not enter into consideration. The characteristics of the polarisation curves are turning points indicating sudden increases in current due to decomposition of the electrolyte. Theory shows that these turning points are not sharp, but that the current–voltage curve is exponential; for comparison the critical point is taken as that at which the tangent to the curve has an angle of 45° to the axes. If the concentration of a reducible substance is less than 10^{-4} g.-equiv./litre, the polarisation curve after rising becomes horizontal again and the current remains constant until the potential of a new reduction is reached. This "wave" type of curve, due to the exhaustion of reducible matter surrounding a drop, is characteristic of a concentration of about 10^{-4}, becomes less with increasing dilution, and vanishes at about 10^{-6} g.-equiv./litre. In the presence of nitrobenzene the polarisation curve exhibits a maximum owing to adsorption phenomena (cf. Shikata, this vol., ii, 304). Strongly oxidising anions have little effect on processes at the dropping cathode, owing to their repulsion from the cathode, but less stable anions, such as zincates, plumbites, and certain metal cyanides, are decomposed at a certain potential into their components and the metallic ion is immediately deposited on the cathode. Owing to periodic change of surface during drop formation, the galvanometer usually oscillates and the form of the oscillation is characteristic of the process, a large oscillation corresponding with a reduction process or evolution of hydrogen, whilst a small oscillation accompanies amalgam formation. The deposition potential of a particular metal becomes more negative as the solution is diluted, a tenfold dilution causing a change of about 57, 26, and 18 millivolts for uni-, bi-, and ter-valent cations, respectively, and marked deviations from these numbers indicate the presence of complex ions or other complicating factors.

W. H.-R.

Dropping Mercury Cathode. II. The Polarograph. J. Heyrovský and M. Shikata (*Rec. trav. chim.*, 1925, **44**, 496—498).—A description of an instrument for recording photographically the polarisation curves from a dropping mercury cathode. The potential across the cell is gradually increased by the motion of a wheel contact along a resistance wire mounted on a rotating drum. A second rotating drum carries a photographic film on which the curve is traced by light from a mirror-galvanometer.

W. H.-R.

Dropping Mercury Cathode. III. Theory of Over-potential. J. HEYROVSKÝ (*Rec. trav. chim.*, 1925, **44**, 499—502).—Hydrogen over-potential is connected with the catalytic influence of different metals upon the combination of hydrogen atoms into molecules. If the combination proceeds according to the scheme (1) $2H \longrightarrow H_2$, theory shows that when the hydrogen-ion concentration changes from c_1 to c_2, the deposition bend in the current–voltage curve should be displaced by $\pi-\pi'=(RT/F)\log c/c'$, by 58 millivolts for a tenfold dilution, which is exactly one-half the actual displacement in the case of the mercury dropping cathode. This discrepancy can be accounted for if it is assumed that some of the hydrogen ions deposited unite with electrons at the cathode to form negative ions, and that the hydrogen molecules are produced, by the union of positive and negative ions at the mercury surface according to the scheme (2) $H^+ + H' \longrightarrow H_2$, for which $\pi-\pi'=2(RT/F)\log c_1/c_2$. This theory applies only to metals with high over-potentials for which the velocity of reaction (2) is greater than that of reaction (1). W. H.-R.

Dropping Mercury Cathode. IV. Changes in Overvoltage with the Concentration of Hydrogen Ions. P. HERASYMENKO (*Rec. trav. chim.*, 1925, **44**, 503—513).—Using the dropping mercury cathode the hydrogen deposition potential has been determined at 16—18° in solutions of hydrochloric, sulphuric, acetic, propionic, boric, and carbonic acids, and in solutions of hydrogen sulphide, and buffer solutions of acetic and propionic acids, the hydrogen-ion concentration being calculated from the dissociation constants. There is close agreement between the observed results and those calculated by means of the formula

$$\pi_1-\pi_2=2(RT/F)\log c_1/c_2,$$

where π_1 and π_2 are the potentials for concentrations of hydrogen ions c_1 and c_2 (cf. Heyrovský, preceding abstract). In order to maintain an approximately equal conductance, the acids used were diluted by a 0·1*N*-potassium chloride solution. The dropping mercury cathode can therefore be used as an indicator for hydrogen ions, the value of the deposition potential of hydrogen changing regularly with the concentration of hydrogen ions. In this way the dissociation constants of hydrogen sulphide, boric acid, and carbonic acid in the presence of potassium chloride have been determined. The work of Glasstone (this vol., ii, 43, 133) is criticised, and the change in overvoltage produced by the addition of sodium sulphate to sulphuric acid solutions is regarded as due to the change in concentration of hydrogen ions owing to the formation of the acid sulphate complex. W. H.-R.

Dropping Mercury Cathode. V. Deposition of Arsenic, Antimony, and Bismuth. V. BAYERLE (*Rec. trav. chim.*, 1925, **44**, 514—519).—The cathodic deposition of arsenic at the dropping mercury cathode is complex in both acid and alkaline solutions, and does not show reversible shifts on the polarisation curves. From acid solutions the deposition of antimony and bismuth proceeds reversibly, the normal deposition potentials (relative to

the calomel electrode) being −0·038 and 0·0 volt, respectively. In alkaline solution the deposition of bismuth resembles metallic deposition from zincates or plumbates, in accordance with the distinctly metallic nature of bismuth, and in contrast with the more complicated results for arsenic and antimony. The solubility products of antimony and bismuth hydroxides are determined as: $[Sb'''][OH']^3=4\times10^{-42}$, and $[Bi'''][OH']^3=4\cdot3\times10^{-31}$.

W. H.-R.

Dropping Mercury Cathode. VI. Electro-deposition of Manganese and the Complexity of Manganous Ions in Ammoniacal Solutions. J. Březina (*Rec. trav. chim.*, 1925, **44**, 520—527).—From neutral or acid solutions of manganous chloride, the electro-deposition of manganese at the dropping cathode proceeds reversibly, the deposition potential from a molar solution being −1·326 volts relative to the normal calomel electrode. The polarisation curves permit the detection of manganous salts in solution down to 10^{-6} g.-mol./litre. The deposition potential becomes more negative in the presence of ammonia owing to the formation of complex cations; this fact is also indicated by cryoscopic measurements. W. H.-R.

Dropping Mercury Cathode. VII. Nickel and Cobalt. N. V. Emelianova (*Rec. trav. chim.*, 1925, **44**, 528—548).—Nickel is not deposited reversibly at the dropping mercury cathode. The turning points on the polarisation curves are abnormally displaced by dilution, and the primary process consists in the reduction of nickel from the bivalent to the univalent state. In neutral or acid solutions this is followed by the deposition of metallic nickel; the deposition potential is much affected by the presence of other salts and of hydrogen ions, and is rendered more negative by the addition of ammonia owing to the formation of complex ions, although very small quantities of ammonia render it more positive. In excess of potassium cyanide nickel salts do not deposit metallic nickel but are only reduced to the univalent nickel complex cyanide. Neutral or acid solutions of pink cobalt chloride deposit cobalt at a potential 0·200 volt more negative than nickel, but abnormal dilution effects are again observed. A solution of the blue chloride in concentrated calcium chloride solution deposits cobalt at a more positive potential than the pink solution, indicating that the blue ions are the more active and are dehydrated. Ammonia renders the deposition potential more negative. From complex cyanides cobalt is not deposited but reduction to the bivalent complex takes place. In meteoric iron, copper, nickel, and cobalt may be detected and roughly determined by observing the deposition potentials at the dropping cathode from solutions of known concentration in hydrochloric acid. W. H.-R.

Dropping Mercury Cathode. VIII. Electrolysis of Some Complex Cyanides. E. B. Sanigar (*Rec. trav. chim.*, 1925, **44**, 549—579).—Iron is not deposited on the dropping mercury cathode from solutions of potassium ferrocyanide at potentials of 0 to

−2 volts relative to the calomel electrode. This indicates that even in the most dilute solutions of ferrocyanides the concentration of ferrous ions is less than 10^{-40} g.-equiv./litre.

Silver is deposited on the dropping cathode from solutions of potassium argenticyanide at a potential of −0·235 volt relative to the calomel electrode. This potential is independent of the concentration of the solution, since the complex $Ag(CN)_2'$ ionises first to AgCN+CN', and only a very small fraction of the molecular AgCN dissociates into Ag^+ and CN' ions, so that the concentration of silver ions is always constant. The corresponding normal deposition potential is +0·485 volt. With increasing voltage the deposition increases rapidly to a maximum intensity which is followed by a sharp fall, after which silver is still deposited until a potential of −1·9 volts is reached, at which potassium begins to be deposited. Similar maxima are met with in the case of auricyanide solutions, and are caused by the adsorption of AgCN' complexes on the surface of the mercury. This absorption becomes less as the potential of the cathodes becomes more negative and finally desorption occurs owing to the electrostatic repulsion. The polarisation curve develops a maximum or a distinct displacement according to the relative magnitudes of the adsorption and desorption processes. W. H.-R.

Dropping Mercury Cathode. IX. Tin. J. Smrz S. J. (*Rec. trav. chim.*, 1925, **44**, 580—590).—Tin is deposited reversibly on the dropping cathode from freshly prepared acidic solutions of stannous chloride, the normal deposition potential being −0·285 volt relative to the calomel electrode. The presence of tin can be detected down to 10^{-6} mole/litre, but on keeping dilute solutions hydrolysis occurs and the wave in the polarisation curve disappears. From freshly-prepared alkali stannite solutions tin is deposited reversibly; a $4\times10^{-4}M$ stannite solution deposits tin at −1·10 and −1·05 volts from N and 0·1N-sodium hydroxide solutions, respectively. On keeping, these solutions are unstable owing to the formation of colloidal stannous hydroxide and to partial auto-oxidation of stannite to stannate. In normal sodium hydroxide solution, the solubility product $[Sn^{\cdot\cdot}][OH']^2$=about 10^{-28}; the acidic solubility product of stannous hydroxide, $[SnO_2H'][H^{\cdot}]=6\times10^{-18}$; the constant for the formation of the complex anion $K_A=[Sn(OH)'_3]/[Sn^{\cdot\cdot}][OH']^3=4\times10^{24}$. Of the hydroxides of lead, zinc, and tin, lead hydroxide is the strongest and stannous hydroxide the weakest, the acidic order being the reverse. W. H.-R.

Dropping Mercury Cathode. X. Some Organic Bases. W. Podroužek (*Rec. trav. chim.*, 1925, **44**, 590—599).—The polarisation curves for solutions of tetramethyl- and tetraethylammonium iodides in the presence of lithium chloride indicate that the organic radicals are deposited reversibly on the dropping cathode, the deposition character being that of an amalgam formation. The normal deposition potentials relative to the calomel electrode are −1·880 and −1·936 volts for the tetramethyl and tetraethyl radicals, respectively. In solutions containing lithium

chloride, quinine is reduced at the dropping cathode, the potential depending on the concentration of hydrogen ions. The polarisation curves show a maximum owing to adsorption (cf. Sanigar, this vol., ii, 676), this effect being detected down to a concentration of 10^{-6} mol. of quinine per litre. W. H.-R.

Dropping Mercury Cathode. XI. Influence of Anions. B. A. Gosman (*Rec. trav. chim.*, 1925, **44**, 600—607).—In solutions of potassium nitrate or chlorate, a sufficiently negative polarisation causes reduction of the anion to take place at the dropping mercury cathode. The mechanism of the process is obscure and the potentials vary greatly with the acidity. In neutral solutions, nitrates do not interfere with the deposition of metals when the *P.D.* is less than −1·45 volts, whilst, if present in small quantities only, neither nitrates nor chlorates interfere with the cathodic deposition of even the most positive metals. Sulphates are quite without effect on cathodic deposition.

The polarisation curves for saturated solutions of lead sulphate show that increased solubility takes place in the presence of sulphuric acid owing to the formation of complex anions.

W. H.-R.

Electrokinetic Phenomenon. Electrocapillarity of Fused Tellurium Dioxide. A. Šimek and (Miss) H. Kadlcova (*Rec. trav. chim.*, 1925, **44**, 608—628).—Drops of fused tellurium dioxide on a platinum surface heated by a direct current at 800—950°, move from the negative to the positive pole. The movement is accompanied by a deformation of the drops, the curvature of the side facing the negative pole being less than that of the other side. Under given conditions, the velocity increases as the drops become larger, but does so less rapidly than the weight of the drops. The velocity of movement and the force by which the drops are driven are both roughly proportional to the current intensity up to a certain limit. Numerous other substances, including selenium dioxide, were examined, but in the pure state did not show the above phenomenon. If tellurium dioxide is added to drops of fused sodium sulphate, chloride, tungstate, or pyrophosphate, the previously flattened drops become much more spherical and, under the influence of a direct current, move more rapidly than pure tellurium dioxide, a velocity of 16 cm./sec. being sometimes attained. The direction of motion depends on the concentration of tellurium dioxide and may be reversed as the latter gradually evaporates. The phenomenon is due to changes of interfacial tension caused by potential differences. W. H.-R.

Electrolysis of Molten Alloys. VI. Copper Alloys (Cu–Zn, Cu–Sn, Cu–Ag, Cu–Al). R. Kremann and R. Gruber-Rehenburg (*Monatsh.*, 1924, **45**, 311—322; cf. this vol., ii, 132).—The interference of zinc oxide in the case of a brass, and of gas bubbles in the case of copper–silver alloys made observations with these alloys impossible. When a copper–tin alloy containing 58% of copper was placed in a fireclay capillary (diameter about 1·5 mm.)

and an electric current passed at 950° for 1·5 to 4 hrs. the change of concentration could scarcely be detected with a current density of 2 amp./mm.^{2}, and was not very marked at 6·9 amp./mm.^{2}, when the more conducting metal, copper, moved towards the anode, the highest difference of concentration between anode and cathode material being 3%. This observation is exceptional, as the better conducting metal usually moves to the cathode. A copper–aluminium alloy treated in the same way at 1050° for 2—4 hrs. showed a continuously increasing concentration of copper at the cathode as the current density was raised to 13·2 amp./mm.^{2}, the excess of copper reaching the value 4%. The electrodes were formed by air cooling the ends of the tubes and so keeping some alloy solid. G. M. B.

Electrolysis of Molten Alloys. VII. Silver–Lead Alloys. R. KREMANN and O. BENDA (*Monatsh.*, 1924, **45**, 339—343).—Electrolysis of a silver–lead alloy containing 50% of lead at 1000°, with iron electrodes, for 4 hrs. showed a migration of silver to the cathode and of lead to the anode which increased in extent up to a current density of 13·2 amp./mm.^{2} without showing sign of attaining a maximum. Differences of composition of 4—5% were observed and the results were not affected when the length of the capillary was increased from 20 to 30 cm. The effects observed here and with the copper–aluminium alloys (cf. preceding abstract) are small compared with those obtained in the electrolysis of alloys of low melting point at similar current densities, the difference being attributed to the greater relative effect of diffusion of the metals at these higher temperatures. G. M. B.

Electrolysis of Molten Alloys. VIII. Tin–Zinc Alloys. R. KREMANN and O. BAUKOVAC (*Monatsh.*, 1925, **45**, 379—383).—The passage of an electric current for 4 hrs. at 400° through a tin–zinc alloy between iron electrodes caused movement of the more highly conducting metal, zinc, towards the cathode. The difference in concentration produced increased to 11·7% of tin when the current density was raised to 12·3 amp./mm.^{2} and would reach a maximum at about 25—30 amp./mm.^{2} Observations on alloys of varying composition showed the effect to be greatest for an alloy containing 50 atoms % of tin. G. M. B.

Electrolysis of Molten Alloys. IX. Tin–Aluminium Alloys. R. KREMANN and J. DELLACHER (*Monatsh.*, 1924, **45**, 385—391).—Electrolysis of a tin–aluminium alloy containing 58·5 atomic-% of tin, for 4 hrs. at 800° causes an increase of concentration of tin at the anode and of aluminium at the cathode, the largest difference of concentration of tin produced being 8% for a current density of 12·3 amp./mm.^{2} The effect appears to reach a maximum near this point. Variation of the initial composition of the alloy shows that the effect is greatest with 50 atomic-% of tin. The results at a chosen current density (8·3 amp./mm.^{2}) are practically the same at 800°, 1200°, 1400°, and 1600°, so that the differences with alloys of high and low melting point depend more on the character of the individual metals than on the temperature. G. M. B.

Action of Gelatin on Electrolytic Cadmium. E. Milliau (*Bull. Soc. chim. Belg.*, 1925, **34**, 143).—Attention is directed to the fact that addition of gelatin or other colloids to electrolytes consisting of solutions of metallic salts of weak acids, such as acetic acid, does not result in the formation of smooth metallic deposits; such deposits are obtained only from solutions of salts of strong acids, such as sulphates, fluosilicates, or fluoborates. A. R. P.

Periodic Electrochemical Phenomena. E. S. Hedges and J. E. Myers (*J. Chem. Soc.*, 1925, **127**, 1013—1026).—Some periodic reactions previously described by the authors (A., 1924, ii, 325, 542) have now been examined electrochemically, using an apparatus in which the electrical and chemical effects of the reactions could be registered simultaneously. In the case of activated metallic couples dissolving in hydrochloric acid or ammonium chloride, the potential difference between the couple and the solution, and between the two components of the couple, undergoes periodic fluctuations which synchronise with the periodic evolution of gas. A potential difference exists between the activated and inactive forms of a metal. Some new reactions, involving the periodic deposition of metals, are described. The change consists in an alternate formation and dissolution of a metallic film which is accompanied by a corresponding oscillation of the electro potential. When magnesium dissolves in dilute hydrochloric acid containing ferrous sulphate in solution, hydrogen is evolved continuously, but in other cases—*e.g.*, when magnesium dissolves in 2% ammonium chloride solution with addition of small quantities of cobalt chloride, ferrous sulphate, nickel chloride, or copper sulphate—the rate of evolution of hydrogen is periodic. Examples are given of "auto-periodic" reactions, in which the dissolving metal is also the activating agent. Copper, when activated by cold rolling, and dissolved in a mixture of nitric and hydrochloric acids, furnishes very regular waves representing both the potential and the pressure of the evolved gas. The best results are obtained with an acid made by mixing 25 c.c. of nitric acid (*d* 1·42), 10 c.c. of hydrochloric acid (*d* 1·16), and 70 c.c. of water. L. L. B.

Behaviour of Silver Iodide in the Photo-voltaic Cell. T. S. Price (*J. Physical Chem.*, 1925, **29**, 557—563).—Polemical against Garrison, A., 1924, ii, 401. The increased negative potential due to the photo-effect cannot be explained by increased solubility of silver iodide in light. A possible explanation is that colloidal silver formed on the decomposition of silver iodide has a higher solution pressure than massive silver. M. B. D.

Technique for Measuring the Hydrogen-ion Concentration of Distilled Water and Unbuffered Solutions not in Equilibrium with the Carbon Dioxide of the Air. L. E. Dawson (*J. Physical Chem.*, 1925, **29**, 551—556).—The p_H value of distilled water, using bromothymol-blue and bromocresol-purple as indicators, has been found to be 7·0. The water was prepared by distilling two-thirds of its volume of distilled water in a "pyrex"

glass flask and using the residual third. Great care must be taken to exclude carbon dioxide when the water is being withdrawn from the container or a more acid value will be obtained.

M. B. D.

Theory of the Velocity of Chemical Reactions. J. N. BRÖNSTED (*Z. physikal. Chem.*, 1925, **115**, 337—364).—A more precise treatment of the author's theory of reaction velocity in solution (A., 1922, ii, 699) is presented. The objection of Bjerrum (A., 1924, ii, 240) to the deduction of the formula depends partly on misunderstanding and partly, as does his "concentration hypothesis," on views relative to reaction velocity and equilibrium which are not generally acceptable. The theory of Christiansen (this vol., ii, 47) is also discussed. It appears possible to develop the author's theory in such a way that the reaction constant can be resolved into two factors one of which depends on the reaction and the other on the solvent. N. H. H.

Effect of Diffusion on Time Rate of Chemical Change. S. SANO (*Japan. J. Phys.*, 1924, **3**, 133—137).—A theoretical discussion of the effect of diffusion on the rate of chemical change.

S. B.

Time Rates of Vaporisation and Chemical Changes on Surface of Contact of Two Fluids. S. SANO (*Japan. J. Phys.*, 1924, **3**, 117—131).—On the basis of several thermodynamical assumptions, the author obtains expressions for the rates of vaporisation and the chemical reactions on the surface of separation of two fluids. S. B.

Rate of Oxidation of Nitric Oxide. I. Method of Measuring the Velocity of a Rapid Gaseous Reaction. M. LATSHAW and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1925, **47**, 1201—1207).—An apparatus suitable for the study of the kinetics of rapid gas reactions is described in which the pressure changes (as indicated in the present instance by a 1-bromonaphthalene manometer) are recorded on a photographic film mounted on the drum of a kymograph. J. S. C.

Rate of Oxidation of Nitric Oxide. II. Velocity of the Reaction between Nitric Oxide and Oxygen at 0° and 30°. R. L. HASCHE and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1925, **47**, 1207—1215).—Using the apparatus and experimental procedure described in the preceding abstract, the experimental numbers obtained in a study of the oxidation of nitric oxide by oxygen at 30° are in good agreement with the assumption of a reaction of the third order. The acceleration in the velocity coefficients at 0° is ascribed to the formation of nitrogen trioxide and also to the imperfect state of nitrogen tetroxide at temperatures so close to its b. p. Increase of the surface : volume ratio by the introduction of glass wool into the reaction vessel caused a marked acceleration in the third-order velocity expression in the latter half of the reaction at 30°, the effect being less pronounced at 0°.

No evidence of autocatalysis was found. The negative temperature coefficient of the reaction is due to intermediate compound formation. J. S. C.

Initial Rate of Decomposition of Nitrogen Pentoxide. E. C. WHITE and R. C. TOLMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1240—1255).—A colorimetric method of analysis for nitrogen dioxide has been developed, capable of measuring partial pressures as low as 0·3 mm. with an accuracy of about 5%. The (unimolecular) thermal decomposition is found to be unimolecular also in its initial stages. The results of the investigation supply no confirmation of the hypothesis that the reaction is autocatalytic. The reaction mixture was formed by mixing freshly-prepared nitrogen pentoxide with oxygen and ozone, the latter serving to re-oxidise the decomposition products until exhausted. The observed rates of reaction are in good agreement with those obtained by Daniels and Johnston (A., 1921, ii, 249). J. S. C.

Explosion of Ammonia with Carbon Monoxide and Oxygen. J. W. BEESON and J. R. PARTINGTON (*J. Chem. Soc.*, 1925, **127**, 1146—1150).—Two volumes of carbon monoxide mixed with one volume of oxygen were exploded with varying quantities of ammonia, at a temperature of 85° and pressure of 380 mm. so that no steam condensed. All mixtures which could be ignited showed approximately the same decomposition of ammonia, viz., 95·3%. With some mixtures containing more than 45% of ammonia, the first spark did not cause explosion, a period of induction being observed, after which the propagation of the flame from the spark to the walls of the bulb was so slow that it could be followed visually. No ignition occurred in mixtures in which the ratio $NH_3/(2CO+O_2)$ exceeded 0·924. W. H.-R.

Gaseous Explosions. I. Initial Temperature and Rate of Rise of Pressure. G. G. BROWN, E. H. LESLIE, and J. V. HUNN (*Ind. Eng. Chem.*, 1925, **17**, 397—402).—The rate of rise of pressure in a gaseous explosion is dependent not only on the rate of the chemical reaction but also on the initial temperature. This can be shown from theoretical considerations which also demand a critical initial temperature. Experiments in a constant volume bulb show that in mixtures containing an excess of fuel this critical initial temperature is 75°, since the maximum rate of rise of pressure is obtained from gases preheated to that temperature. M. B. D.

Effect of Nitrogen and Carbon Dioxide Dilutions on Explosion Limits of Acetone and Methyl Alcohol and their Mixtures. H. CROUCH and E. K. CARVER (*Ind. Eng. Chem.*, 1925, **17**, 641—642).—The explosion limits of acetone and methyl alcohol in air are 2·5 and 6·1%, respectively, for the lower limit and 10·4% for the upper limit for acetone. No explosion takes place if the air contains less than 11% of oxygen. The lower limit is scarcely changed by varying the oxygen content of the air down to about 13%. This effect is not observed when carbon dioxide acts as a diluent in place of nitrogen owing to its higher heat capacity.

The law of mixtures of Le Chatelier, which states that a mixture of any two limit mixtures (both upper or both lower) will itself be a limit mixture, was found to hold for the mixtures studied.

M. B. D.

Ignition of Carbon Disulphide Vapour and its Phosphorescent Flame. H. B. Dixon (*Rec. trav. chim.*, 1925, **14**, 305—322).—An apparatus designed to measure the "lag" prior to the ignition of mixtures of carbon disulphide vapour with hydrogen, carbon dioxide, methane, and other gases both in air and oxygen is described, in order to obtain information concerning the effects due to the gradual heating of the mingling gas by the pre-flame combination and to contact with the wall of the silica tube during this period, which were not considered in earlier work (cf. Dixon and Coward, T., 1909, **95**, 514), and the observed lag and corresponding ignition temperatures for a large number of various mixtures both in air and oxygen are recorded. Carbon disulphide maintains the ignition point at a low temperature approximating to its own. When the lag exceeded 2 or 3 sec. the gases often failed to unite, but normal behaviour was restored by prolonged sweeping out of the cylinder with air or oxygen, and the cause of non-ignition is shown not to lie in the formation of a deposit of carbon monosulphide on the active surface of the silica (cf. Dixon and Russell, T., 1899, **75**, 603). Ethylene and acetylene possess a strongly inhibitive effect on the ignition of carbon disulphide mixtures, 1% of ethylene raising the ignition temperature of a mixture of carbon disulphide and hydrogen from 215° to 410°. Mixtures of carbon disulphide and methane are used to investigate the phenomena of phosphorescent flame which is observed when the temperature of the furnace reaches 180—190°, the flame always starting some way above the jet. The products of this phosphorescent combustion are mainly carbon monosulphide (collected as a brownish-red film) and sulphur dioxide, a large quantity of carbon disulphide escaping unburnt; practically no carbon is combusted, and the absence of steam in the products shows that the methane passes through the flame unburnt. The brown deposit is formed only when phosphorescence is visible and can itself become luminous and start the phosphorescent flame. A trace of gaseous "poison" (ethylene, acetylene, coal gas, or nitrogen peroxide) introduced into the mixture of gases before they mingle inhibits both phosphorescence and the formation of the deposit, but the toxic gas has no action if introduced into the phosphorescent flame itself. Assuming the main reaction of incipient combustion to be $CS_2+O_2=CS+SO_2$, an explanation of this action of the poison by its condensation on the surface of the active carbon monosulphide molecule is elaborated.

J. W. B.

Influence of a Magnetic Field on certain Chemical Reactions. M. A. Parker and H. P. Armes (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 203—207).—Investigations on the influence of magnetic fields on the rate of certain chemical reactions have shown conclusively that the reduction of ferric chloride in hydrochloric

acid solution by metallic iron or aluminium and the reduction of permanganate in acid solution by metallic iron are hastened in the field, there being a definite relationship between the extent of reduction and the strength of the field. The phenomena observed during the reduction of ferric chloride in hydrochloric acid solution by magnesium are attributed to the formation of a magnetic deposit on the metal. The effect of stirring the solutions during reduction diminishes the difference in the extent of reduction in a given time in and out of the field. J. S. C.

Hydrogen Peroxide as an Oxidising Agent in Acid Solution. II.—I. Oxalic Acid. II. Formic Acid. W. H. HATCHER and G. W. HOLDEN (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 231—246; cf. *ibid.*, 1923, [iii], **17**, III, 119).—I. The oxidation of oxalic acid to carbon dioxide and water in presence of hydrogen peroxide proceeds according to the conditions for a unimolecular reaction, the velocity being considerably increased in the presence of nitric or of hydrochloric acid. Evidence is put forward in favour of the view that hydrogen peroxide forms a complex, which is not a per-acid, with the non-ionised molecules of oxalic acid, which complex later breaks down into water and carbon dioxide.

II. The oxidation of formic acid proceeds along similar lines, the effect of addition of nitric acid being, however, to stabilise the peroxide, the reaction velocity being thereby lessened. Hydrochloric acid rapidly causes decomposition of hydrogen peroxide and scarcely any oxidation is effected. The complex formed is probably performic acid. J. S. C.

Accelerating Action of Carbohydrates on the Oxidation of Acetoacetic Acid. Z. ERNST and J. FORSTER (*Magyar Orvosi Archivum*, 1924, **25**, 363—367).—Mannitol, glycerol, mono- and tri-butyrin have the same accelerating action on the oxidation of acetoacetic acid by hydrogen peroxide as observed by Shaffer with dextrose. On the contrary, mono- and di-hydric alcohols, di- and poly-saccharides and organic acids do not produce an acceleration. CHEMICAL ABSTRACTS.

Velocity of Saponification of Ionic Esters. J. N. BRÖNSTED and A. DELBANCO (*Z. anorg. Chem.*, 1925, **144**, 248—256).—The first stage in the hydrolysis of the ester of a dibasic acid is a reaction between hydroxyl ion and undissociated ester, but the second stage takes place between two ions, hydroxyl ion and the ester ion, R(OEt)O′, and its velocity may therefore be expected to show a positive, exponential salt effect. This has been verified for the hydrolysis of the potassium derivative of nitrourethane (A., 1896, i, 207) by sodium hydroxide; the nitrocarbamate ion at first formed decomposes very rapidly with liberation of nitrous oxide and the reaction is thus readily followed: $-NO_2{:}N{\cdot}CO_2Et + OH' \longrightarrow -NO_2{:}N{\cdot}CO_2- + EtOH$; $-NO_2{:}N{\cdot}CO_2- \longrightarrow N_2O + CO_3''$. This reaction is equally accelerated by the addition of potassium chloride, sulphate, or cobalticyanide, salts having the same cation but anions of different valencies, but tetrammineplatinum chloride and luteocobaltic chloride, salts with cations of higher valencies, have much

greater effects; this was to be expected because the reacting ions are negative (cf. A., 1922, ii, 481, 699). A. G.

Kinetic Study of the Reduction of Mercuric Bromide by Sodium Formate. F. BOURION and J. PICARD (*Compt. rend.*, 1925, **180**, 1599—1602; cf. A., 1924, ii, 613).—The reaction between mercuric chloride and sodium formate in excess has been studied by the Ostwald isolation method. The reaction is definitely bimolecular, although the equation suggests that it is termolecular. The discrepancy is explained by the formation of a complex salt $HgBr_2,H{\cdot}CO_2Na$, which reacts with a molecule of sodium formate. The effective reaction would then be bimolecular. At 40° the rate of reduction of mercuric bromide by sodium formate is about half the rate observed for mercuric chloride. R. A. M.

Kinetics of Swelling and Shrinking of Gels. I. S. LIEPATOFF (*Kolloid-Z.*, 1925, **36**, 222—226).—The velocity of swelling when the process takes place in the pure state, satisfies the formula $K=1/t\,.\,log_e m/(m-Q)$, where m is the swelling-maximum, Q the degree of swelling at the time t. If the swelling is accompanied by any secondary process, the equation $\gamma K=1/t\,.\,log_e m/(m-Q\gamma)$ holds better, where γ is the velocity coefficient of the secondary process. Experiments to test the validity of these equations were undertaken with glue and gum tragacanth in pure water, 0·025N-potassium hydroxide, hydrochloric acid, potassium dichromate, and potassium ferricyanide, and the second equation was found to embrace all cases of gel swelling. The shrinking of the gel in ethyl alcohol of various strengths, in methyl alcohol, and in formaldehyde, shows that the velocity of shrinking may be expressed by the equation $K=\{1/(a-E)t\}\log_e(a-Z)E/(E-Z)a$, where a is the initial water-content of the gel, E the water given up in time t_∞, and Z the water given up in time t. In many cases the equation $\gamma K=\{1/(a-E)t\}\log_e(a-\gamma Z)E/(E-\gamma Z)a$ is more satisfactory. L. L. B.

Velocity of Decomposition of Solids. I. Dissociation of Magnesium Carbonate. M. CENTNERSZWER and B. BRUŽS (*Z. physikal. Chem.*, 1925, **115**, 365—376; cf. this vol., ii, 206).—The velocity of the dissociation of natural and of artificial magnesium carbonate has been studied by means of an apparatus which measures the volume of carbon dioxide evolved in a given time. The velocity does not depend on the surface of the solid phase or on the rate of diffusion of the carbon dioxide, but corresponds with a reaction of the first order. The dissociation proceeds in three stages as follows: (i) $2MgCO_3=MgO,MgCO_3+CO_2$; (ii) $2(MgO,MgCO_3)=3MgO,MgCO_3+CO_2$; (iii) $3MgO,MgCO_3=4MgO+CO_2$. The temperature quotients for 10° are: stage (i) (experiments on magnesite), about 3; stages (ii) and (iii) (experiments on artificial magnesium carbonate), 4·3 and 3·2 respectively. N. H. H.

Action of Ammonium Chloride Vapour on Metals and the Conformity of Ammonium Salts with Hydroxonium Salts as Acids. K. A. HOFMANN, F. HARTMANN, and K. NAGEL (*Ber.*, 1925, **58**, [*B*], 808—817).—Comparison of the action of dry hydrogen

chloride with that of ammonium chloride vapour on metals at 250—350° by measurement of the volume of hydrogen evolved under similar conditions shows the latter to be one hundred times more active than the former with respect to copper, about forty times as active in the cases of nickel and silver, and at least five times as active in the case or iron. The action cannot therefore be due to the primary dissociation of ammonium chloride into hydrogen chloride and ammonia; this is confirmed by the absence of appreciable quantities of nitrogen from the gaseous products of the change and by the observation that the activity increases with increasing concentration of ammonium chloride vapour and hence with increase in concentration of undissociated ammonium chloride molecules. Since the metalammine chloride is a primary product of the change the latter consists in a substitution process in which the metal displaces hydrogen from the ammonium complex. The ability of the metal to form a chloride and an ammine complex and of the metallic surface to facilitate the displacement of hydrogen by solution followed by emission as the hydrogen molecule appear to be the essential factors underlying the change, thus accounting for the observation that, whereas the reactivity of the metals towards gaseous hydrogen chloride at 200° follows the order Fe>Ni>Cu>Ag>Hg, which accords with the heats of formation of the chlorides from metal and hydrogen chloride, the sequence towards ammonium chloride vapour is Fe>Cu>Ni>Ag>Hg or As. Ammonium chloride, and probably all ammonium salts, behave therefore as acids since they permit the replacement of hydrogen by metal. It is therefore directly comparable with aqueous hydrochloric acid which, according to Hantzsch (this vol., ii, 359), contains the hydroxonium salt $[OH_3]Cl$. Since the hydroxonium complex is less stable than the ammonium group, ammonium chloride requires a higher temperature than hydrogen chloride for the development of an appreciable activity towards metals. Thus, at 200°, copper is quantitatively converted into cuprous chloride with evolution of hydrogen by aqueous hydrochloric acid, whereas the corresponding change with ammonium chloride solution does not take place below about 250°. H. W.

Influence of Impurities in Zinc on its Solubility in Acids. R. Vondráček and J. Izák-Križko (*Rec. trav. chim.*, 1925, **44**, 376—389).—The velocity of the dissolution of pure zinc and its alloys in 0·5*N*-sulphuric acid has been studied by casting the metal into a cylinder 2 cm. in diameter one face of which, ground (and sometimes polished), was alone left free to attack by the acid, the remainder of the cylinder being protected, and measuring the volume of hydrogen evolved per sq. cm. per unit time during the period of dissolution. With pure zinc (Fe 0·002, Pb 0·038, Cd 0·002, Cu 0·003%, Sb traces) the solution velocity increases for the first hour, remains constant for 6 hrs., and again increases slightly about the eighth hour. When the surface is polished 2 hrs. elapse before the normal intensity is reached; thus the "induction period" is dependent on the mechanical treatment of the surface. Mercury

and aluminium have a decided lowering influence on the velocity of dissolution, the former completely inhibiting the evolution of gas after 2·6 c.c./cm.^{2} have been evolved. Lead is practically indifferent, whilst cadmium, arsenic, tin, antimony, iron, and copper (after a certain passivity of the alloy has been observed at the beginning of the solution process) increase the solution velocity in the order given, the reaction velocities compared with that of pure zinc as unity being 1·15, 1·75, 2·80, 6·4, 11·5, and 12·2, respectively, for alloys containing 1% of the metal when solution to a depth of 0·2 mm. has occurred. For alloys of zinc with tin and cadmium, the maximum solution velocity is not markedly influenced by increasing the content of these metals from 0·5 to 1·0%, whereas, in the case of iron, the increase is almost directly proportional (within the limits 0·01 to 1·23%) to the amount of the metal present. The contradictory results of previous investigators are discussed in the light of the above results. J. W. B.

Influence of Thermal and Mechanical Treatment on the Rate of Dissolution of Aluminium in Hydrochloric Acid. X. WACHÉ and G. CHAUDRON (*Compt. rend.*, 1925, **180**, 1495—1497).—The rate of dissolution of aluminium in hydrochloric acid is decreased by hammering or heating the metal to a high temperature for some time. Generally speaking, the more rapidly the fused metal is cooled the greater will be the rate of dissolution in acid. Pure aluminium is much less readily attacked than the commercial specimens containing small amounts of silicon and iron. The rate of dissolution appears to be independent of grain size. J. S. C.

Water-line Corrosion of Iron and Steel, with special reference to the Action of the so-called "Inhibitors" of Corrosion. U. R. EVANS (*J. Soc. Chem. Ind.*, 1925, **44**, 163—169T).—Two distinct types of corrosion are discussed under the expression "water-line attack." On areas above the water-line which become wetted through splashing or variations in water-level, the conditions are favourable for rapid corrosion. If the rust forms as a uniform blanket over the whole of the wetted surface and continues to adhere, the subsequent rate of corrosion will be determined by the rate at which dissolved oxygen can pass through the blanket to the metallic surface, although the softened layer contains sufficient graphite or uncorroded iron to render it a conductor. Cast iron undergoes softening, but the changes in structure may escape notice until it is tested with a knife. In many fresh- and salt-waters the zone just below the water-line is remarkably free from corrosion owing to the formation of a protective, adherent oxide-film. In such waters, the area rather lower down suffers corrosion in consequence of electric currents flowing between these unaërated areas as anode and the aërated portions at the water-line as cathode. If "inhibitive chemicals," such as sodium carbonate or potassium carbonate, which tend to reduce total corrosion through the formation of a protective film, are added to waters containing chlorides, the corrosion may be localised at the water-line, because close adhesion of the protective film is most

likely to fail at that point. In such cases, although the total corrosion, indicated by loss of weight, may be reduced, the metal may be perforated more rapidly than in the absence of the inhibitor. Potassium chromate appears to be a safer inhibitor than sodium carbonate, but actual experiment is advisable before either of them is added to a corrosive water, in order to ensure that corrosion is absolutely prevented and not simply localised, with consequent greater damage. R. B.

Corrosion of Iron [Erosion]. W. R. WHITNEY (*Ind. Eng. Chem.*, 1925, **17**, 385—388).—When a water jet impinges on an iron surface, erosion takes place only when the water contains dissolved oxygen. Erosion of metals is probably due to the removal of the products of corrosion and not so much to disintegration by the formation of vacuum pockets by the rapidly moving propeller etc. M. B. D.

Corrosion of Iron in Absence of Oxygen. J. W. SHIPLEY, I. R. MCHAFFIE, and N. D. CLARE (*Ind. Eng. Chem.*, 1925, **17**, 381—385).—When iron is introduced into buffer solutions free from oxygen it evolves gaseous hydrogen from solutions more acid than p_H 9·4, which is the hydrogen-ion concentration of a saturated solution of ferrous hydroxide. In the presence of oxygen, ferric hydroxide is formed and between p_H 9·4 and 7·0 the rate at which the dissolved oxygen diffuses to the metal surface controls the reaction. Ferric hydroxide is soluble in solutions more acid than p_H 7·0 in which the hydrogen-ion concentration again controls the rate of corrosion and the reactions concerned are independent of the oxygen supply. No change in the potentiometer readings could be discovered when hydrogen or nitrogen was bubbled over one electrode as was found by Bancroft (A., 1924, ii, 686). M. B. D.

Oxygen Distribution as a Factor in the Corrosion of Metals. U. R. EVANS (*Ind. Eng. Chem.*, 1925, **17**, 363—372).—Qualitative experiments on the water-line corrosion of iron and zinc show that the results can be explained by the theory of differential aëration. The appearance of the corroded specimen can be divided into four zones: the dry top portion; the portion above the water-line which is wetted by creeping of the cathodically produced alkali upwards over the surface; the portion below the water surface which is aërated and cathodic and develops an oxide film showing interference colours; the lower portion, which is not reached by oxygen and is therefore anodic. The junction between the third and fourth zones is covered by a mantle of the metallic hydroxide, which is deposited by the metal salt from the anodic portion coming into contact with the sodium hydroxide from the cathodic portion. The oxide film becomes thick enough to give interference colours owing to the combined effect of dissolved oxygen and cathodic treatment, which renders it only partly protective and it is thus able to increase its thickness. If a disc of metal is whirled in an aërated liquid, it corrodes evenly all over its surface and the corrosion product is

far more adherent than when the metal is subjected to differential oxidation. In the case of iron under these conditions, the relatively soluble ferrous hydroxide is probably oxidised to ferric hydroxide before it is out of the reach of adhesional forces. M. B. D.

Acid Corrosion of Metals. Effect of Oxygen and Velocity. W. G. WHITMAN and R. P. RUSSELL (*Ind. Eng. Chem.*, 1925, **17**, 348—354).—A survey has been made of the effect of dissolved oxygen on the corrosion of mild steel, chromium steel, aluminium, lead, copper, nickel, monel metal, and tin in various acids from 20° to 50°. With metals, such as iron, which evolve hydrogen as gas in the presence of acids, the effect of dissolved oxygen is more important in the weaker acids where hydrogen evolution is slow. The effect of dissolved oxygen is not important with oxidising acids. Oxygen decreases the corrosion rate in the case of aluminium and chromium steel in strong nitric and sulphuric acids owing to the formation of a film of aluminium oxide and a passivity effect, respectively. Copper and nickel, which do not evolve hydrogen from acids, are quite resistant to non-oxidising acids in the absence of oxygen but may be rapidly attacked when oxygen is present. In some cases the corrosion of a metal in the presence of oxygen is from 100 to 200 times the rate that held when it was absent. The effect of the velocity of stirring of test pieces of copper in aërated sulphuric, hydrochloric, and acetic acids was found to increase the corrosion in the cases where the dissolved oxygen had a large effect when the metal was at rest. This is due to the fact that the velocity decreases the thickness of the stationary film of liquid on the metal surface through which the oxygen has to diffuse. The effect of velocity of stirring of steel in 80—100% sulphuric acid is also given. M. B. D.

Oxidation of Copper–Nickel Alloys at High Temperature. N. B. PILLING and R. E. BEDWORTH (*Ind. Eng. Chem.*, 1925, **17**, 372—376).—Both nickel and copper oxidise at temperatures of about 1000° so that the square of the amount of oxidation is proportional to the time of exposure. Copper oxidises about thirty times as fast as nickel. Copper–nickel alloys oxidise in a similar manner to their constituent metals except those containing from 30 to 80% of nickel in which the rate of oxidation increases much more rapidly with temperature. The rate of oxidation can be followed by measuring the increase in the electrical resistance of a standard wire test piece as well as by the increase in weight. M. B. D.

Catalytic Effects in the Oxalate–Permanganate Reaction. G. N. RIDLEY (*Chem. News*, 1925, **130**, 305—306).—Data obtained for the velocity of the reaction between oxalic acid and potassium permanganate at varying temperatures appear to indicate that the reaction is catalysed, not only by manganous ions, but also by undissociated manganous sulphate. The velocity of the reaction at 25° is considerably increased by passing a small current through the solution, probably owing to increase in the rate of movement of the cations induced by the current. A. R. P.

Promoter Action in Homogeneous Catalysis. II. Mechanism of the Promotion of Copper Salts in the Catalytic Decomposition of Hydrogen Peroxide by Ferric Salts. A. C. ROBERTSON (*J. Amer. Chem. Soc.*, 1925, **47**, 1299—1314; cf. A., 1924, ii, 29).—Cupric acid is present in cases where the catalytic decomposition of hydrogen peroxide by ferric salts is promoted by copper and the formation of this acid is catalysed by the presence of minimal amounts of ferric salt. As the concentration of iron is reduced, the region of maximum promotion approaches the value 2Fe:3Cu. The reaction $2FeO_3+3CuO \rightarrow Fe_2O_3+3CuO_2$ is a possible mechanism of the promotion. "Promotion" is defined and the conditions under which promotion occurs are discussed. J. S. C.

Negative Catalysis of Oxidation Reactions. N. R. DHAR (*Z. anorg. Chem.*, 1925, **144**, 289—303).—The oxidation of phosphorus, chloroform, sulphites, stannous salts, and various organic reducing agents by atmospheric oxygen is hindered or retarded by the presence of easily oxidised compounds such as sodium arsenite, quinol, glycerol, and sugars. The decomposition of nitrous acid into nitric acid and nitric oxide and of phosphorous and hypophosphorous acids into phosphine and phosphoric acid is also retarded by addition of a mild reducing agent. The mechanism of these and other negatively catalysed reactions may be best explained by assuming that molecular complexes are formed between the original substance and the catalyst and that these are more slowly oxidised than either compound separately. This view is supported by the investigations of other workers. A. R. P.

Synthetic Catalysts. G. CUSMANO (*Gazzetta*, 1925, **55**, 218—224; cf. A., 1919, ii, 61).—Further investigations have been made on compounds acting as catalysts to the reaction $SO_2+Cl_2=SO_2Cl_2$. The life of such catalysts depends on their resistance to chlorination by either the chlorine or, more commonly, the sulphuryl chloride, and the nature of the carbon skeleton is of importance mainly in relation to this resistance. Ethylenic and alicyclic linkings, by uniting with chlorine, lead to the destruction of the catalyst. Phenyl benzyl ketone rapidly loses its catalytic activity owing to halogenation of the methylene group, whereas dibenzoyl, like other α-diketones, such as camphoquinone, diketocineole, and isatin, is almost inert, although highly resistant to chlorination. On the other hand, β- and γ-diketones, like benzoylacetone and acetonylacetone, favour the synthesis, but ultimately undergo chlorination.

That some relationship is established between the contiguous carbonyl groups of the α-diketones at the expense of those affinity residues which, in monoketones or in diketones with the carbonyl groups further apart, effect the catalytic action, is shown by the fact that oximes of ketones and both mono- and di-oximes of α-diketones catalyse the synthesis of sulphuryl chloride. Similar properties are exhibited by the nitrones and furazans, particularly by the furazan of diketocineole.

The experimental data are to be published later. T. H. P.

Decomposition of Nitrous Acid by Light and by Catalysts. K. B. MUKERJI and N. R. DHAR (*Z. Elektrochem.*, 1925, **31**, 255—258; cf. Rây and others, T., 1917, **111**, 413).—The reaction $3HNO_2 \rightleftharpoons HNO_3+2NO+H_2O$ is of the first order and has a subnormal temperature coefficient, the value of which increases with rise of temperature. The velocity coefficient in both light and the dark increases slowly with increase of concentration of the nitrous acid. The velocity coefficients are considerably greater (from 200 to 400%) when the reaction is carried out in open vessels than when closed vessels are employed. This is attributed to a displacement of equilibrium owing to the removal of nitric oxide under the former conditions. The velocity of the reaction is markedly accelerated by light, and to a greater extent when closed vessels are used. The following substances act as positive catalysts for the reaction: ferric nitrate, cobalt nitrate, nickel nitrate, chromium chloride, copper sulphate, nitric acid, potassium chlorate, potassium nitrate, sulphuric acid, ferric hydroxide sol, molybdic and titanic acids, bromocamphor, thiocarbamide, dinitrophenol, carbamide, phthalic anhydride, citric, tartaric, and formic acids, potassium oxalate, potassium formate, boric acid, and tartar emetic. The following act as negative catalysts: sucrose, dextrose, glycerol, alcohol, hydrogen peroxide, ethyl ether, quinol, phenol, brucine, strychnine, narcotine, and quinine sulphate. Manganese nitrate and barium sulphate are without effect. The results indicate that reducing agents retard reactions involving auto-oxidation and reduction processes. F. G. T.

Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. III. Carbon Monoxide as a Catalyst Poison. R. N. PEASE and L. STEWART (*J. Amer. Chem. Soc.*, 1925, **47**, 1235—1240).—A continuation of the investigations on the poisoning of catalysts (A., 1923, ii, 862). Quantitative measurements of the influence of carbon monoxide on the activity of a copper catalyst towards a mixture of ethylene and hydrogen at 0° show that the catalyst is very sensitive to the poison, less than 0·05 c.c. of carbon monoxide being sufficient to reduce the catalytic efficiency of 100 g. of copper by 90%. It is shown that the metallic surface owes 90% of its efficiency as a catalyst to less than 1% of the regions which are active in adsorption. Adsorption measurements, even at pressures as low as 1 mm., furnish no trustworthy index of catalytic activity for hydrogenation catalysts. Carbon monoxide is a "temporary" poison, pumping out at 250° being sufficient to restore the activity of the catalyst. J. S. C.

Thermal Decomposition of Ammonia upon Various Surfaces. C. N. HINSHELWOOD and R. E. BURK (*J. Chem. Soc.*, 1925, **127**, 1105—1117).—The thermal decomposition of ammonia has been investigated in silica vessels, and on the surfaces of heated platinum and tungsten wires. In all cases equilibrium corresponds with almost complete decomposition of the ammonia, whilst up to the highest temperature reached, 1050° in a silica vessel, no sign of a homogeneous reaction was observed, the decomposition being

entirely a surface reaction. The reaction on a silica surface is of the first order with respect to ammonia, and strongly retarded by hydrogen, the retarding influence, C, being expressed by a relation of the type, $-d[NH_3]/dt=k[NH_3]\{1-C[H_2]\}$. The results for silica surfaces, in general, agree with those of Bodenstein and Kranendieck (A., 1912, ii, 1155), but the nature of the particular silica surface exerts a remarkable effect on the temperature coefficient of the reaction, the retarding effect of the products, and the effect of temperature on the retarding effect. In contradiction to the work of Bodenstein (*loc. cit.*) the authors find that in suitable silica vessels, (1) added hydrogen may have just as large a retarding effect as hydrogen formed *in situ* by the reaction, (2) the temperature coefficient may be very high, and (3) the retarding influence of the products may be constant over a range of 200°.

The reaction on a heated platinum wire is of the first order as regards ammonia, and is retarded by hydrogen, but differently from the retardation in the case of silica, the equation being $-d[NH_3]/dt=k[NH_3]^n/[H_2]$, where n is approximately equal to 1. Nitrogen has practically no effect on this reaction, which corresponds with a heat of activation of 140,000 cal. The reaction on a heated tungsten wire is of zero order with respect to ammonia, and is uninfluenced by the products of reaction. It is much more rapid than with platinum, but the temperature coefficient is smaller and corresponds with a heat of activation of 38,700 cal. W. H.-R.

Catalysis by the Action of Subdivided Metals. III. Heat of Adsorption of Hydrogen on Nickel. B. Foresti (*Gazzetta*, 1925, **55**, 185—201).—The author's results (A., 1923, ii, 747; 1924, ii, 320) are discussed in relation to those of Beebe and Taylor (A., 1924, ii, 159), and further results are given showing the relation between the temperature of evacuation of the finely-divided nickel and the heat of adsorption, as well as the effect on the latter of reheating the metal. These results render it highly probable that the surface of the nickel or other metal in similar condition is composed of adsorbent centres of varying force, and that the catalytic activity is determined by such centres as are able to adsorb gases and retain them firmly. T. H. P.

Induced Oxidation and its Mechanism Explained on the Basis of the Formation of Ions during Chemical Reactions. A. N. Dey and N. R. Dhar (*Z. anorg. Chem.*, 1925, **144**, 307—312).—Sulphur, sucrose, dextrose, ethyl alcohol, starch, potassium oxalate, sodium tartrate, sodium arsenite, and similar mild reducing agents are oxidised at the ordinary temperature by passing air through their solutions in which finely-divided copper, cuprous chloride, cuprous oxide, zinc, or yellow phosphorus is suspended. Finely-divided copper dissolves in cold solutions of sodium arsenite, sodium phosphite, sodium citrate, potassium tartrate, citric acid, tartaric acid, and sucrose only in the presence of oxygen, but it dissolves in cold ammonium nitrite solution also in the absence of oxygen,

probably owing to the direct action of the nitrous acid set free by hydrolysis. The oxidising action of the phosphorus, copper, zinc, and other reducing agents in the above cases is probably due to the formation, by the oxidising action of the air, of ions which can oxidise molecular oxygen and the activated oxygen molecule then attacks the sulphur, alcohol, etc. A. R. P.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. VII. Effects of Numerous Substances on the Platinum Catalysis of the Reduction of Benzaldehyde. W. H. CAROTHERS and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 1047—1063; cf. A., 1924, i, 968).—The effect of various substances on the catalytic reduction of benzaldehyde in 95% alcohol by hydrogen in presence of platinum oxide has been studied. A catalyst which has lost its activity by contact with aldehyde (cf. A., 1923, ii, 310) is not reactivated by the addition of ferrous chloride, but if the mixture containing the exhausted catalyst is shaken with air, either before or after the addition of the ferrous chloride, a permanent partial restoration of the catalytic activity is achieved. Ferrous and ferric hydroxides increase the rate of reduction at first, thereafter retarding it, apparently by covering the catalyst with a gelatinous film, as the addition of hydrochloric acid, which by itself has a depressing effect, completely restores the activity. Metallic iron, ferric oxide, chloride, and acetate, ferrous chloride and sulphate, all promote the catalysis. Ferric nitrate in small amount (0·1—1·0 millimol.) causes the reduction to cease before all the aldehyde is reduced, whilst a larger proportion (10 millimols.) carries the reduction further, with production of toluene. It is concluded that the promoter effect is due to iron ions. Manganese, nickel, cobalt, vanadic acid, chromic chloride, uranyl acetate, and alkalis are promoters. Palladium is a promoter, but may be acting as an independent catalyst. Sodium chromate and zinc acetate in small amount (0·1 millimol.) are promoters, but larger proportions (1·0 millimol.) almost completely suppress the reduction. Copper chloride is a promoter, the acetate a depressant. Titania, molybdenum, silver, tungsten, osmium, iridium, aluminium, and gold, as well as mineral acids, are without effect on the catalysis. Mercury and lead act as catalyst poisons, but a considerable proportion of either is necessary to suppress the reduction completely. Of sodium salts, the chloride and bromide increase the induction period, but are otherwise inert. The iodide acts as a weak depressant, probably through the liberation of iodine. The nitrate is a weak depressant, whilst the nitrite, inert in small amounts, completely inhibits the reduction when 1·0 millimol. is present. The sulphate and chlorate are inert, the cyanide is a poison. Using a catalyst which has been promoted with ferrous chloride, hydrochloric acid decreases the rate of reduction, but causes the latter to go beyond the alcohol stage. Sodium nitrate causes some acetal formation, whilst the nitrite is again a powerful depressant. The first reduction product is in all cases the primary alcohol, any formation of hydrocarbon always taking place subsequently, and

more slowly. The results are discussed in relation to those of Faillebin (A., 1923, i, 92). F. G. W.

Hydrogen Electrode. H. T. BEANS and L. P. HAMMETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1215—1226).—An attempt has been made to classify some of the conditions which give rise to variable potentials of hydrogen electrodes with platinum catalysts and to show how these variabilities may be eliminated. The formation of platinum-black necessitates the presence of some impurity, since pure chloroplatinic acid gives only bright electro-deposits. Bright metallic deposits of platinum prepared electrolytically are catalytically active for the hydrogen–hydrogen ion reaction, and their life, although much shorter than that of platinum-black, is sufficient to allow of their use as hydrogen electrodes. Consideration of the various methods for obtaining active surface shows that it is not so much the extent of the surface as the quality that determines activity, and freshly-prepared surfaces are most active. The rate of attainment of equilibrium depends on removal of oxygen, which is in turn determined by cell-design, nature of the surface, and hydrogen-ion concentration of the aqueous medium. Hydrogen electrode measurements are possible in unbuffered solutions in the neutral range provided the electrodes are perfectly clean. J. S. C.

Tervalent Copper. M. VRTIŠ (*Rec. trav. chim.*, 1925, **44**, 425—434).—The compound of tervalent copper obtained by the anodic or persulphate oxidation of copper sulphate in alkaline solution in the presence of tellurates has been investigated. The rôle of the latter is that of a peptising and stabilising agent only, the production of tervalent copper being determined only by the alkalinity of the solution. Periodates act similarly to tellurates. This is confirmed by potentiometric measurements which show that the concentration of the $Cu^{\cdots}$ ions is unaffected by changes in the concentration of the tellurate ions. From these and other observations it is inferred that the formula most nearly expressing the composition of the tervalent copper compound (in potassium hydroxide solution) is $K[Cu(OH_4)]$. N. H. H.

Electrolytic Deposition of Tungsten. J. A. M. VAN LIEMPT (*Z. Elektrochem.*, 1925, **31**, 249—254).—Tungsten powder (99·3% pure) may be obtained, up to 80% of the theoretical yield, by electrolysing at 950° molten sodium tungstate at a current density of 15 amp./cm.^{2}, in a quartz crucible between tungsten electrodes. The tungsten results from the reduction of the molten tungstate by the nascent sodium liberated at the cathode: $6Na+5Na_2WO_4=W+4Na_4WO_5$. Pure tungsten is obtained so long as the mass remains neutral or weakly alkaline. If it becomes too strongly alkaline the tungsten redissolves. In acid fusions, reduction of W_2O_7'' ions by the sodium occurs with the formation of "tungsten bronzes" of the type $M_2(WO_3)_n$ (cf. Brunner, *Diss.*, Zürich, 1903). The electrical resistance of these "bronzes" decreases rapidly with rise of temperature owing to the gradual liberation of tungsten. The anode reaction is $WO_4''+Na_2WO_4=Na_2W_2O_7+0{\cdot}5O_2$. When

unattackable electrodes are used in a cell without a diaphragm, the products of these electrode reactions react, making the mass alkaline: $4Na_4WO_5+3Na_2W_2O_7=10Na_2WO_4+Na_2O$. Electrolysis may be made continuous under these conditions by gradually adding tungstic oxide. In the presence of WO_4'', a tungsten anode is oxidised, the oxide dissolving to keep the fused mass neutral. Tungsten may be deposited in an adhesive, polishable layer on copper, nickel, or cobalt by using these metals as cathodes in the electrolysis of fused acid tungstates at 1000°. Lithium acid tungstates give the best results. Repeated layers of tungsten may be thus deposited if the surface layers of "tungsten bronzes" are removed between each electrolysis. The tungsten is formed by the decomposition of "tungsten bronzes" primarily deposited. Crystal growth of a monocrystalline tungsten filament may be obtained by electrolysis at low current densities in neutral or acid melts (cf. A., 1924, ii, 558). F. G. T.

Reduction of Uranyl Salts by Means of a Dropping Mercury Cathode. P. Herasymenko (*Chem. Listy*, 1925, **19**, 172—179).—Uranyl salts are reduced at a dropping mercury cathode first to derivatives of quinquevalent uranium. Further reduction ensues only when the polarisation becomes very considerable. The polarisation curves of the reduction show a very marked maximum when the metal is all in the quinquevalent form, but this maximum disappears in the presence of certain electrolytes such as potassium or lithium chlorides, probably owing to adsorption of the reduced products at the surface of the electrode. A. R. P.

Instability of Phthalate Solutions towards the Hydrogen Electrode. C. Z. Draves and H. V. Tartar (*J. Amer. Chem. Soc.*, 1925, **47**, 1226—1230; cf. Merrill, A., 1922, i, 326; Oakes and Salisbury, A., 1922, ii, 468; Clark, *ibid.*; Wood and Murdick, A., 1922, ii, 735).—Measurements with the cell $Hg|Hg_2Cl_2,KCl(1{\cdot}0N)|KCl(1{\cdot}0N)|$phthalate solution$|H_2$ show that the instability of phthalate solutions towards the hydrogen electrode is dependent on the relative amount of platinum-black on the latter. Complete reduction of potassium hydrogen phthalate to the corresponding hexahydro derivative has been accomplished in aqueous solution using heavily platinised gauze as electrode. J. S. C.

Photochemical Decomposition of Nitrosyl Chloride. E. J. Bowen and J. F. Sharp (*J. Chem. Soc.*, 1925, **127**, 1026—1028).—The photochemical decomposition of nitrosyl chloride has been studied in an all-glass apparatus using light of spectral range approximately 4400—5200 Å. Approximately two quanta are absorbed for each molecule decomposed. The heat of reaction is $NOCl+45{,}000$ cal. $\longrightarrow NO+Cl$, from which the maximum wavelength capable of causing the decomposition is calculated as 6270 Å., which corresponds almost exactly with the point at which the absorption of nitrosyl chloride begins, but the absorption in red light is too weak to enable the decomposition to be studied. Since the quantum of blue light is greater than the minimum quantum

necessary for decomposition, it is probable that the decomposition is a true unimolecular process, $NOCl+h\nu \longrightarrow NO+Cl$, followed by spontaneous reactions re-forming nitrosyl chloride, possibly through the intermediate compound $NOCl_2$. The rate of reaction does not therefore follow the unimolecular equation, in contradiction to the assumption of Kiss (A., 1923, ii, 598), whose further conclusions are criticised. W. H.-R.

Mercury Helide. J. J. MANLEY (*Nature*, 1925, **115**, 947; cf. this vol., ii, 57, 314).—A correction; the simplest formula assignable to mercury helide is $HgHe_{10}$. A. A. E.

Action of Natural Waters on Copper. H. HENSTOCK (*J. Soc. Chem. Ind.*, 1925, **44**, 219—220T).—Boiling water containing 0·0024 part per 100,000 of sodium chloride, or equivalent quantities of magnesium chloride or potassium chloride, attacks copper with the formation of soluble copper compounds, but copper is not attacked by solutions of calcium chloride, magnesium sulphate, sodium sulphate, calcium sulphate, magnesium hydrogen carbonate, or calcium hydrogen carbonate of approximately equivalent dilution, nor by sodium or magnesium chloride solution if equal quantities of calcium hydrogen carbonate or calcium hydroxide are also present. No action on copper could be detected with water containing solely organic matter in solution. In certain cases where natural soft waters have been found to attack copper apparatus, the cause has always been attributable to the presence of traces of sodium or magnesium chloride, and can be prevented by the addition of small quantities of lime. L. A. C.

Mechanism of the Formation of Malachite from Basic Cupric Carbonate. J. R. I. HEPBURN (*J. Chem. Soc.*, 1925, **127**, 1007—1013).—When equivalent solutions of cupric sulphate and sodium carbonate are mixed at the ordinary temperature, the precipitated basic cupric carbonate (over a range of concentration from 0·005*N* to 3*N*) consists of a hydrogel of highly hydrated material of low refractive index and opaque in polarised light. If immediately washed free from adhering reagents and suspended in pure water, this initial precipitate is stable, but normal crystals of malachite are gradually formed if the precipitate is suspended in a solution of carbon dioxide. If left in contact with the precipitating reagents, the change to malachite is accelerated by increasing concentration, and in this case the product consists entirely of malachite sphæro-crystals. When malachite is formed at 100° from the blue solutions prepared by dissolving the basic carbonate in a saturated solution of sodium hydrogen carbonate, the product (in the absence of foreign nuclei) consists of a surface film of sphæro-crystals of size about 6μ; the film is disrupted into individual sphæro-crystals on boiling. In both cases the presence of gelatin retards but does not prevent the formation of malachite. W. H.-R.

Mixed Basic Silver–Copper Salts. G. MALQUORI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 392—396).—Investigation of the

system cupric hydroxide, silver nitrate, water at 20° indicates the existence of only one basic salt, $3Cu(OH)_2,2AgNO_3,3H_2O$, which is decomposed by water but is stable in presence of silver nitrate solutions having concentrations not less than 0·78%. T. H. P.

Solubility of Silver in Water. I. H. KŘEPELKA and F. TOUL (*Chem. Listy*, 1925, **19**, 182—184).—After contact with pure silver foil for 24 days, carefully redistilled water contained 0·035 mg. of silver per litre; in 14 days 0·021 mg., and in 7 days 0·012 mg. were dissolved. Previous heating of the silver in an atmosphere of pure hydrogen appreciably reduced its solubility in water. As the experiments were conducted in vessels of Bohemian glass, it is possible that the alkali derived from the vessels had an influence on the solubility. A. R. P.

Hydrates of Calcium Carbonate. J. HUME (*J. Chem. Soc.*, 1925, **127**, 1036—1039).—A solution of sucrose (25 g.) in water (100 c.c.) was shaken with lime and filtered, the filtrate being treated with carbon dioxide at 0°, and then exposed at 0° to the action of atmospheric carbon dioxide. After 2 or 3 days crystals of calcium carbonate hexahydrate were deposited, d^{15} 1·789. In contact with water at or above 0°, the hexahydrate slowly changes into anhydrous calcium carbonate, but in the above sugar–lime mixture the hexahydrate is stable below 10·4° and the anhydrous salt above 17°; between 10·4 and 17° the stable phase is a pentahydrate, d^{15} 1·834, which changes into the anhydrous form in contact with water. Between 10·4° and 25° the hexahydrate is first precipitated from the above sugar–lime mixtures, and then slowly changes into the form stable at the particular temperature. No evidence of lower hydrates has been obtained. W. H.-R.

Direct Formation of Mercuric Oxybromides. H. PÉLABON (*Compt. rend.*, 1925, **180**, 1500—1501).—Employing a method analogous to that previously reported (this vol., ii, 222), the existence of the oxybromides, $HgO,HgBr_2$ and $4HgO,HgBr_2$, has been demonstrated, and evidence obtained for the existence of a third of which the exact composition is uncertain. J. S. C.

Constitution of Boric Acid and Some of its Derivatives. P. H. HERMANS (*Z. anorg. Chem.*, 1925, **142**, 399—300).—In explanation of previous work (this vol., i, 500) it is stated that acids formed from co-ordinated boron compounds, $[(HO)_2BO]H$ and its derivatives are strong, but derivatives of boron trihydroxide, $B(OH)_3$, are neutral. Equilibrium exists between the two forms where an oxygen atom neutralises two of the co-ordination valencies. L. J. H.

New Type of Alkali Borate: Pentaborates. V. AUGER (*Compt. rend.*, 1925, **180**, 1602—1604).—Alkali borates are known of the following types: MBO_2, $M_2B_4O_7$, $M_2B_{10}O_{16}$, $Li_2B_8O_{13}$ (Le Chatelier, A., 1897, ii, 448), and probably $Na_2B_8O_{13}$ and $Na_2B_6O_{10}$ (A., 1915, ii, 449). Fractional crystallisation of potassium tetraborate in the presence of a large excess of boron trioxide yields boric

acid, decaborate, and tetraborate between the temperature limits −3° and +80°. Solutions in which the ratio B/K is 2·5/1 yield at 115—120° microcrystalline prisms having the composition $K_2HB_5O_9,2H_2O$. If a concentrated solution of potassium tetraborate is heated in a sealed tube at 115—120° and seeded with the pentaborate this substance is very readily formed.

The sodium salt is formed by simple heating of borax and water to 115° in a sealed tube. R. A. M.

X-Ray Investigation of the Crystalline Nature of China Clays etc. G. SHEARER (*Trans. Ceram. Soc.*, 1923—1924, **23**, 314—317).—The *X*-ray spectra of powdered (1) china clay, (2) equimolecular mixtures of china clay and alumina, (3) mixtures of china clay (1 mol.) and alumina (2 mols.) and (4) alumina, after being heated at 1200° and 1700°, were obtained, together with that of natural sillimanite. Sillimanite is the principal constituent of china clay after heating at 1200° or 1700°. The mixture (2) consisted of free sillimanite and free alumina, as did the mixture (3) after heating at 1200°. A new crystalline constituent had been produced in (3) on heating at 1700°. The crystals present in the clay were neither very large nor very small. H. S. H.

Dehydration of Kaolinite. J. V. SAMOILOFF (*Trans. Ceram. Soc.*, 1923—1924, **23**, 338 339).—From a study of the thermal phenomena observed on heating various minerals it is concluded that on dehydration kaolinite is decomposed into Al_2SiO_5 and silica. The characteristic exothermic reaction about 900° is due to the molecular rearrangements of Al_2SiO_5, the same exothermic reaction being observed with allophane. H. S. H.

Action of Heat on Kaolinite and Other Clays. I. J. W. MELLOR and A. SCOTT (*Trans. Ceram. Soc.*, 1923—1924, **23**, 322—329).—The dehydration of kaolinite does not take place at a fixed temperature and is completed above 500°. Kaolinite when heated at about 500° decomposes into silica, alumina, and water. The critical point about 900° is connected with a transformation in the form of the alumina set free about 500°. Sillimanite of the same composition as the natural mineral can develop below 1200°, and probably forms above that temperature solid solutions with $3Al_2O_3,2SiO_2$. A new compound, which may be $3Al_2O_3,2SiO_2$, is formed when kaolinite is heated at 1700°. H. S. H.

Reaction of Siloxen with Halogen Compounds. H. KAUTSKY and H. THIELE (*Z. anorg. Chem.*, 1925, **144**, 197—217; cf. A., 1924, ii, 852).—The ⋮SiH groups in siloxen, $Si_6H_6O_3$, react with halogen acids, alkyl and aryl halides, and halogenoacetic acids according to the equation ⋮SiH+RX=⋮SiX+RH, where X is chlorine, bromine, or iodine. When gaseous hydrogen bromide is used monobromosiloxen is formed quantitatively, proving the presence of 6 silicon atoms in the molecule of siloxen. In the presence of water, ammonia, or amines, the halogen compounds first formed are decomposed: ⋮SiX+H_2O=SiOH+HX, ⋮SiX+2R·NH_2=⋮SiNHR+R·NH_3X. The reaction with organic halogen compounds does not

take place between the pure substances in the dark, but may be made sensitive to long wave-lengths by the presence of substances which absorb these, such as oxysiloxen or suitable dyes; the reaction products, oxy-, halogen-, or amino-siloxens, being absorbent, act as auto-sensitisers. The reaction may also be induced in the dark by other reactions, such as the oxidation of a trace of the siloxen with oxygen or the production of the siloxen *in situ* from calcium silicide and hydrochloric acid. The system siloxen–oxygen can act as a powerful oxidising agent, chloroform or carbon tetrachloride being oxidised in the dark to carbonyl chloride. A. G.

Action of Some Gases on Silicates. H. VON WARTENBERG (*Z. anorg. Chem.*, 1925, **142**, 335—336).—Metals cannot be kept in a reducing atmosphere at 1200° or 1300° in vessels of silica or porcelain without the production of appreciable quantities of silicon. The presence of ferrous oxide in porcelain also leads to reactions such as the absorption of chlorine, which has been observed at 1000°. Owing to slow penetration of the walls by the gas the action may continue over a very considerable time. L. J. H.

Treatment of Malacon. Separation of Celtium [Hafnium] from Zirconium. (MLLE.) M. MARQUIS, P. URBAIN, and G. URBAIN (*Compt. rend.*, 1925, **180**, 1377—1380; cf. A., 1922, ii, 463; 1923, ii, 80).—Malacon is a zirconium silicate from Madagascar, containing small amounts of celtium, thorium, rare earths (mainly yttrium group), iron, titanium, niobium, uranium, and traces of tantalum. It can be decomposed by sulphuric acid or potassium hydrogen sulphate. The strong aqueous solution of sulphates is treated with potassium sulphate in excess, when the double sulphates of zirconium and celtium are precipitated. The double sulphate of zirconium and potassium is distinctly less soluble than the celtium analogue. The fractionation must be carried out in strongly acid solutions or else hydrolysis occurs. Complex oxalates, tartrates, and carbonates can be prepared, but separation is best effected through the double carbonates. If a mixture of zirconium and celtium salts is repeatedly treated with saturated sodium carbonate solution the first liquors are rich in zirconium and poor in celtium. The zirconium complexes are more stable than those of celtium and celtia is a stronger base than zirconia. Alkali precipitates zirconium before celtium from mixtures of simple salts, but in complex salts the reverse is true. The method of separation which follows from the above results is described.

The authors regard photographic quantitative analysis by *X*-ray spectra (Coster and Hevesy) as untrustworthy. R. A. M.

Quadrivalent Lead. J. ŠTĚRBA-BOHM and M. AUERSPERGROVÁ (*Rec. trav. chim.*, 1925, **44**, 390—399).—An unsuccessful attempt has been made to prepare lead disulphide (PbS_2) by the action of hydrogen sulphide on lead dioxide. The action of gaseous hydrogen sulphide in an atmosphere of carbon dioxide results in a product containing some combined and some free sulphur. The total sulphur found at the ordinary temperature was 4·16% (ratio

of combined to free =1 : 1·61) and with increasing temperature rose to a maximum of 20·87% (ratio of combined to free =1 : 1) at about 100°. With higher temperatures, the total sulphur and the proportion of free sulphur showed a decrease owing to evaporation of the latter. It is probable that the following reactions occur: (i) $PbO_2+H_2S=PbO+S+H_2O$; (ii) $PbO_2+2H_2S=PbS+S+2H_2O$; and that at 100° (ii) is predominant. By the action of liquid hydrogen sulphide at the ordinary pressure reaction (i) appears to prevail. An aqueous solution of potassium sulphide reacts very slowly with lead peroxide forming, probably, lead sulphide. In all cases the action is incomplete. Gaseous hydrogen sulphide gives lead sulphide only with a methyl-alcoholic solution of lead tetrachloride. Improved methods for the determination of lead and sulphur are described. N. H. H.

Chromates of the Metals of the Cerium Group. F. Zambonini and G. Carobbi (*Rend. Accad. Sci. Fis. Napoli*, 1925, [iii], **31**, 17—24).—The anhydrous chromates of lanthanum, praseodymium, and neodymium were obtained by heating intimate mixtures of the chlorides of these metals with potassium chromate to temperatures above 600°. A similar attempt to prepare anhydrous cerium chromate at 1000° resulted in the formation of a mixture of chromium sesquioxide and cerium dioxide. In addition to the octahydrates of the above salts prepared by Britton (A., 1924, ii, 763), the following new hydrates were prepared by precipitation methods from cold solutions. $La_2(CrO_4)_3,H_2O$, $Nd_2(CrO_4)_3,10H_2O$, $Pr_2(CrO_4)_3,10H_2O$, $Sm_2(CrO_4)_3,9H_2O$. F. G. T.

Solid Hydrides of Arsenic and Antimony. G. Druce (*Chem. Listy*, 1925, **19**, 156—157).—With aqueous sodium hydroxide trihydrogen arsenide yields sodium arsenide, which is immediately hydrolysed with the formation of solid dihydrogen diarsenide and the evolution of hydrogen. In a similar way, trihydrogen antimonide yields sodium antimonide, which with hydrochloric acid gives the solid dihydrogen diantimonide and hydrogen. The solid antimonide is also obtained when a solution of sodium hydroxide is electrolysed with an antimony cathode. A. R. P.

Solid Antimony Hydride. E. J. Weeks and J. G. F. Druce (*J. Chem. Soc.*, 1925, **127**, 1069—1072).—Stibine was passed over solid sodium hydroxide, which became coated with a grey deposit. When the latter was treated with water, hydrogen was evolved, and the grey residue, after washing with dilute hydrochloric acid and drying in a vacuum desiccator, consisted of amorphous antimony dihydride, Sb_2H_2. The reactions involved may be expressed by (1) $SbH_3+3NaOH \longrightarrow SbNa_3+3H_2O$, and (2) $2SbNa_3+6H_2O \longrightarrow Sb_2H_2+6NaOH+2H_2$. The same compound may also be obtained by the electrolysis of sodium hydroxide at an antimony cathode. Antimony dihydride is slightly decomposed when heated in hydrogen at a dull red heat, and completely decomposed at a higher temperature. W. H.-R.

Amphoteric Hydroxides. II. Tantalic Acid and Alkali Tantalates. G. JANDER and H. SCHULZ (*Z. anorg. Chem.*, 1925, **144**, 225—247; cf. A., 1923, ii, 772).—Preparations of tantalic acid made by the addition of nitric acid to aqueous sodium tantalate at 0° and 100° both showed hysteresis loops in the moisture content–vapour pressure curves. Alkali tantalates were prepared by fusing the hydroxides with tantalum pentoxide and crystallising from water; tantalic acid is precipitated from the aqueous solutions by acids, including carbonic acid, but the precipitate is soluble in excess of strong acid. Different proportions of potassium hydroxide and tantalum pentoxide always lead to the same crystalline tantalate; from highly concentrated solutions crystals of different form were obtained but these were readily converted into the first form and probably differed only in water of crystallisation. By the addition of sodium hydroxide to aqueous potassium tantalate two sodium salts, also differing only in water of crystallisation, were obtained and a lithium tantalate was similarly prepared. Analysis showed that each of these salts contained alkali metal and tantalum in the atomic proportion 7 : 5, and not 4 : 3 as has been found previously; the data agree with the formulæ $7K_2O,5Ta_2O_5,24H_2O$; $7Na_2O,5Ta_2O_5,22H_2O$; $7Na_2O,5Ta_2O_5,40H_2O$, and $7Li_2O,5Ta_2O_5,40H_2O$.

The acid is probably a complex acid in which the oxygen atoms of orthotantalic acid have been replaced by TaO_4 groups: $H_7[Ta(TaO_4)_4]$. The molecular weight of the potassium salt, as determined by comparing the diffusion coefficient with that of sodium hexamolybdate periodate, is 1750 compared with the calculated value of 1450 and is thus of the right order of magnitude; conductivity data indicate that the acid is at least hexabasic.

A. G.

Preparation and Properties of Disulphur Difluoride. M. CENTNERSZWER and C. STRENK (*Ber.*, 1925, **58**, [*B*], 914—918; cf. A., 1924, ii, 167).—The approximate physical constants of disulphur difluoride, obtained by heating silver fluoride with sulphur, are m. p. −105·5°, b. p. −99°, d^{-100} 1·5, mol. wt. 93·2. The gas yields a yellow or white deposit when introduced into a dry, vacuous flask, but decomposition ceases after 12—24 hrs. and the "purified" gas then gives no deposit when brought into a second flask and does not attack mercury (contrast *loc. cit.*). Disulphur difluoride does not appear to be completely stable towards heat. Its production from sulphur and silver fluoride is probably accompanied by that of other fluorides of sulphur, some of which are relatively difficultly volatile.

H. W.

Formation and Decomposition of Polythionates. F. FOERSTER (*Z. anorg. Chem.*, 1925, **144**, 337—340).—Although the intermediate formation of sulphoxylic acid in the reaction between sulphur dioxide and hydrogen sulphide in aqueous solution cannot be detected, the author considers that the assumption is justified by analogy with the reaction between sulphur dioxide and selenium dioxide. That thiosulphuric and sulphuric acids are the primary

products of the hydrolysis of trithionic acid may be shown by maintaining a mixture of potassium trithionate and potassium acetate at 50° for some days; in the absence of potassium acetate, the sulphuric acid formed in the reaction decomposes the thiosulphuric acid with the formation of sulphur dioxide and sulphur owing to the sensitiveness of thiosulphuric acid to hydrogen ions (cf. Riesenfeld, this vol., ii, 229; Foerster, *ibid.*, 148; and Foerster and Hornig, A., 1923, ii, 23). A. R. P.

Influence of Hydrogen Ions on the Mechanism of the Reduction of Ferric Salts by Sodium Thiosulphate. J. HOLLUTA and A. MARTINI (*Z. anorg. Chem.*, 1925, **144**, 321—326).—The mechanism of the reduction of ferric salts by sodium thiosulphate may be expressed as follows: (1) $Fe^{\cdot\cdot\cdot}+2HS_2O_3' \rightleftharpoons [Fe(S_2O_3)_2]'+2H^{\cdot}$; (2) $[Fe(S_2O_3)_2]'+Fe^{\cdot\cdot\cdot}=2Fe^{\cdot\cdot}+S_4O_6''$; (3) $H^{\cdot}+S_4O_6''=HS_4O_6'$. The reaction is retarded by the addition of acids in a similar way to the action of neutral salts; with excess of hydrogen ion reaction (1) goes from right to left, whereas a small amount of acid (0·05 mol. per litre) increases the concentration of the ferric ions by repressing hydrolysis and consequently accelerates reaction (2). As the acidity of the solution increases, a side reaction of the fourth order commences to take place thus, (4) $2Fe^{\cdot\cdot\cdot}+2HS_2O_3'=2Fe^{\cdot\cdot}+HS_4O_6'+H^{\cdot}$, and when the acidity exceeds 0·5*N* this becomes the sole reaction that takes place. With very high acidity, the thiosulphate slowly decomposes into sulphite and sulphur and the velocity constant of (4) rapidly falls. A. R. P.

System Chromium-Hydrogen. G. F. HÜTTIG and F. BRODKORB (*Z. anorg. Chem.*, 1925, **144**, 341—348).—Chromium, electrolytically deposited at −50° from concentrated solutions of chromic acid containing a little chromic sulphate, may contain up to about 0·45% H, which appears to be present in the form of a supersaturated solid solution. At the ordinary temperature, the hydrogen pressure of this chromium is less than 1·0 mm., but at 58° a sudden evolution of hydrogen takes place, although a temperature of 350° is required in order to remove the whole of the gas. No reproducible relations between temperature, pressure, and hydrogen concentration could be established. *X*-Ray examination showed that hydrogen increases very slightly the lattice parameter of chromium. Electrolytic chromium free from gas has d_4^{25} 7·138±0·003 and d_4^{50} 7·156±0·001, hence its atomic volume is 7·286 at 25° and 7·268 at −50° and its coefficient of expansion between −50° and +25° is $1·2\times10^{-5}\pm0·3\times10^{-5}$. A. R. P.

Composition of Rust. R. STUMPER (*Bull. Soc. chim. Belg.*, 1925, **34**, 150—158).—Analyses of many samples of iron rust show that this material has a very variable composition but always contains ferrous oxide and a greatly preponderating amount of ferric oxide; representing its composition as xFeO,yFe$_2$O$_3$,zH$_2$O, $x=1$, $y=2$ to 20, and $z=2$ to 30. On allowing iron to rust in water the percentage of ferrous oxide to total oxides falls hyperbolically with the time; thus after 1 day the rust contains

43·3% FeO, after 5 days 22·7% FeO, and after 15 days 9·5% FeO. Extrapolation of this curve to zero time indicates that the oxide first formed during the rusting of iron is ferrous oxide and this becomes further oxidised to ferric oxide at a rate that decreases rapidly at first with the time, then more slowly, finally approaching an equilibrium. A. R. P.

Precipitation of Ferric Salts with Ammonium Sulphide. H. Křepelka and W. Podroužek (*Rec. trav. chim.*, 1925, **44**, 416—424).—The composition of the precipitate obtained by the interaction of colourless ammonium sulphide solution and ferric salt solutions (in an atmosphere free from oxygen) is investigated. The composition of the precipitate depends on the hydrogen-ion concentration, and therefore on the iron salt employed, the concentrations of the solutions, and the velocity of addition. Concentrated ferric salt solutions and very dilute solutions of ammonium sulphide give a mixture of ferrous sulphide and free sulphur, the reaction occurring in acid medium and the ferric ion attaining an oxidation potential sufficiently high to oxidise the sulphide ion of the ammonium sulphide. If the ferric salt be precipitated with a concentrated solution of ammonium sulphide (ordinary analytical conditions), the hydrogen-ion concentration falls below the necessary minimum before the reaction is complete, and the precipitate consists of a mixture of ferrous and ferric sulphides and free sulphur. The free sulphur cannot be abstracted in stoicheiometric amount because of the presence of water (probably of hydration) which cannot be removed by washing the precipitate with alcohol. Very concentrated solutions of ammonium sulphide and dilute ferric salt solutions (and therefore the slow addition of the ferric salt solution to the ammonium sulphide) yield only ferric sulphide. If all the ferric salt is not separated from the solution the ferric sulphide is unstable and undergoes the spontaneous reaction: $Fe_2S_3=FeS+FeS_2$ (cf. Mecklenburg and Rodt, A., 1918, ii, 167), and the ferrous sulphide then reacts with the surplus of ferric ions: $2FeS+2Fe_2(SO_4)_3=6FeSO_4+2S$ (cf. Budnikov and Krause, A., 1922, ii, 782). J. W. B.

Potassium Chlororuthenates and the Co-ordination Number of Ruthenium. S. H. C. Briggs (*J. Chem. Soc.*, 1925, **127**, 1042—1048).—In contradiction to the co-ordination theory, apparently isomeric forms of the compound K_2RuCl_5,H_2O, were reported by Howe (A., 1902, ii, 86) and by Miolati and Tagiuri (A., 1901, ii, 246), and this discrepancy is examined. According to the conditions, the addition of potassium chloride to a cold acidified solution of ruthenium trichloride results in the formation of one or both of the two compounds K_2RuCl_5,H_2O and $2K_2RuCl_5,3H_2O$, both of which belong to Miolati's series, and give yellow solutions unaffected by chlorine or bromine vapour. The only salt of Howe's series has composition $2K_2RuCl_5,3H_2O$, and is prepared either by the action of alcohol and hydrochloric acid on Miolati's salt or on a mixture of ruthenium trichloride and potassium chloride. In either case, the mixture is boiled, the alcohol distilled off, and the

solution kept for 1 week before being evaporated to crystallisation. Howe's salt gives an intensely black coloration with chlorine or bromine, the colour becoming yellow after prolonged action, and Miolati's salt can then be isolated from the yellow solution. A hot acidified solution of Howe's salt is oxidised on exposure to air, yielding a *compound*, K_2RuCl_5,K_2RuCl_5OH. These compounds require a higher co-ordination number than 6, and 8 is the most probable value. W. H.-R.

Intermediate Compound of High Molecular Weight in the Decomposition of [Pt en$_2$]I$_2$ by Acids. A. SCHLEICHER and W. SCHMITZ (*Z. anorg. Chem.*, 1925, **142**, 367—372; cf. A., 1923, i, 1120). —By the treatment of [Pt en$_2$]I$_2$ with dilute sulphuric acid a compound is obtained to which the structural formula

$$\begin{matrix} & \text{en} & 5H_2O & \text{en} & \\ [H_2O\text{---}Pt & \text{---} & I & \text{---} & Pt\text{---}H_2O]I,5H_2O \\ & \text{en} & 5H_2O & \text{en} & \end{matrix}$$

is assigned. Simultaneously precipitated iodine leads to decomposition to platinous iodide and the formation of ethylenediamine sulphate, a reaction brought about immediately by strong acids. The propylenediamine compound behaves similarly. L. J. H.

Preparation of Dust-free Liquids by Distillation. J. D. GARRARD (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 126—127).—An investigation of the conditions under which dust-free water may be obtained by distillation in a vacuum without ebullition shows that, provided "bumping" be avoided, neither the temperature of distillation nor the temperature difference between the two bulbs employed as distillation vessel and receiver has any appreciable effect on the number of motes in the distillate, and the distillation bulb may safely be taken to complete dryness. "Steaming-out" is the most satisfactory method of cleaning prior to filling. Determinations of the scattering of light in water prepared in various types of glass show that whereas the use of soft soda, Pyrex, or Jena ware yields sensibly identical values, water obtained in lead-glass apparatus has a scattering power 20—40% higher. The dust-free water is invariably contaminated with particles on shaking even after agitation, rinsing back, and redistilling as often as twenty times. J. S. C.

Purification and M. P. of Potassium and Sodium Cyanides. GRANDADAM (*Compt. rend.*, 1925, **180**, 1598—1599; cf. this vol., 419). —Neutralisation of hydrocyanic acid by alcoholic potassium hydroxide results in a product which is only 99% pure. A better product is obtained by purifying the commercial product (95%) in an absolutely anhydrous medium. Fractional vacuum distillation was unsatisfactory (Bucher, *J. Ind. Eng. Chem.*, 1917, **9**, 233). In opposition to Bronn, the alkali cyanides are appreciably soluble in liquid ammonia at −33·5° (roughly 4%). The usual impurities (carbonate, cyanate, hydroxide) are much less soluble. Recrystallisation from anhydrous ammonia gave products 99·9% pure by

determination with silver. The only two ordinary metals in the presence of which this degree of purity could be maintained were silver and gold. No reaction occurred in the absence of oxygen and moisture. The gold–silver couple possesses feeble thermo-electric properties, but this difficulty was overcome by the aid of a very sensitive galvanometer. The m. p. found were, sodium cyanide $563{\cdot}7\pm0{\cdot}3°$; potassium cyanide $634{\cdot}5\pm1°$. R. A. M.

Formation of Aluminium Borides. H. FUNK (*Z. anorg. Chem.*, 1925, **142**, 269—279).—Mixtures of aluminium turnings, magnesium powder, sulphur, and boron trioxide were heated in a crucible lined with aluminium oxide to which a small proportion of pipe-clay was added as binding material. From the regulus crystals of aluminium borides could be obtained. On melting these the liquid formed two layers, the upper layer yielding mainly crystals of the formula AlB_2. Crystals of composition closely approximating to AlB_{12} were also obtained. High temperature and excess of boron favour the formation of the latter, low temperature and excess of aluminium the former. L. J. H.

Preparation and Properties of Carbides. E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **144**, 169—189).—Carbides of titanium, zirconium, vanadium, tantalum, and niobium were prepared pure by heating the oxides with the calculated weights of carbon at temperatures of 1100° to 1900°; impure *scandium carbide* was obtained by fusing the oxide–carbon mixture at 3000° and probably has the formula Sc_4C_3. Carbides of molybdenum, tungsten, and silicon were prepared from the metals. Melting points were determined by measuring the energy radiated at the m. p. (cf. this vol., ii, 419) or with an optical pyrometer; those of niobium and tantalum carbides, 4000—4100°, are the highest recorded for chemical compounds. All the above carbides, except that of silicon, are good conductors of electricity. A. G.

Separation of Zirconium from its Ores as Phosphate. J. H. DE BOER [with A. E. VAN ARKEL] (*Z. anorg. Chem.*, 1925, **144**, 190—196).—For the separation of zirconium, the ore is fused with potassium hydrogen sulphate, the fused mass extracted with water, and the metals precipitated as hydroxides and redissolved in concentrated hydrochloric acid. From the strongly acid solution zirconium is precipitated as the phosphate, $Zr(HPO_4)_2$, and is thereby separated from all other metals except hafnium. The phosphate is readily washed by decantation with hydrochloric acid and water and may then be dissolved in hydrofluoric acid and the zirconium reprecipitated as hydroxide. Similarly, hafnium may be isolated, and zirconium and hafnium may probably be separated by utilising the different solubilities of the complex acids formed when the phosphates are dissolved in hydrofluoric acid. A. G.

Generation of Hydrogen Sulphide. A. HENWOOD, R. M. GAREY, W. GOLDBERG, and E. FIELD (*J. Franklin Inst.*, 1925, **199**, 685—686).—A copious supply of pure hydrogen sulphide may be obtained by gently heating a mixture of sulphur and paraffin wax.

Removal of the spent charge is facilitated by the previous admixture of ignited asbestos. F. G. T.

Production of Ozone by Silent Discharge at Low Pressures. E. WARBURG and W. RUMP (*Z. Physik*, 1925, **32**, 245—251).—Siemens tubes were used in which the passages for the gas varied from 1 to 3·5 mm. in width. The oxygen contained 3·5% of nitrogen, and the potential varied from 5000 to 9000 volts. As the pressure was reduced the current across the tube increased, but the yield of ozone diminished, at first slowly, then more rapidly, and for pressures below 200 mm. it was proportional to the pressure. With air the yield of ozone is greater than the value corresponding with the partial pressure of the oxygen. E. B. L.

Theory of Chemical Action in Siemens Ozone Tubes. E. WARBURG (*Z. Physik*, 1925, **32**, 252—261).—The problem is treated as one of ionisation by collision, and it is assumed that negative ions are all electrons and that positive ions are oxygen molecules. Calculation shows that 6 to 9% of the electron impacts and very few of the collisions of the positive ions produce ozone. As the number of impacts is inversely proportional to the free path it is directly proportional to the pressure, thus accounting for the reduced yield when the pressure is reduced (cf. preceding abstract). The theory does not account satisfactorily for the effect of width of the layer of gas nor for the inefficiency of high-frequency alternating current. E. B. L.

[Ultra-balance.] W. H. F. KUHLMANN (*Ber.*, 1925, **58**, [*B*], 961).—A comment on the communication of Holtz and Kuhlmann (this vol., ii, 319). H. W.

Calcspar Lenses for Intense Polarised Light. W. SCHÜTZ (*Z. Physik*, 1925, **32**, 502—504).—When passed through a calcspar lens cut parallel to the optic axis, the ordinary ray forms an image nearer to the lens than that of the extraordinary ray. The former can be blocked out and the latter used as a source of polarised light. Still more effective is a combination of two lenses which may be made to act either as a parallel plate or as a diverging lens for one ray while converging the other. As the ratio of the refractive indices of the two rays varies but slightly with the wave-length, the one system can be used throughout the spectrum. E. B. L.

Photographic Plates for Detection of Mass Rays. F. W. ASTON (*Proc. Camb. Phil. Soc.*, 1925, **22**, 548—554).—In early work on positive-ray spectra, "landscape" plates, Schumann plates made by the original method, and "half-tone" plates were successively used. Very slight changes in the gelatin employed in the emulsion affect the sensitivity of plates to mass-rays. Emulsions containing much gelatin are very insensitive to the mass-rays of the heavier elements, and in studying these it was finally found necessary to "schumannise" the "half-tone" plates by dissolving away the gelatin in sulphuric acid. The details of this somewhat difficult procedure

are given. The sensitivity of the plates so prepared is very variable and cannot be completely controlled, but at their best they are very sensitive. S. B.

Constant-level Water Baths. H. J. WING (*Ind. Eng. Chem.*, 1925, **17**, 630).—An easily constructed modification of Brooks' apparatus (cf. A., 1924, ii, 669) may be made by using a Gooch crucible filtering tube, a small wide bottle, etc., as the main part, and four suitable glass tubes. The amount of water entering must not be greater than can be carried off by the fall tube, which should empty as far below the water surface as possible, and not be large enough to allow the back passage of air. The overflow tube must be longer than that which carries off the excess water from the bath. D. G. H.

Micro-furnace for High Magnifications. H. S. ROBERTS and T. STADNICHENKO (*J. Opt. Soc. Amer.*, 1925, **10**, 605—608).—To permit the use of a 16-mm. objective, a microscope stage furnace was constructed, the heating element of which was a doubled strip of nichrome ribbon. The charge was inserted into the fold of the heater between two strips of silica glass. Oxidation was prevented by the circulation of helium through the furnace. A current of 40 amp. through the heater produced a temperature of 800°. F. G. T.

Vacuum Door. R. F. MEHL and D. P. SMITH (*Ind. Eng. Chem.*, 1925, **17**, 598).—An inner steel tube and a surrounding glass tube stand in mercury. The outer tube is prolonged at the top into a bulb connected to the vacuum system and containing the plugged end of the steel tube together with the section just below, bored with small holes. Evacuation raises the mercury level in both tubes to barometric height, which is just below the bulb, and a slow stream of the gas to be admitted to the system is bubbled up the steel tube. Mercury and gas are discharged into the bulb, and the mercury level quickly adjusts itself to the new pressure. D. G. H.

Laboratory Pump. D. H. CAMERON (*Ind. Eng. Chem.*, 1925, **17**, 585).—The circulating liquid flows by gravity to the beaker containing the inlet valve of the pump which is operated by suction from a water vacuum pump. The pump consists of a vertical glass cylinder with a check valve at the bottom (cf. A., 1923, ii, 65) and connected at the top with the vacuum system, and also by means of an inverted U-tube and vertical tubing, to a flexible rubber tube carrying the short-stemmed inlet funnel. This is provided with a cork float and is clamped so that it swings in the beaker with the altering liquid level. When air is no longer free to pass through the inlet valve, liquid is drawn in until suction is broken by the level in the beaker falling below the upper edge of the funnel; air is then again admitted, the check valve opens, and the liquid is discharged from the pump by gravity. D. G. H.

Use of Long Mercury Manometers. E. SWAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1341—1342).—A method is given for the construction of a mercury manometer. J. S. C.

Improved Fischer Vacuum Fractionator. L. SATTLER (*Ind. Eng. Chem.*, 1925, **17**, 583).—The chief modifications consist in two traps to prevent the distillate from being carried into the vaccum pump, and a reservoir in which the distillate collects during the changing of the receiver, whilst strain is removed from the apparatus by introduction of a coil between two stopcocks. D. G. H.

Microturbidimeter. O. E. CONKLIN (*J. Opt. Soc. Amer.*, 1925, **10**, 573—580).—Rapid measurements of the comparative turbidities of small amounts of liquids may be made with a microscope cell consisting of a plano-convex lens placed convex side downwards on a piece of plate glass. The sample fills the space between these, its thickness increasing outwardly from the point of contact. The cell is placed over an electric lamp having a straight filament, so that the filament crosses the point of contact. For a constant current consumption of the lamp, the length of filament visible through the cell is inversely proportional to the square root of the turbidity of the liquid. A piece of flashed opal glass in which a concave lens has been ground just cutting through the opal coating is used as a turbidity standard. A lever device is described for measuring the length of the visible filament in the absence of a stage micrometer. For photographic emulsions the turbidity is proportional to the concentration of the silver halide. The relative and specific turbidities of a number of fluids are compared, measurements being reproducible to within 2%. F. G. T.

Automatic Devices for Extracting Alkaloidal Solutions. S. PALKIN, A. G. MURRAY, and H. R. WATKINS (*Ind. Eng. Chem.*, 1925, **17**, 612—614).—Aqueous solutions may be extracted with an immiscible solvent by connecting the solvent boiling flask with the side arm of the tubular extractor which contains the solution to be extracted. In the case of heavy solvents a long wide tube open at each end is employed, whilst for light solvents a long funnel tube provided at the bottom with small holes is placed through the two layers of liquid, projecting well above them. Substances more difficult of extraction demand rather more complicated apparatus in which the solvent enters the liquid wholly or partly in the form of vapour. D. G. H.

Modified Soxhlet Extraction Apparatus. B. KÖHLER (*Collegium*, 1925, 187—188).—The apparatus consists of a small squat flask fitted with a wide tube and ground glass connexion. The tube is bent at right angles and passes into the upper portion of the Soxhlet receptacle which contains the material to be extracted, and is fitted with condenser and ground glass connexion. From the bottom of the receptacle, a siphon tube leads back to the flask. The end of the siphon tube can be attached to a filter-pump after extracting the material and the extracted material can be recovered quantitatively. D. W.

Discovery and Properties of Hafnium. G. HEVESY (*Chem. Reviews*, 1925, **2**, 1—41).

Mineralogical Chemistry.

Structure of Iron-Nickel Meteorites. R. VOGEL (*Z. anorg. Chem.*, 1925, **142**, 193—228).—There is a break in the composition curve of mixed crystals of iron and nickel at 1455°, corresponding with the δ—γ inversion. At the transition point the δ-mixed crystals contain 6%, and the γ-mixed crystals 30% Ni. The structure of the meteoric material does not differ essentially from that of synthetic alloys. Kamazite and taenite are respectively the δ- and γ-mixed crystals, with their nickel content variable as a result of supersaturation. The former is deposited primarily from the fused mass, the latter mainly secondarily as a result of the phase change at the transition point. Plessite consists of supercooled, supersaturated crystals, either from the fused mass as a whole or, more usually, from the mass remaining after the separation of the kamazite. All these structures are unstable at the ordinary temperature and are converted, by suitable annealing, into homogeneous γ-mixed crystals, the rate of conversion depending on the nickel content as well as on the temperature, being faster for the alloys poorer in nickel. Impurities also greatly affect the rate of conversion. Etching figures are discussed in relation to structure, and a system of classification of the meteoric alloys is offered. L. J. H.

Lead Sulphobismuthite of Volcanic Origin. F. ZAMBONINI, O. DE FIORE, and G. CAROBBI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1925, [iii], **31**, 24—29).—A crystalline mineral, for which the name cannizzarite is proposed, has formed since 1921 in the lower parts of fumaroles on Vulcano (Isole Eolie, Lipari Islands), where the emission of acid volcanic gases is greatest and access of air is prevented. The temperature of the region is 550—615°. The crystallographic constants were not determined accurately, but the mineral appears to be of rhombic habit, and isogonal with bismuthinite and antimonite in the 001 zone. d^{10} 6·54. The analysis corresponds with the formula $PbS,2Bi_2S_3$. It is probably formed by the action at high temperatures of hydrogen sulphide on the chlorides of bismuth and lead. F. G. T.

Properties and Occurrence of Zeolites. O. WEIGEL (*Sitzungsber. Ges. Beförder. ges. Naturwiss. Marburg*, 1924, 73—101; from *Chem. Zentr.*, 1924, ii, 2239).—In the formation of zeolites, the solvent remains within the interstices of a comparatively rigid silicate lattice without participating in its structure. The atoms of the silicate lattice lose energy, necessary for overcoming the internal pressure of the solvent, which serves for the formation of the lattice. The lattice on account of its rigidity remains unaffected under different conditions, whereby the energy of internal pressure becomes free, so that saturation by adsorption of other substances is possible. The readiness with which base exchange can take place is explained by the weakening of the linkings in the silicate lattice. The re-

lationship between temperature, vapour pressure, and the content of adsorbed molecules may be expressed by a modification of van der Waals' equation: $n=n/b-R(T-T_s)v^2/(v-nb)\sqrt{aa'}$, where n is the number of molecules adsorbed by each silicate molecule, T' is the temperature corresponding with the actual saturation pressure of the liquid phase of the adsorbed substance in the region of the adsorbing crystal, and R, T, v, a, and b have their usual significance. Experimental data gave good agreement with results calculated from the equation. G. W. R.

Combination of Water in the Zeolites. V. ROTHMUND (*Rec. trav. chim.*, 1925, **44**, 329—339).—A theoretical paper in which various views concerning the manner in which water is combined in the zeolites are critically examined and discussed. Examination of the vapour-pressure curves to determine whether definite hydrates exist has led to opposite conclusions in the hands of different investigators, some (Damour, Friedal, Tammann, Rinne) obtaining a continuous curve, others (Beutell and Blaschke) obtaining a "step" curve denoting the existence of definite hydrates. In the zeolites Böhm has shown that the loss and readsorption of water is not reversible, a "hysteresis" lag being observed over certain temperature ranges. Theories of absorption and solid solution are discussed and in this connexion it is noted that the dehydrated zeolites can reabsorb, in place of water, alcohol, bromine, iodine, etc. or ammonia, hydrogen, nitrogen, methane, and other gases (ammonia being most strongly absorbed), the quantity absorbed being of the same order of magnitude as in the case of charcoal and governed by the usual formula, $v=\alpha p^{1/n}$. In spite of their crystalline nature the zeolites closely resemble colloidal substances such as silica gel and permutite, and the author suggests that the processes of absorption of water by all "swelling" substances such as starch, albumin, etc. are similar phenomena. J. W. B.

Analysis of Alvite. S. BEDR-CHAN (*Z. anorg. Chem.*, 1925, **144**, 304—306).—A sample of pure alvite had the following composition: 25·65% SiO_2, 0·63% $TiO_2+Nb_2O_5+Ta_2O_5$, 2·08% CaO, 1·11% MgO, 2·05% ThO_2, 0·71% Ce_2O_3 etc., 7·57% Fe_2O_3, 41·92% ZrO_2, 4·66% HfO_2, 4·55% $BeO+Al_2O_3$, 6·30% H_2O, total 97·23%. The hafnia was determined by X-ray analysis and the other constituents by the usual methods. A. R. P.

Analytical Chemistry.

Apparatus for Accurate Analysis of Small Quantities of Gas. D. S. CHAMBERLIN and D. M. NEWITT (*Ind. Eng. Chem.*, 1925, **17**, 621).—An improved form of the Bone and Wheeler gas analysis apparatus (A., 1908, ii, 221) is described, with which samples of from 1 to 5 c.c. of gas can be analysed with an accuracy of 0·01%. M. B. D.

Automatic Burette and Flask for Standard Alkali Solutions. H. R. McMillin (*Ind. Eng. Chem.*, 1925, **17**, 592).—The burette is connected by a 3-way tap to a "pyrex" glass flask containing the standard solution. The flask is provided with a "suberite" ring, and evaporation from it is checked by means of potassium hydroxide solution, which together with a calcium chloride tube also excludes carbon dioxide. The apparatus is free from attachment and can readily be shaken. D. G. H.

Quantitative Spectral Analysis. W. Gerlach (*Z. anorg. Chem.*, 1925, **142**, 383—398).—Contrary to statements in the literature, the "ultimate" rays (last observed lines of an impurity as it is continuously removed) are the strongest under the conditions of exposure. Quantitative measurements of the amount of impurity remaining are possible by comparison of the intensity of these lines with that of neighbouring lines of the main substance, but standard exposures of specimens of known composition with the same principal substance are essential. L. J. H.

Graphic Comparison of Potential Scales and Electrode Potentials. L. J. Bircher (*Ind. Eng. Chem.*, 1925, **17**, 622).—The graphic representation of typical potential scales as vertical lines and the single potentials of typical half-cells as horizontal lines, with numbers indicating the potential values of the latter on the three standard scales, provides a sufficient number of typical junctions to enable others to be placed. D. G. H.

Electrometric Titration. J. C. Brünnich (*Ind. Eng. Chem.*, 1925, **17**, 631—632).—Electrometric titrations can be made without the use of hydrogen gas or a calomel cell by combining a pure graphite electrode with a platinum spiral electrode through a millivoltmeter. The potential given by this arrangement is approximately zero in neutral solutions, +0·18 volt in 0·01*N*-acid, and −0·13 volt in 0·01*N*-alkali. M. B. D.

Rapid Electroanalysis. Separations by Graded Potentials. A. Lassieur (*Ann. Chim.*, 1925, [x], **3**, 235—324).—A simple apparatus is described for rapid electroanalysis which permits of the use of graduated potentials. The experimental conditions are worked out for the determination of copper, bismuth, antimony, lead, and tin, and certain mixtures of these (cf. A., 1924, ii, 15, 568; this vol., ii, 159). Electrodes coated with antimony can retain lead when the concentration of the latter in the electrolyte is 2 g. per litre. Stannic chloride is reduced during the deposition of tin when the potential difference is 320 millivolts or more; antimony catalyses the reaction. The complex formed by adding hydrofluoric acid to an antimonious solution which has been oxidised by potassium chlorate is partly reduced on the passage of the current. This does not occur when potassium dichromate is used as the oxidising agent. [Cf. *B.*, July 24th.] S. K. T.

Calomel Electrodes. C. J. Schollenberger (*Ind. Eng. Chem.*, 1925, **17**, 649).—A satisfactory calomel electrode may be

made from a separating funnel by removing the stopcock, fusing on a length of glass tubing, inserting an inner tube projecting into the body of the funnel, and out through the stem. In this is placed the potassium chloride and the tube is jointed to the stem and plugged with a ground-in rod. This stopper is lightly pressed upon when the cork is inserted in the funnel. Calomel and mercury are placed in the funnel and contact with the mercury is established by means of a bent tube in the cork. [Cf. *B.*, July 24th.] D. G. H.

Calomel Half Cells for Industrial Hydrogen-ion Measurements. H. C. PARKER and C. A. DANNERTH (*Ind. Eng. Chem.*, 1925, **17**, 637—639).—Four easily controlled types of cells are described, the first for laboratory use with a ground glass joint sealed with mercury, the second a flow type with porous cup, the third a combined hydrogen electrode and calomel half cell, and the fourth a rugged industrial half cell entirely surrounded with bakelite casing. [Cf. *B.*, July 24th.] D. G. H.

Salt Error of Cresol-red. W. D. RAMAGE and R. C. MILLER (*J. Amer. Chem. Soc.*, 1925, **47**, 1230—1235).—The salt error of cresol-red in solutions containing 5 to 35 parts per 1000 of sea-salts has been determined from a comparison of the Sörensen values of samples of sea-water of known salinity as determined by electrometric and colorimetric methods using this indicator. The correction to be applied to the colorimetric determinations over the range of salinity indicated varies from −0·11 to −0·27 Sörensen unit. J. S. C.

Detection and Determination of Chloride, Bromide, and Thiocyanate in the Presence of Cyanide. E. SCHULEK (*Z. anal. Chem.*, 1925, **66**, 169).—The priority of Polstorff and Meyer's formaldehyde method (A., 1912, ii, 988) is acknowledged, but priority is claimed for the boric acid method previously described (this vol., ii, 432). A. R. P.

Determination of Iodide. E. SCHULEK (*Z. anal. Chem.*, 1925, **66**, 161—169).—The methods of Winkler (A., 1916, ii, 109) and of Bugarszky and Horváth (A., 1909, ii, 932) for the determination of iodide in the presence of chloride and bromide have been modified so that the whole operation can be conducted at the ordinary temperature. When much iodide is present together with bromide, the very faintly acid solution is treated with chlorine water until bromine begins to be displaced, and the liberated bromine is removed by addition of a 5% solution of phenol. The iodate formed is determined iodometrically after addition of potassium iodide and phosphoric acid. If only a small amount of iodide is present bromine water or alkali hypobromite may be used for the oxidation. The presence of magnesium or calcium salts interferes with the reaction. [Cf. *B.*, 1925, 543.] A. R. P.

Action of Some Oxidising Agents on Sulphate and its [Volumetric] Determination with Iodate. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1925, **47**, 1319—1325; cf. *J. Ind. Eng. Chem.*, 1922, **14**, 1152).—Previous work is continued. The amounts of

bromate and dichromate are less than those required for the complete conversion of sulphite into sulphate. This is probably due to the formation of some dithionic acid which resists further oxidation. Iodate completely oxidises to sulphate, and this fact permits of the accurate determination of sulphites by this oxidant. Solutions of potassium iodate maintain their concentration over indefinite periods of time. An electrometric method of end-point determination may be used for the determination of sulphites in coloured solutions. J. S. C.

Nessler's Reagent Without Potassium Iodide. L. W. WINKLER (*Z. Unters. Nahr. Genussm.*, 1925, **49**, 163—165).—The modified reagent is prepared by dissolving mercuric iodide in a solution containing potassium bromide and sodium hydroxide, preferably made with tap-water of medium hardness. With natural waters, the reagent may cause some precipitation. To prevent this, use is made of a second solution containing sodium potassium tartrate and sodium hydroxide in which mercuric iodide is dissolved. A. G. P.

Iodometric Methods Depending on the Formation and Determination of Cyanogen Iodide. III. R. LANG (*Z. anorg. Chem.*, 1925, **142**, 280—298; cf. below).—The method is extended to the determination of hydrazine and hydroxylamine (separately or together), selenium, hydrogen peroxide, cyanides, thiocyanates, and ferrocyanides. The last three may be determined in the presence of each other. L. J. H.

Determination of Oxides of Nitrogen (except Nitrous Oxide) in Small Concentration in the Products of Combustion of Coal Gas and in Air. A. G. FRANCIS and A. T. PARSONS (*Analyst*, 1925, **50**, 262—272).—The absorption of oxides of nitrogen in large volumes of air and products of combustion by solutions of sodium hydroxide and hydrogen peroxide (Allison, Parker, and Jones, *U.S. Bur. Mines, Tech. Paper* 249) leads to formation of nitrite. Oxidation is complete when the gases are shaken in a closed bottle with acidified hydrogen peroxide for 3 hrs. Proportions of less than 1 in 10^6 are determined by passing a measured volume of gases through tubes immersed in liquid air, and treating the condensate with the same hydrogen peroxide mixture. The normal proportion of nitric oxide in the air was found to be 1—2 in 10^8, falling to 0·3 after heavy rain, and rising to 15—16 during fog. S. I. L.

Iodometric Methods Depending on the Formation and Determination of Cyanogen Iodide. II. R. LANG (*Z. anorg. Chem.*, 1925, **142**, 229—256).—Previous work (A., 1922, ii, 782) is extended by the use of iodine monochloride and hypoiodous acid as oxidising agents, the iodine liberated being determined by titration with potassium iodate in acid solution in the presence of a cyanide. Antimony, arsenic, copper, and iron, or mixtures of the last three together, may be titrated in this way. The modifications necessary in the presence of other heavy metals, both for these reactions and

in the direct determination of iodide, are described, but the details are too numerous for abstraction. L. J. H.

Theory of the Titration of Boric Acid. M. CIKRTOVÁ and K. ŠANDERA (*Chem. Listy*, 1925, **19**, 179—182).—Boric acid may be titrated accurately with sodium hydroxide in the presence of a saturated solution of certain inorganic salts, such as calcium or lithium chloride, which are strong dehydrating agents, as is also glycerol, which is commonly added to the solution in order to increase the strength of the acid. This action appears therefore to be due to the dehydration of boric acid and not to the formation of complexes. A. R. P.

Determination of Boric Acid in Presence of Aluminium, Iron, or Chromium Salts. H. FUNK and H. WINTER (*Z. anorg. Chem.*, 1925, **142**, 257—268).—The removal of aluminium, chromium, or iron is necessary before boric acid can be determined by the method of Rosenbladt and Gooch (A., 1887, ii, 299), but precipitation with alkali carries down some boron which cannot be removed. A successful separation is obtained if iron be precipitated as phosphate from slightly acid solution, and chromium is precipitated as hydroxide by the addition of iodide and iodate. Both methods are satisfactory for aluminium. L. J. H.

Apparatus for Determining Carbon Dioxide. W. W. REED (*Chem. and Ind.*, 1925, **44**, 422).—In place of washing out the carbon dioxide by aspirating air through the apparatus, the gas is withdrawn by suction from the bottom of the flask, the calcium chloride tube being sealed to another tube, the height of which above the liquid is adjustable. R. B.

Determination of Dissolved Carbon Dioxide. R. LEGENDRE (*Compt. rend.*, 1925, **180**, 1527—1529).—A critical account of various methods of determination of dissolved carbon dioxide (cf. Winkler, A., 1904, ii, 215; 1912, ii, 1210; Haas, A., 1917, i, 433; Osterhout and Haas, A., 1918, ii, 24; Hall, A., 1923, ii, 507; Shipley and McHaffie, A., 1923, ii, 649; Lehmann and Reuss, A., 1923, ii, 697; Spoehr and McGee, A., 1924, ii, 275). In comparing the dissolved carbon dioxide content of different liquids it is of value to find the amount of alkali necessary to lower the hydrogen-ion concentration to a fixed level. The method of comparison chosen is that of passing air through the different samples of water maintained at a definite hydrogen-ion concentration and determining the amount of carbon dioxide carried over. This method is of use in analysing biological fluids and waters, and in investigating the respiratory exchange of aquatic animals. L. F. H.

Separate Determination of Potassium and Sodium in Urine. O. VON DEHN.—(See i, 855.)

Quantitative Variations of Homogeneous Mixtures of Two Salts and a New Indirect Method of Quantitative Analysis. G. COMELLA (*Annali Chim. Appl.*, 1925, **15**, 123—136).—A method is described for calculating from the titre of a solution containing

two salts, such as sodium and potassium chlorides, the proportions of the two in the mixture. *N*-Solutions of sodium and potassium chlorides contain respectively 58·46 g. and 74·56 g. of the salt per litre, and replacement of 0·1 c.c. of *N*-sodium chloride by 0·1 c.c. of *N*-potassium chloride decreases the amount of sodium chloride present by 0·005846 g., increases that of potassium chloride by 0·007456 g., and increases the sum of the two by 0·00161 g.; these quantities may be regarded as the common differences of three arithmetic progressions. Thus, if 63·29 g. of the mixed chlorides per litre are found to give a *N*-solution, the corresponding terms in these progressions will be in position 3001, since (63·29—58·46)/0·00161+1=3001. The amount of sodium chloride in 63·29 g. of the mixture is hence 58·46—(3000×0·005846)=40·922 g., and that of the potassium chloride, 3000×0·007456=22·368 g. T. H. P.

Nephelometric Determination of Calcium and Magnesium. L. KEISS.—(See i, 852.)

Determination of Small Quantities of Magnesium as Magnesium Ammonium Phosphate in Presence of Much Aluminium. G. JANDER, E. WENDEHORST, and B. WEBER (*Z. anorg. Chem.*, 1925, **142**, 329—334).—Contrary to Hahn (this vol., ii, 69), magnesium may be accurately determined as magnesium ammonium phosphate in presence of large quantities of aluminium (held in solution by tartaric acid), but the precipitate requires several days to form. L. J. H.

Quadrivalent Lead. [**Determination of Lead and Sulphur.**] J. ŠTÉRBA-BOEHM and M. AUERSPERGROVÁ.—(See ii, 699.)

Simultaneous Electrolytic Determination of Copper and Lead. H. BILTZ (*Ber.*, 1925, **58**, [*B*], 913—914).—Difficulties arise in the simultaneous anodic deposition of lead dioxide and cathodic separation of copper from solutions of the metals in nitric acid owing to the solvent action of nitrous acid on the dioxide. They may be overcome by electrolysing initially in moderately concentrated acid solution to which carbamide is added previously to dilution for completion of electrolysis; the process is continued until the copper has been deposited completely. H. W.

Qualitative Tests for Copper, Iron, and Cobalt. M. L. NICHOLS and S. R. COOPER (*J. Amer. Chem. Soc.*, 1925, **47**, 1268—1270).—Aqueous solutions of copper, iron, and cobalt salts give respectively brown, green, and orange-red precipitates (or colorations if in very dilute solution) with aqueous solutions of dinitrosoresorcinol. In neutral solution the reagent is capable of detecting 0·0040 mg. of copper, 0·0035 mg. of iron, and 0·0033 mg. of cobalt in 1 c.c. of solution. In dilute acid solution, the sensitiveness of the tests for cobalt and iron is increased by addition of sodium acetate. When testing for cobalt in presence of an excess of nickel, the concentration of the latter should be first reduced by treatment with dimethylglyoxime. J. S. C.

Titration of Mercury with Potassium Cyanide and Jellinek's Titration of Weakly Dissociated Salts. E. RUPP [with W. WEGNER and P. MAIHS] (*Z. anorg. Chem.*, 1925, **144**, 313—318).—The statements of Jellinek and Krebs (A., 1923, ii, 871) and of Jellinek and Kühn (A., 1924, ii, 695) that titration of mercuric chloride with potassium cyanide using phenolphthalein as indicator gives results that are 3% too low is shown to be erroneous provided that the cyanide used is pure, *i.e.*, that its cyanogen contents calculated from the argentometric and acidimetric titrations are nearly identical. The low results obtained by Jellinek are ascribed to the presence of free alkali in the cyanide, but correct results may be obtained with this impure cyanide if the mercuric chloride solution is added to an excess of the cyanide solution and the excess then titrated with hydrochloric acid and methyl-orange, or if the cyanide is first rendered neutral to methyl-orange with dilute sulphuric acid. Mercuric chloride may also be determined accurately by addition of dilute hydrocyanic acid to the neutral solution until the liquid has a slight odour, followed by titration of the liberated hydrochloric acid with standard alkali and methyl-orange. The titration of lead nitrate with trisodium arsenite (Jellinek and Kühn, *loc. cit.*) and of ferric chloride with thiosulphate (Jellinek and Vinogradov, A., 1924, ii, 703) both give variable results depending on the concentrations of the reacting substances. A. R. P.

Potentiometric Determination of Cerium. O. TOMIČEK (*Rec. trav. chim.*, 1925, **44**, 410—415).—A simple potentiometric method for the determination of tervalent cerium consists in the oxidation of the cerous sulphate or chloride in a very concentrated solution of potassium carbonate, in an oxygen-free atmosphere, by titration with potassium ferricyanide solution. About three-quarters of the amount of 0·05 or 0·1*N*-ferricyanide solution necessary for the reaction, $2K_3Fe(CN)_6+K_2CO_3,Ce_2(CO_3)_3=2K_4Fe(CN)_6+2Ce(CO_3)_2$, is added to the cerium solution, carbon dioxide passed in until all air is expelled, and potassium carbonate added with continual stirring until the mixture contains 35% of carbonate. The titration is then completed in the manner described by Kolthoff and Tomiček (*ibid.*, 1924, **43**, 775). The sensitivity of the titration is unaltered by the presence of ferric iron, thorium or other cerite earths, and since ferrous iron is more easily oxidised than the tervalent cerium the method permits the simultaneous determination of both metals. The results are accurate to ±0·2%. J. W. B.

Volumetric Determination of Cerium. J. ŠTĚRBA-BOEHM and V. MATULA (*Rec. trav. chim.*, 1925, **44**, 400—409).—To obtain satisfactory results for the determination of cerium in the presence of thorium and other rare earths the experimental conditions fully described in the original must be followed exactly. The earths, in the form of sulphates or chlorides, are dissolved in cold water, and a solution of potassium persulphate is added, followed by sodium hydroxide until the hydroxides just begin to be precipitated, then one drop of phenolphthalein, and again sodium hydroxide in excess. Sufficient base must be present to neutralise the sulphuric acid

formed by the reaction, $K_2S_2O_8+H_2O=K_2SO_4+H_2SO_4+O$, a slight excess not being objectionable. The solution is boiled for 25 min., cooled, and potassium iodide and hydrochloric acid are added. With gentle mixing, the precipitated hydroxides dissolve, and the liberated iodine is titrated with $N/40$-thiosulphate solution. This yields an approximate result ($\pm 2\%$ of the actual cerium content), and exact results may now be obtained by using 1·5—2 g. of potassium persulphate (and the appropriate quantity of sodium hydroxide) for each gram of cerium present and regulating the period of ebullition according to the cerium content. When the cerium content is greater than 25% the sample should first be diluted with a small quantity of rare earth sulphates free from cerium. The results are accurate to $\pm 0{\cdot}16\%$ and the method is applied to the analysis of several cerium ores. Iron may be determined iodometrically in the presence of cerium if the oxidation be carried out by means of chlorine water in dilute hydrochloric acid solution. [Cf. *B.*, July 24th.] J. W. B.

Analytical Chemistry of Indium. J. Heyrovský (*Chem. Listy*, 1925, **19**, 168—172).—Indium may be deposited from acid or alkaline solutions on a dropping mercury cathode. The reaction is reversible and requires a cathodic potential of $-0{\cdot}503$ volt for the deposition of the metal from a molar solution. The method will detect indium in a solution containing as little as 0·01 mg. of metal in 25 c.c. Indium salts yield with excess of potassium or sodium hydroxide solutions of true salts of an acid derived from indium sesquioxide, but the salts are progressively hydrolysed on keeping until the solution contains less than $0{\cdot}25\times10^{-4}$ g.-equivalent of indium in true solution in N-sodium hydroxide. The ionic decomposition product of an alkaline solution of a freshly-prepared specimen of indium hydroxide is 10^{-33} and of an acid solution of an aged specimen $0{\cdot}25\times10^{-18}$. A. R. P.

Separation of Gallium from Aluminium and Iron. R. Fricke (*Z. anorg. Chem.*, 1925, **144**, 267—268).—Gallium is not conveniently separated from large amounts of iron or aluminium by precipitating the latter with excess of ammonium hydroxide, but the method may be used when the gallium is nearly pure. A. G.

Colorimetric Determination of Small Amounts of Iron. W. B. Walker (*Analyst*, 1925, **50**, 279—283).—In the thiocyanate method, the use of nitric acid containing nitrous acid is recommended to ensure rapid oxidation of all ferrous compounds, nitrous acid being then oxidised by hydrogen peroxide before addition of thiocyanate. Since phosphates interfere, the ferrocyanide method is to be preferred; nitrous acid should be removed by boiling before addition of the ferrocyanide. S. I. L.

Electrometric Titration in the Determination of Ferrous and Ferric Iron in Magnetites. H. R. Adam (*J. S. Afr. Chem. Inst.*, 1925, **8**, 7—10).—The direct determination of ferric iron is carried out by running a slight excess of standard stannous chloride

solution into the almost boiling ferric iron solution, and titrating back with dichromate or iodine. If dichromate is used, the end-point is determined electrometrically, and the back titration may be continued to determine the total iron, there being two sharp rises of potential, the first when the excess of stannous chloride has been oxidised, and the second when the iron is completely oxidised. Back titration with iodine is simpler, but in this case the electrometric method has no advantage over the use of starch as indicator. The total iron may also be determined in the solution used for the ferrous iron, for after the determination of the latter with dichromate, titration with stannous chloride may be carried out as above. Titanium in solution does not affect the reduction of iron by stannous chloride. B. F.

Colorimetric Determination of Molybdenum. E. WENDEHORST (*Z. anorg. Chem.*, 1925, **144**, 319—320).—Hydrogen sulphide is passed into the ammoniacal molybdate solution, which is then acidified and the precipitate collected and roasted to oxide. This is dissolved in ammonia, the solution evaporated to dryness, and the residue dissolved in a known volume of water. An aliquot part of the solution is treated with a quantity of 5% glycerol solution saturated with hydrogen sulphide; 0·2*N*-sulphuric acid is then added drop by drop until the yellow colour reaches its maximum intensity. The colour is compared in a colorimeter with that of a standard solution of molybdenum trioxide treated in a similar manner. A. R. P.

Separation of Molybdenum from Vanadium as Sulphide. A. E. STOPPEL, C. F. SIDENER, and P. H. M.-P. BRINTON (*Chem. News*, 1925, **130**, 353—355).—Precipitation of molybdenum as sulphide in a sulphuric acid solution containing vanadium gives good results if the cold solution is saturated with hydrogen sulphide and then heated under pressure. The precipitate contains a few tenths of a mg. of vanadium, but a similar quantity of molybdenum fails to precipitate, so that there is a compensation of errors. If an ammoniacal solution of molybdic and vanadic acids issaturated with hydrogen sulphide and then treated with 2—3 g. of tartaric acid and hydrochloric acid until acid, all the molybdenum is precipitated as sulphide, retaining, however, 1—1·5 mg. of vanadium, which may be removed by reprecipitation. A. R. P.

Determination and Separation of Rarer Metals from other Metals. V. Separation of Zirconium and Hafnium from Titanium, Cerium, and Thorium. L. MOSER and R. LESSING (*Monatsh.*, 1924, **45**, 323—337).—Zirconium salts are precipitated by sodium arsenate from boiling hydrochloric acid solutions as a hydrated normal arsenate, $Zr_3(AsO_4)_4$, whilst from strong nitric acid solutions a zirconyl salt, $ZrO{\cdot}HAsO_4$, is obtained which is more easily filtered. Fractional precipitation of a commercial "pure" zirconium preparation, by the latter method, gave fractions in which the equivalent of the metal varied from 98·68 to 90·56, which shows that hafnium is precipitated with zirconium and that its arsenate is still less soluble than that of zirconium. Conditions have been

worked out and tested in detail for the use of this precipitation of zirconium as arsenate in separating it from titanium, cerium, and thorium. In presence of titanium and cerium, an excess of hydrogen peroxide must be present to ensure their conversion into pertitanic acid and cerous salts respectively. The separation from thorium is satisfactory only when the acidity of the solution is adjusted within a narrow range near 1·13*N*-nitric acid.

G. M. B.

Precipitation of Gold and Silver by Metallic Sulphides. [Detection of Traces of Gold and Silver in Solution.] A. Steigmann (*Chem.-Ztg.*, 1925, **49**, 423).—For the detection of traces of gold in a solution, hydrogen peroxide is added followed by solutions containing (*a*) sodium sulphite and "metol" and (*b*) sodium sulphite and silver nitrate. The characteristic colour of the colloidal solution of silver obtained from the reagents added is considerably modified by the presence of gold and the colour also develops much more rapidly. Traces of silver may be detected in a solution by the same process, except that the silver nitrate in the reagents is replaced by mercuric chloride. A. R. P.

Elementary Analysis of Organic Substances by Combustion with Copper Oxide in a Vacuum. J. Švéda and O. Prováke (*Chem. Listy*, 1925, **19**, 163—167).—A small quantity of the substance is introduced in a small platinum boat into a hard glass combustion tube one end of which is packed with copper oxide wire. The tube is then filled with alternate layers of copper oxide and reduced copper obtained from copper oxide wire and finally each end of the tube is plugged with copper gauze. After weighing, the whole is introduced into a silica tube, which is then connected by well fitting stoppers and stopcocks to a manometer, a drying tube containing phosphorus pentoxide, and a Sprengel vacuum pump. After evacuation, the tube is heated at 750—800° in an electric furnace and the gases evolved (carbon dioxide and nitrogen) are withdrawn into a eudiometer for analysis. Hydrogen is determined from the loss in weight of the glass combustion tube and its contents after making allowance for the oxygen required for the combustion of the carbon and for the weight of the substance. A. R. P.

Proving Identity of Two Organic Compounds. E. Murmann (*Oesterr. Chem.-Ztg.*, 1925, **28**, 86—87).—Where very small quantities only are available, the m. p. and behaviour towards a large number of solvents are compared for the substance under examination and the substance with which it is suspected to be identical. Figures are allotted to the behaviour with each solvent, and the succession of these is usually sufficient to prove identity or otherwise.

S. I. L.

Determination of Alcohol. M. Martini and A. Nourisson (*Ann. Falsif.*, 1925, **18**, 235—237).—The alcohol is distilled into an oxidising potassium dichromate solution, the excess of dichromate reduced by potassium iodide, and the liberated iodine titrated with sodium thiosulphate solution. [Cf. *B.*, 1925, 520.] D. G. H.

Micro Determination of Sugar or Reducing Substance in Blood. L. LORBER.—(See i, 852.)

Determination of α-Cellulose. C. G. SCHWALBE (*Papier-Fabr.*, 1925, **23**, 232—233).—A discussion of Jentgen's method (*Kunststoffe*, 1911, **1**, 165) and various modifications, *e.g.*, washing with sodium hydroxide solution after draining off the first filtrate and the prolongation of the time of treatment. Mechanical kneading is not recommended. [Cf. *B.*, 1925, 539.] J. F. B.

Determination of Pentosan. F. W. KLINGSTEDT (*Z. anal. Chem.*, 1925, **66**, 129—160).—All carbohydrates and vegetable substances that give hexoses on hydrolysis yield, on distillation with 12% hydrochloric acid, hydroxymethylfurfuraldehyde and probably also other compounds which form condensation products with phloroglucinol, so that under certain conditions the determination of pentosans by this method will give very erroneous results. The solubilities of the phloroglucides of furfuraldehyde and its derivatives in alcohol vary considerably; thus the methylfurfuraldehyde compound is readily soluble in warm alcohol, even after it has been dried for 8 hours, whilst the furfuraldehyde compound is insoluble after drying, but slightly soluble when moist. Hydroxymethylfurfuraldehyde and *s*-difuryldimethyl ether compounds are almost completely soluble in alcohol when moist, but less soluble when dried. Extraction of a mixed condensation product with alcohol, however, and calculation of the insoluble residue to pentosan invariably yields high results, whether the condensation is carried out at the ordinary temperature or in a warm solution and whether the product is dried or not before extraction. Fairly correct results for pentosan may be obtained by a careful regulation of the distillation, not more than about 150—180 c.c. being collected. When all the furfuraldehyde has distilled, the distillate gives no further green precipitate with a hydrochloric acid solution of phloroglucinol. The condensation should be carried out in cold solutions and the moist precipitate extracted with alcohol. The residue gives the minimum amount of pentosan in the substance tested. [Cf. *B.*, Aug. 7th.] A. R. P.

Colorimetric Determination of Acetone in Urine. M. H. P. SITSEN.—(See i, 855.)

Determination of Urea in Blood, etc. P. B. REHBERG, also G. Y ROIG and K. HELMHOLZ. (See i, 853.)

Jaffe's Reaction for Creatinine. II. Effect of Substitution in the Creatinine Molecule and a possible Formula for the Red Tautomeride. I. GREENWALD.—(See i, 839.)

Standard Solution for Sahli's Hæmometer. A. K. J. KOUMANS.—(See i, 851.)

Determination of Xanthrophyll. F. M. SCHEETZ.—(See i, 871.)

General, Physical, and Inorganic Chemistry.

Excitation Maxima for Spectral Lines in the Striæ of the Positive Column of Hydrogen. E. Lau (*Ann. Physik*, 1925, [iv], **77**, 183—194).—Spectrophotometric records have been obtained of the distribution of light-intensity arising from the emission of single lines at various positions in the striæ of the positive column in a hydrogen discharge tube. Similar data have been obtained for the continuous spectrum. An ingenious device was employed to maintain a constant pressure in the stream of hydrogen. The Balmer series lines, $H\alpha$, $H\beta$, $H\gamma$, are most intense at different points in the striation. The most important lines in the Fulcher band spectrum, 6430, 6327, 6224, 6121, 6018, and 5656, 5548, 5420, 5302, occur most strongly at different places. The shortest wave-lengths in a band system, *e.g.*, 6018 and 5302, correspond with the smallest electron-velocities. The maximum of the continuous spectrum occurs at the same place for all wave-lengths between 4000 and 5000 Å. The positions of maximum intensity for series lines are reversed when striæ with a lower potential drop are investigated. The probable change of the electron velocity within a striation is only 1 volt. This may mean an acceleration or a retardation according to the type of striation.

The small electron velocity is regarded as due to collisions of electrons with hydrogen molecules. The energy resulting from the loss in velocity reappears as the continuous radiation, which is thus ascribed to a purely collisional mechanism. In the Balmer series and in the continuum, there are two excitation maxima in a double striation, but there is only one maximum for the Fulcher bands. In the first striation from the cathode, whether it be single or double, the lines of the Balmer series (especially $H\alpha$ and $H\beta$) are much weakened near the cathode. There is no evidence of electrons existing in the positive column with velocities greater than those of the exciting electrons. (Cf. Seeliger and Okubo, *Physikal. Z.*, 1924, **25**, 337, who found it necessary to assume that a current of faster electrons traverses the striation.) R. A. M.

Hydrogen Spectrum of Constant Frequency-difference. J. W. Nicholson (*Month. Not. Roy. Astr. Soc.*, 1925, **85**, 656—659).—Among the lines of the secondary spectrum of hydrogen showing a normal Zeeman effect, and therefore probably of atomic origin, a number may be picked out between 3732·25 and 4966·98 Å. which have an approximately constant wave-number difference of 1313. Another large group nearer the red end has a wave-number difference which is nearly the same, namely, 1300. The lines of these two groups, which have certain members in common, are also most characteristically unaffected by the presence of helium. They appear to belong to a series spectrum nearer to the neon than

to the helium type, and they show a certain resemblance to the nebular and to the Wolf-Rayet spectra. Another class of lines previously described (this vol., ii, 468), which show no Zeeman effect, form widely separated bands of molecular origin. M. S. B.

Hydrogen-like Spectra from the Point of View of the Polarisability of the Atom-core. E. SCHRÖDINGER (*Ann. Physik*, 1925, [iv], **77**, 43—70).—The polarisability of the core of atoms of noble gases has been calculated for the *p*-, *d*-, and *f*-series. It is fairly constant within a series; in many cases it is accurately so. In the same spectrum, the variation from series to series is usually in the sense that the constant polarisability for one series is a multiple of that of another series. The polarisability of the core in outer orbit series may be accepted as fairly constant. Evidence is brought forward showing that the outer orbits of lithium and sodium are weakly bound. The remarkable disturbance of the Bergmann Series for AlII can be explained on the basis of a very great polarisability for exciting frequencies which are smaller than the resonance frequency, and a negative polarisability for frequencies greater than the resonance frequency. This explanation is tentatively extended to the arc spectra of the alkaline earths. All calculations are based on whole number impulse quanta and an attempt is made to state the case for and against this method of treatment. R. A. M.

Structure of the Band Spectrum of Helium. III. The Doublet Bands. W. E. CURTIS and R. G. LONG (*Proc. Roy. Soc.*, 1925, **A**, **108**, 513—541; cf. A., 1923, ii, 351).—New data of the doublet bands of helium, which are unique in conforming to a line-series law, have been secured, extending the main series to the eighth member, and their structure has been studied in detail. Previous difficulties of interpretation have been to a large degree overcome. New and much more accurate values of the molecular moments of inertia and separation of the nuclei have been obtained. Support is afforded to Lenz's suggestion (*Verh. d. Phys. Ges.*, 1919, **21**, 632) that the structure of the helium molecule may be related to that of the hydrogen molecule. Light is thrown on the nature of the perturbations occurring in two of the bands. The second series of doublets is re-examined, and, although the data are much less extensive, the results of the analysis are closely similar to those obtained from the main series. It is concluded that the two series must originate from the same molecule, but a different radiating electron. L. F. G.

Characteristic *X*-Rays from Lithium. G. K. ROLLEFSON (*Physical Rev.*, 1925, [ii], **25**, 740—746).—By photoelectrical determination, values for radiation and ionisation potentials of lithium are, respectively, 39·2, 43·07, 46·0 volts and 48·4 volts. Extension of the Moseley curve for the $K\alpha$ lines gives, on interpolation, the following wave-lengths: lithium, 286·5 Å; beryllium, 132·8; boron, 74·4; carbon, 49·0; nitrogen, 33·2; oxygen, 24·4; fluorine, 18·6; neon, 14·8 Å. A. A. E.

Further Spectra Associated with Carbon. R. C. JOHNSON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 343—355).—The spectra associated with carbon, which are developed in vacuum tubes containing helium and a trace of carbon, have been studied in the ultra-violet. A number of new faint lines are recorded in the region 4000—2400 Å., but it has not been found possible to deduce any general laws governing the alteration of the intensity distribution caused by helium. Several new members of the Comet Tail bands are recorded in the near ultra-violet, and a new spectrum is described which is associated with these bands, and is of similar structure, but degraded in the opposite direction. The new bands lie between 4235 and 3314 Å. Their presence in the cometary spectrum is uncertain. The negative carbon bands were well developed in the same tube, and have been remeasured and arranged in series.

S. B.

Origin of the Auroral Green Line 5577 Å., and other Spectra Associated with the Aurora Borealis. J. C. MCLENNAN and G. M. SHRUM (*Proc. Roy. Soc.*, 1925, **A**, **108**, 501—512).—In studying the effect of large admixtures of helium or of neon on the spectrum of oxygen, a hitherto unknown line, of wave-length $5577{\cdot}35\pm0{\cdot}15$ Å., has been photographed; it is very sharp and is subject to great fluctuations in intensity. Evidence is produced to prove that this line is identical with the auroral green line $\lambda=5577{\cdot}350\pm0{\cdot}005$ Å. This line is attributed to some hitherto unknown spectrum of oxygen, and is not a limiting member of the ordinary band spectrum of this substance. It has been observed faintly in highly-purified oxygen when using currents of high density. Helium has been used to bring out the bands of nitrogen (cf. Merton and Pilley, this vol., ii, 333) with an intensity distribution similar to that found in the aurora. The possibility of metastable helium acting as the exciting agent in the auroral spectrum is discussed. L. F. G.

Resonance Lines of Neon. G. HERTZ (*Z. Physik*, 1925, **32**, 933—939).—The spectrum of a low-voltage arc in neon was photographed in a vacuum grating spectrograph and two strong lines were found at 735·7 and 743·5 Å. Their difference in frequency agrees with the difference of the terms $1s_2$ and $1s_4$, and are the combinations of these terms with the ground term. They are resonance lines. The two ionisation potentials of neon are 21·47 and 21·57 volts, in agreement with the value 21·5 obtained by the electron impact method. E. B. L.

Spectrum of Sodium at Low Voltages. F. H. NEWMAN (*Phil. Mag.*, 1925, [vi], **50**, 165—173).—The sodium low-voltage spectrum was determined in a three-electrode discharge tube in which sodium vapour was subjected to electron bombardment by electrons emitted from a heated tungsten wire cathode, and accelerated by a potential difference applied between the grid and cathode. On the basis of Bohr's theory of atomic structure, it is shown that by bombarding the vapour by electrons of increasing energy, lines of the arc spectrum should be emitted by the permitted inter-

orbital transfers, up to an electron energy of 5·12 volts, at which value the whole of the arc spectrum should appear. Photographic observations showed the development of the spectrum in the order of the potentials predicted by theory. At 2·2 volts, wave-lengths 5896 and 5890 Å. only appear. At 4·0 volts, the lines 3303 and 3302 Å. are excited, and the lines 6161, 6154, and 5688, 5683 Å. are emitted at 4·4 and 4·6 volts, respectively. F. G. T.

Spectra of Doubly and Trebly Ionised Phosphorus. M. O. SALTMARSH (*Proc. Roy. Soc.*, 1925, **A**, **108**, 332—343).—Observations have been made on the spectrum of phosphorus from a vacuum tube containing the vapour of yellow phosphorus and a variable amount of hydrogen, excited by a condensed discharge with and without self-induction. By making use of the intensity changes with alteration of the discharge, the lines corresponding with the different states of ionisation have been selected. The series system of doubly ionised phosphorus, III, is a doublet system, in accordance with the spectroscopic displacement law. Approximate values of the various series terms have been obtained. Three members of the triplet series of trebly-ionised phosphorus have been identified. It has now been observed that, for three groups of elements, the sharp terms are greater than the diffuse terms with the same Rydberg numbers for the neutral and singly ionised atom, but smaller for the doubly and trebly ionised atom. S. B.

Intensity Relations of Triplet Components of the Alkaline Earths and Spark Doublets of Calcium. H. B. DORGELO (*Physica*, 1924, **4**, 281—286; cf. A., 1924, ii, 282; Burger and Dorgelo, *Z. Physik*, 1924, **23**, 258).—Rules previously given are confirmed. The intensity ratio for the triplets *ps* and *pd* is 5 : 3 : 1, for the *db* triplet 7 : 5 : 3. The spark doublet of the principal and sharp series of calcium has the same ratio (2 : 1) as the arc doublet of the alkali metals. The complex spark doublet 1π—2δ of calcium gave the same value as the complex arc doublet of cæsium.

CHEMICAL ABSTRACTS.

Structure of the Spectrum of Scandium. II. M. A. CATALÁN (*Anal. Fís. Quím.*, 1924, **22**, 497—505; cf. A., 1923, ii, 104).—A revision of the classification of the terms of the spectrum of ionised scandium. Two new multiplets are given. The selection principle as modified by Laporte (A., 1924, ii, 364) is valid for this spectrum. G. W. R.

Reported $K\beta_4$ Line in the X-Ray Spectra of Molybdenum and Palladium. S. K. ALLISON (*Nature*, 1925, **115**, 978—979).—No evidence has been obtained, in the case of molybdenum, for the existence of the β_4 line described by Leide (this vol., ii, 457); however, in the region in which it should occur, a discontinuity in the general radiation always appeared, due to the absorption by the target of its own radiation. It is possible that the effect might be mistaken for a faint line on the short wave-length side of the γ line. A. A. E.

Stages in the Excitation of the Spectra of Cadmium. A. E. RUARK and R. L. CHENAULT (*J. Opt. Soc. Amer.*, 1925, **10**, 653—659).—Errors may be introduced into the determination of the energy of electron impact required for the excitation of a spectrum line, by the occurrence of successive impacts upon a given atom. Tables giving the appearance voltages of lines should therefore be accompanied by data of the current densities at which the observations were made. Such observations are supplied for the cadmium lines developed in a three-electrode tube with applied voltages of 8—65 volts. S. B.

Nature of the Iodine Line 2062 Å. L. A. TURNER and K. T. COMPTON (*Physical Rev.*, 1925, [ii], **25**, 791—794).—The authors' experimental results are explicable on the assumption that the iodine line 2062 Å. is not a resonance line, but that the atoms which absorb it are in a state of which the energy level is 0·545 volt above the normal. The existence of a resonance line of atomic iodine between 1750 Å. and 1890 Å. is indicated. A. A. E.

Tungsten *X*-Ray Emission and Absorption Spectra. R. V. ZUMSTEIN (*Physical Rev.*, 1925, [ii], **25**, 747—752).—An investigation of the *M* series lines of tungsten, using a vacuum spectrometer. In the emission spectrum, faint lines η_1=6·857 A. and η_2=6·789 Å. have been observed, and Hjalmar's two components of the α and β lines measured at α'=6·948 Å., β'=6·720 Å. Lines were observed in the absorption spectrum at 6·708, 6·475, 5·416, 4·800, and 4·365 Å. There is also an unpredicted component, M_3'=5·380 Å. A. A. E.

The Mercury Line 2270 Å. ($1s-2p_1$). T. TAKAMINE and M. FUKUDA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 293—298).—This line, not hitherto observed directly, has been found in the mercury arc spectrum. The wave-length appears to be shifted by about 0·1 Å., according as the line is produced by a condensed discharge or in the side-glow of an arc. W. A. C.

Rotating Arc between Carbon Electrodes. PAUTHENIER (*Compt. rend.*, 1925, **180**, 1833—1836).—Details of a new method. R. A. M.

Complex Structure of Spectra. S. GOUDSMIT (*Z. Physik*, 1925, **32**, 794—798).—A variation of Pauli's treatment of electron grouping and quantum numbers for an atom under the influence of a strong magnetic field is developed and applied to the spectra of neon and lead. E. B. L.

Intensities of Lines in Multiplets. I. Theory. H. N. RUSSELL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 314—322).—Formulæ are developed which represent fairly closely all the available data. J. S. C.

Intensities of Lines in Multiplets. II. Observed Data. H. N. RUSSELL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 322—328).—The theory developed (preceding abstract) is compared with the observed data, the agreement being close. J. S. C.

Classification of Enhanced Lines of Various Elements. I. M. KIMURA and G. NAKAMURA (*Japan. J. Phys.*, 1924, **3**, 197—215).—Examination of the spark spectra of about thirty elements has shown that their enhanced lines may be grouped according to their lengths. All members of a group behaved similarly when either the self-induction, capacity, or spark gap was varied. From consideration of the fact that the larger is the enhanced line the smaller will be the amount of energy required to excite it, a classification of the groups as II, III, IV, or spark, super spark, and super-super spark indicates that the lines in each group are emitted by singly, doubly, and triply ionised atoms, respectively. From these considerations, the number of electrons easily detachable from an atom under an intense electrical discharge increases with the positive valency of the element and reaches a maximum with groups IV or V of the periodic table. A. E. M.

Classification of Enhanced Lines of Various Elements. II. Spectra of Intermittent Arc Shunted by a Condenser. M. KIMURA (*Japan J. Phys.*, 1924, **3**, 217—225).—Using an intermittent condensed arc and varying the voltage up to 440 volts, certain classes of enhanced lines appeared in succession. Spark lines appeared first, then super spark, and finally super-super spark. In the cases of zinc and copper, no super spark lines appeared even in the 440 volts arc, whilst with the other elements, antimony, bismuth, platinum, cadmium, and tin, these were obtained easily at 220 volts. Super-super spark lines appeared in the 440 volt arc of lead, but not in the arcs of antimony, bismuth, or tin.
A. E. M.

Doublets and Triplets in the Spectra of Different Elements. Y. SUGIURA (*Japan J. Phys.*, 1924, **3**, 155—185).—Mathematical. Doublets and triplets are deduced as being emitted by atoms having one and two valency electrons, respectively. Expressions for the wave-number differences of doublets and triplets are obtained from the energy difference due to the intra-atomic magnetic fields set up by the elliptic orbits of the electrons. These calculated values are in good agreement with those observed for the doublets of the alkali elements and for the copper, silver, and aluminium groups. Calculated values of the wave-number differences $\Delta\nu_p^{2\cdot3}$ and $\Delta\nu_d^{2\cdot3}$ for the elements of the second column of the periodic table are in fair agreement with observation. The bearing of the work on the orientation of electron orbits in atoms is discussed. A. E. M.

Spark Spectra in the Schumann Region. L. and E. BLOCH (*J. Phys. Radium*, 1925, [vi], **6**, 105—120; cf. A., 1921, ii, 3, 286, 364; Lang, *Phil. Trans.*, 1924, A, **224**, 371).—Valuable additions to the data of spark spectra in the region 1850—1300 Å. have been made by the use of two vacuum spectrographs with fluorite optical parts. In the later model, the fluorite was of very good quality and the absence of fluorescence together with the use of a very fine slit have enabled the authors to obtain plates which show a decided advance in respect of detail. Hundreds of new lines are

recorded and many lines hitherto regarded as simple have been resolved into doublets or triplets. The radical changes involved in the spectra have necessitated the publication of new lists of wave-lengths for iron, nickel, cobalt, and tungsten. Data for copper, silver, gold, platinum, manganese, and chromium will appear later. In the new arrangement, the prism consists of two 30° fluorite prisms and a mirror; in the spark gap, the current of hydrogen employed formerly has been replaced by nitrogen. An important experimental difficulty in the work was the increasing opacity of the fluorite window. An invisible deposit is formed which is only removed by dismounting the window and washing both sides with benzene. The photographs were calibrated by means of the following lines determined by means of a vacuum grating spectrograph. 1807·70, 1751·80, 1657·86, 1561·35, and 1335·70 (carbon); 1935·79, 1930·97, and 1858·13 (aluminium); 1742·81 and 1494·63 (nitrogen). A series of secondary standards in the aluminium spectrum was also used. These may be as much as 0·2 Å. in error. Hence the absolute values of the wave-lengths recorded may be in error owing to uncertainty in the standards, but the intervals between lines are known accurately to within a few hundredths of an ångström. The table for iron extends from 1895·53 to 1505·16; for nickel about 270 new lines are recorded down to 1370·31; cobalt shows 346 lines from 1882·14 to 1424·82, of which 150 are new. The tungsten spectrum shows a very large number of lines down to 1450. (Cf. A., 1924, ii, 214.) R. A. M.

Theory of the Continuous *X*-Ray Spectrum. M. Bronstein (*Z. Physik*, 1925, **32**, 881—885).—It is shown that a small correction should be applied in deducing the sharp edge of the continuous spectrum from Einstein's $h\nu$ relation, dependent on the angle between the beam of *X*-rays and the direction of the cathode rays. E. B. L.

Spectroscopic Evidence of *J*-Transformation of *X*-Rays. M. Siegbahn (*Nature*, 1925, **116**, 11—12).—Responsibility is denied for some of the *K* wave-length values ascribed to the author by Khastgir and Watson (this vol., ii, 336). Leide's new and more accurate values yield no trace of such discontinuities as are described by Khastgir and Watson. A. A. E.

Spectroscopic Evidence of *J*-Transformation of *X*-Rays. W. W. Nipper (*Nature*, 1925, **116**, 12).—Siegbahn's (preceding abstract) contentions are supported. Although the greatest deviation of the values employed from more recent wave-length determinations occurred, by coincidence, at points corresponding with two of the critical absorbabilities for *J*-transformation of *X*-rays, there is no spectroscopic evidence for the existence of the phenomenon. A. A. E.

Spectroscopic Evidence of *J*-Transformation of *X*-Rays. S. R. Khastgir and W. H. Watson (*Nature*, 1925, **116**, 47).—Polemical and explanatory (cf. this vol., ii, 336, and preceding abstracts). A. A. E.

The Term Problem of Doublet Spectra, with Particular Reference to *X*-Ray Spectra. G. WENTZEL (*Ann. Physik*, 1925, [iv], **76**, 803—828).—A complete representation of the terms of the *X*-ray, as well as of the alkali spectra, can be obtained if the energy of the n_k orbit is calculated by the separation method, taking into account the relativity effect and penetration into inner electron shells. If the energy is calculated from the relativistic fine structure constant $\alpha^2=(2\pi e^2/hc)^2$, the principal term (non-relativistic) involves fractional azimuthal quantum numbers, as in the suggestion of Heisenberg (this vol., ii, 3). By assuming that the charge on the shell of the atom is very small compared with that on the kernel, the calculation for the *X*-ray and Millikan ultra-violet spectra is much simplified. The whole of the alkali and *X*-ray terms may be expressed as functions of two quantum numbers n and k, if negative as well as positive values of k are admitted. The expression found by the author for the screening doublets $(\Delta\sqrt{\nu/R})/0{\cdot}6$=integer (*Z. Physik*, 1923, **16**, 46) is obtained by assuming that k^2 is very small compared with n^2. The Sommerfeld fine structure theory follows from the application of these ideas to the hydrogen atom. F. G. T.

***X*-Rays Terms and Intensities.** H. R. ROBINSON (*Phil. Mag.*, [vi], 1925, **50**, 241—250; cf. A., 1923, ii, 818).—Previous work has been extended and made more accurate by the production of secondary *X*-ray spectra from targets of uranium oxide, thorium nitrate, gold, arsenic oxide, manganese oxide, and titanium oxide. The general distribution of intensity among the sub-groups of the secondary rays follows closely the results of the previous work, showing clearly that so long as the critical absorption frequency of a group is not too far removed from the frequency of the incident radiation, most of the secondary electrons come from the softer sub-groups. As the critical absorption frequency decreases, the maximum intensity in the sub-groups shifts gradually from the softer towards the harder members. This holds generally in the *M* and *N* as well as in the *L* sub-groups. A comparison of visual and photometric observations of intensities indicates that the former somewhat exaggerates the differences in intensity. The photometer curves especially indicate the diffuseness of the low-velocity side of the lines, due mainly to the straggling of electrons from deeper layers of the target. F. G. T.

Exact Determination of Characteristic Atomic Frequencies in the Spectral Region between Visible Light and *X*-Rays. HOLWECK (*J. Chim. Phys.*, 1925, **22**, 311—318; cf. Holweck, *Compt. rend.*, 1921, **173**, 709).—The critical potentials of some elements have been determined by a modification of the "gaseous anticathode" method of Mohler and Foote. The gas was contained in the chamber of a negatively charged electroscope through which was passed a beam of *X*-rays, issuing from a molybdenum anode as the result of the collision of a stream of electrons, emitted at a difference of potential V. If V is comparatively small the *X*-ray

radiation forms a continuous spectrum, and the critical potential is indicated by a break in the curve connecting V with the degree of ionisation. The following values were found for the L_{III} critical potentials in volts: argon, 246·5±1; chlorine, 203±1; sulphur, 163±1; phosphorus, 128±2; silicon, 98±2; aluminium, 68±2. The substances used were argon, hydrogen chloride, hydrogen sulphide, hydrogen phosphide PH_3, and hydrogen silicide SiH_4; for aluminium the beam was passed through a thin sheet of the metal. The author's previous value for aluminium (*loc. cit.*) is in error owing to a wrong correction. W. H.-R.

Generally Accepted Explanation of the Zeeman Triplet on a Quantum Basis. W. M. HICKS (*Nature*, 1925, **115**, 978).—In the usual way of applying Larmor's theorem to the explanation of the Zeeman effect, it is tacitly assumed that after the imposition of the magnetic field the rotating system is the same as before, with simply the rotation superposed. This assumption is incorrect, and it is objected that the new orbit ceases to be quantised, and that the total energy is supposed to be altered by the action of a magnetic field on a moving electron. A consideration, however, of actual orbits leads to the result that no effect is to be expected, or if so that the magnitude must depend on the second or higher powers of H. A. A. E.

Quantum Theory of Multiplet Structure and the Anomalous Zeeman Effect. W. HEISENBERG (*Z. Physik*, 1925, **32**, 841—860).—The theory of the interaction between an electron and the atomic core involves the ambiguity that for one definite stationary state of the core and of the outer electrons there are two values for the energy of their interaction, and, conversely, for one value of this energy there are two systems of stationary states for the electron and the core. Schemes are developed which yield an interpretation of some of the observed regularities of multiplets. E. B. L.

Intensity of the Components in the Zeeman Effect. L. S. ORNSTEIN, H. C. BURGER, and W. C. VAN GEEL (*Z. Physik*, 1925, **32**, 681—683).—The intensities of the components of the zinc triplet 4810, 4722, 4680 Å. ($2p_i$—ss) were determined, using a grating spectrograph and a Moll microphotometer. The results show satisfactory agreement with theory (cf. Hönl, *ibid.*, 1925, **31**, 340; Ornstein and Burger, this vol., ii, 340). E. B. L.

Polarisation of Resonance Radiation and the Duration of Excited State. K. R. RAMANATHAN (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 93—102).—The changes of polarisation of the resonance radiation of mercury vapour in weak magnetic fields (Wood and Ellett, *Proc. Roy. Soc.*, 1923, **A**, **103**, 396) can be explained by taking into account the Larmor precession of the orbit of the electron round the direction of the magnetic field, and the finite duration of the excited condition of the atom. The duration of the excited state required to explain the decrease of polarisation in mercury vapour resonance when a magnetic field is applied

parallel to the direction of observation, and perpendicular to the incident beam of light, is consistent with Wien's determination of the same quantity (A., 1924, ii, 362). The changes in intensity and polarisation of the resonance radiation when the mercury vapour is mixed with hydrogen, helium, argon, or air (Wood, *Phil. Mag.*, 1922, [vi], **44**, 1107) can be explained by assuming a finite time of excitation of the atom, and that the effect of a collision is either to destroy the radiation or to disturb the polarisation so as to make its direction random. F. G. T.

Excitation and Ionisation Potentials of Rare Gases. G. HERTZ and R. K. KLOPPERS (*Physica*, 1924, **4**, 367—372; cf. A., 1922, ii, 733; 1923, ii, 281; *Z. Physik*, 1923, **18**, 307).—The method previously employed is modified by the use of an equipotential nickel cathode. Values of the resonance potentials are: argon, 11·5, 13·0, 13·9 volts; krypton, 9·9, 10·5, 11·5, 12·1 volts; xenon, 8·3, 9·9, 11·0 volts. Ionisation potentials (±0·1 volt) are: argon, 15·4; krypton, 13·3 (p=0·07 mm.); xenon, 11·5 (p=0·12 mm.). These values do not correspond with a single spectral term, but with average values for groups of neighbouring terms.

CHEMICAL ABSTRACTS.

Experimental Study of Directions of Emission of Photo-Electrons. P. AUGER (*Compt. rend.*, 1925, **180**, 1939—1941; cf. this vol., ii, 618).—The expression $P=\sin^3\omega d\omega \cdot \sin^2\lambda d\lambda$ for the probability of emission of a photo-electron in a small solid angle $d\omega d\lambda$ making an angle ω (the colatitude) with the direction of the exciting X-ray pencil was deduced in the earlier paper. The experimental distributions are considered in two stages, as functions of ω and λ, respectively. The integral of $\sin^3\omega$ is expressed as $\frac{1}{3}(1-\cos\omega)[1-\frac{1}{2}\cos\omega(1+\cos\omega)]$ and that of $\sin^2\lambda d\lambda$ as $\frac{1}{2}(\lambda-\sin\lambda\cos\lambda)$. The experimental and theoretical curves are of the same type. R. A. M.

Distribution of Initial Velocities among Thermionic Electrons. L. H. GERMER (*Physical Rev.*, 1925, [ii], **25**, 795—807).—Measurements were made of the number of electrons from a tungsten filament at 1440—2475° Abs. which arrived at a coaxial cylindrical electrode against various retarding potentials. The experiments showed that the thermionic electrons emitted from tungsten into a high vacuum have velocity components distributed according to Maxwell's law for the distribution of velocities in an electron atmosphere in temperature equilibrium with the hot filament. A. A. E.

Schottky's Method of Determining the Distribution of Velocities among Thermionic Electrons. C. DAVISSON (*Physical Rev.*, 1925, [ii], **25**, 808—811).—Schottky's formula for the thermionic current from a filament to a coaxial cylinder fails when the potential at any distance x from the axis is less than $Vr^2(R^2-x^2)/x^2(R^2-r^2)$, where V is the potential of the filament with respect to the cylinder, r and R are the radii of filament and cylinder, respectively, and $r<x<R$. A. A. E.

Modification of the Laws of Emission of Ions from Hot Metals by the Quantum Theory. S. C. Roy (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 61—81).—The probability of identity between photo-electric and thermionic work-functions is discussed. W. A. C.

Vaporisation of Electrons. N. v. Raschevsky (*Z. Physik*, 1925, **32**, 746—752).—It is assumed that the emission of electrons from a hot body can be treated as being analogous to ordinary vaporisation of molecules, that the electrons behave like a monatomic gas, and that energy transference between the electrons and atoms inside the hot body is negligible. In the equation for the thermionic current, $i=Ae^{-b/T}T_a$, a is only equal to 2 when the energy of the internal electrons is taken as being independent of temperature; if these electrons are regarded as free, $a=\frac{1}{2}$; if they form a lattice, $a=-1$. E. B. L.

Electron Reflection in Gases. H. Baerwald (*Ann. Physik*, 1925, [iv], **76**, 829—848).—The reflection of electrons in hydrogen has been studied by comparing the total current produced by the passage through the gas of electrons from a hot filament with the current due to electrons reflected on impact with hydrogen molecules. The latter current was measured by means of an annular collector shielded from, and surrounding, the filament. The amount of reflection increases with the gas pressure, but the ratio of reflected to direct current is independent of the velocity of the electrons. The integral and differential curves are given for the variation of both direct and reflected current with change of the electron velocity obtained by varying the grid voltage. The differential curves of the direct current show maxima which flatten and occur with more slowly moving electrons as the gas pressure increases. The reflection is associated with a loss of energy which becomes accentuated when the electrons are accelerated by more than 11 volts. Above 16 volts, positive ions appear in the gas. This ionisation voltage was determined for a number of gas pressures and for varying filament currents. From a consideration of the free paths of the hydrogen molecules in these circumstances it is concluded that energy loss from slowly moving electrons occurs on grazing contact with the sphere of action of the hydrogen molecule. F. G. T.

Isotope Effect in the Spectrum of Silicon Nitride. R. S. Mulliken (*Nature*, 1925, **116**, 14).—The equations previously given (*Physical Rev.*, 1924, [ii], **23**, 554) for the silicon nitride bands are incorrect. The equation $\nu=24234{\cdot}2+1016{\cdot}30\ n'-17{\cdot}77\ n'^2+0{\cdot}41\ n'^3-0{\cdot}0049\ n'^4-1145{\cdot}00\ n''+6{\cdot}570\ n''^2$ holds for the position of the null-lines of the $Si^{28}N$ bands, n' being the vibrational quantum number of the initial, n'' that of the final, state of the molecule. Various abnormalities now disappear, an analogy of the SiN bands to the violet CN bands is evident, and the isotope effect is normal. In the case of SiN, but not in that of BO, integral vibrational quantum numbers are preferred. A. A. E.

Band Spectra of Lead Isotopes. E. S. BIELER (*Nature*, 1925, **115**, 980).—The assumption that the carrier of the band at 4270 Å. is the PbH molecule instead of the Pb_2 molecule affords a satisfactory explanation of the results of Grebe and Konen (A., 1922, ii, 4) on the band spectra of lead isotopes. A. A. E.

Determination of the Atomic Weight of a Mixture of Lead Isotopes Present in Clevite from Aust-Agdar, Norway. (MLLE.) E. GLEDITSCH, (MME.) DORENFELDT, and O. W. BERG (*J. Chim. Phys.*, 1925, **22**, 253—263).—Taking the atomic weight of ordinary lead as 207·18, the atomic weight of the mixture of lead isotopes in Norwegian clevite was determined as 206·17 by two different methods: (1) by conversion of a carefully purified chloride into the sulphate, and, (2), more accurately by measuring the densities of saturated solutions of the nitrates, from which the atomic weight can be calculated, if it is assumed that the molecular solubilities are the same. The single result obtained by method (2) agreed with the mean of slightly differing results obtained by method (1). The clevite was remarkable for its small content of thorium. W. H.-R.

Number of Ions Produced in a Spherical Volume by Radium Emanation (Radon). M. W. MUND (*Ann. Soc. Sci. Bruxelles*, 1925, **44**, 336—344).—Theoretical. The total number of ions produced in a spherical volume of gas by the α-particles of emanation homogeneously distributed in it and of radium-*A* and radium-*C* on the enclosing walls has been calculated. Two cases are considered: one, when the gaseous volume has a larger radius than the ranges of the α-particles, and the other when this radius is smaller. Equations are given connecting the number of ions produced with the ranges of the α-particles, the radius of the spherical enclosure, the constant of the gas ionised, and the number of atoms of radium emanation present. A. S. R.

Magnetic Spectrum of β-Particles from Radium-*E*. (MLLE.) I. CURIE and J. D'ESPINE (*Compt. rend.*, 1925, **181**, 31—33).—The upper limit of the principal band is very sharply defined at $\beta=0{\cdot}936$ (β=ratio of the velocities of the particle and of light), the lower edge being somewhat indefinite at $\beta=0{\cdot}70$. The portion of maximum intensity between $\beta=0{\cdot}86$—$0{\cdot}80$ is due to the partial overlapping of a sharply-defined band extending from $\beta=0{\cdot}936$—$0{\cdot}80$ and a less sharply-defined band extending from $\beta=0{\cdot}86$—$0{\cdot}70$. The band corresponding with radiations, $\beta=0{\cdot}50$, is possibly due to some secondary effect. There is also a band corresponding with radiations of higher velocity, $\beta=0{\cdot}986$—$0{\cdot}97$. J. S. C.

Paramagnetism and the Electronic Configuration of the Atom. L. C. JACKSON (*Nature*, 1925, **115**, 981).—It is suggested that the different magnetic states of the ions of iron ($Fe^{\cdot\cdot}$) and cobalt ($Co^{\cdot\cdot}$) may correspond with different internal configurations of the electrons. Thus ordinary ferrous iron would possess the configuration 2, 8, 14, 0, and the other magnetic state might be produced by the transference of one of the 14 electrons in the

incomplete third quantum orbit to the fourth quantum orbit, or by a redistribution of the third quantum orbit electrons among the various levels, 3_1, 3_2, and 3_3, of this orbit (cf. Russell, this vol., ii, 406). A. A. E.

Structure of Strontium. H. COLLINS (*Chem. News*, 1925, **131**, 3—6).—Tables of atomic and molecular volumes, heats of formation, of neutralisation and of solution, and magnetic rotation are compiled to support the speculation that the strontium atom is formed by the union of calcium and titanium atoms. S. I. L.

The Statistical Distribution Function in the Theory of Radiation and Atomic Heat. E. CSÁSZÁR (*Z. Physik*, 1925, **32**, 872—880).—Polemical against Schrödinger (*ibid.*, 1924, **25**, 173). E. B. L.

Quantum Theory of the Laue Effect. M. BRONSTEIN (*Z. Physik*, 1925, **32**, 886—893). E. B. L.

Application of Quanta to the Electron Theory of Metals. L. S. ORNSTEIN (*Z. Physik*, 1925, **32**, 673—677).—Expressions are obtained for the conditions of equilibrium between electrons, atoms, and radiation. The theory of metallic conduction is developed from the point of view that the mean free path of an electron ends when it approaches nearer than a certain small distance to a metallic ion. As with other theories, it fails to account for the Hall effect, or for super-conductivity at very low temperatures. E. B. L.

New Light on Two-electron Jumps. R. A. MILLIKAN and I. S. BOWEN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 329—334; cf. A., 1924, ii, 710; this vol., ii, 342; *Physical Rev.*, 1925, [ii], **25**, 591).—An extension of previous work, the radiating properties of two-valency-electron, and three-valency-electron atoms being investigated. The former systems are characterised by a spectral flag consisting of five nearly equally spaced bars, the central one being about twice as heavy as the others, and systems of the second type are characterised by a flag consisting of four bars, the middle two being fairly close together. These flags are produced by simultaneous jumping of two electrons. The jumps consist in a jump of one of the two electrons between a $2p$ and a $2s$ level, or a $3p$ and a $3s$ level combined with a simultaneous jump of a second electron between two of the levels: $2p_1$, $2p_2$, $2p_3$, or $3p_1$, $3p_2$, and $3p_3$. The significance of the two-electron jump is considered, a more detailed analysis being promised later. J. S. C.

Physical Interpretation of Bohr's Stationary States. G. P. THOMSON (*Phil. Mag.*, 1925, [vi], **50**, 163—164).—The stationary states of an electron in the hydrogen atom can be regarded as determined, without postulating waves with a velocity greater than light, by supposing the electron to be attached to the nucleus by a tube of force forming a connexion of limited, although possibly varying, cross-section between the two charges. If the tube possesses mass, and its tension provides the attraction between the electron and the

nucleus, it will be able to transmit waves, and the condition determining the possible states is that the vibrations in the tube shall be in tune with the period of the orbit. F. G. T.

Relative Transition Probabilities in the Sodium Atom. G. R. HARRISON (*Physical Rev.*, 1925, [ii], **25**, 768—782).—Direct precise measurements were made of line absorption intensities, whence the constants C_1 and C_2 in Slater's formula for transition probabilities, $Nxh\lambda_0 B_{ij}=c\pi\log_e 10\times\sqrt{C_1/C_2}$ and relative values of B_{ij} were determined for the various lines 2 to 16 in the principal series of sodium. No decrease in relative probability of the higher numbers with increasing vapour pressure was found. Relative values of A_{ij} were computed from Einstein's relation $c^3A_{ij}=8\pi h\nu_0{}^3B_{ij}$. In these expressions, A_{ij} is the probability of a spontaneous transition from state j to state i with the emission of radiation, B_{ij} that of the reverse process, c the velocity of light, N the number of absorbing atoms, x the length of the absorbing path, h Planck's constant, and λ_0 the central wave-length of the absorption line. A. A. E.

Methods for Determining Transition Probabilities from Line Absorption. J. C. SLATER (*Physical Rev.*, 1925, [ii], **25**, 783—790).—A discussion of the various steps encountered in translating the experimental data into atomic constants, and a statement of the formulæ in a form adapted for practical use. A. A. E.

Relation of Spectral Lines to Mass Variations within the Atom. L. B. HAM (*Physical Rev.*, 1925, [ii], **25**, 762—767).—An investigation of the mass variations of the electron and nucleus involved in the transitions represented by Bohr's frequency condition $h\nu=E_b-E_e$, on the assumption that the total mass variations of the electron are composed of "kinetic" and "potential" variations. An apparent discrepancy between the quantum theory and the theory of relativity is thus eliminated, and it is shown that the electronic mass may be considered as quantified. The fine structure of the hydrogen doublet is explained, and absolute values of the changes of mass of the electron at aphelion and perihelion for various orbital transitions for $H\alpha$ are tabulated. A. A. E.

Orbits in the Hydrogen Atom as Affected by the Motion of the Nucleus. E. REICHENBÄCHER (*Z. Physik*, 1925, **32**, 907—917; cf. *ibid.*, 505). E. B. L.

Electronegative Hydrogen. A. E. VAN ARKEL and J. H. DE BOER (*Physica*, 1924, **4**, 382—392).—Electronegative hydrogen (as in lithium hydride) accounts for the properties of B_2H_6 on the basis of Kossel's screening effect. For the hydrocarbons, hydrogen behaves like a small halogen rather than an infinitely small positive charge. Simple rules are given for calculating the b. p. of halogen derivatives of methane; the method is less successfully applied to derivatives of silicon hydride. CHEMICAL ABSTRACTS.

Possible Explanation of the Ingersoll Non-magnetic Nickel Film. C. W. OSEEN (*Z. Physik*, 1925, **32**, 940—941).—A film

of nickel formed by cathode spluttering is not magnetic. If the M ring contains 18 electrons the atom would not be expected to be magnetic. If one or more of these electrons has a higher quantum number, which is probable in crystals and in chemical compounds, the atom would be paramagnetic. E. B. L.

Atomic Structure Factor in the Intensity of Reflection of X-Rays by Crystals. D. R. HARTREE (*Phil. Mag.*, 1925, [vi], **50**, 289—306).—The use is indicated, in examining complicated crystal structures, of F-curves, which represent the variation with glancing angle of the factor F, the scattering power of an atom, defined as the ratio of the amplitude of the wave scattered by that atom to the amplitude of the wave scattered by an electron. By assuming that the individual electrons in an atom scatter according to classical theory, it is shown that the F-curves for any given atom can be calculated from the dimensions of, and the progress of time in, the core orbits. It is possible by a numerical analysis of the terms of the optical and X-ray spectra to determine approximately the field of an atom, and from this the dimensions of the core orbits may be calculated (A., 1924, ii, 2). The results of this analysis indicate that the maximum radii of all non-circular core orbits with the same principal quantum number are very nearly the same. This, in conjunction with the result that the contribution to the scattering power of an atom from a non-circular orbit is a function of the maximum radius of the orbit only, permits all non-circular core orbits of the same principal quantum number to be regarded as equivalent as regards their contribution to the scattering power of the atom. Maximum radii of the core orbits are represented by the formula $\rho_0=\kappa/(N-\gamma)$, where N is the atomic number, and κ and γ are constants for core orbits of the same quantum number in different atoms. Values of the constants are given for a number of orbits. Tables are given for the contributions to the scattering power from circular and non-circular orbits, respectively, and the F-curves based on Stoner's distribution of electrons are given for the ions Cs^+, Cu^+, S^{--}, S^{++++++}, and O^{--}. In these curves, there is a slow initial decrease of F with increasing glancing angle for compact ions compared with that for ions of greater size. For the same element in different states of ionisation there is little difference in value of F except for small glancing angles. The observed values of F for Na^+ and Cl^- are smaller than those calculated either from the Bohr or the Stoner electron distribution. F. G. T.

Interpretation of Intensity Measurements in X-Ray Analysis of Crystal Structure. W. L. BRAGG (*Phil. Mag.*, 1925, [vi], **50**, 306—310).—A discussion of factors to be considered in using Hartree's results for the relative scattering powers of atoms based on a calculation of orbit dimensions (cf. preceding abstract). The influences are of two types, dependent on the glancing angle and the structure factor, respectively. Those dependent on the glancing angle are due to the method and crystal sample used, and on the polarisation of the scattered radiation. The dependence of the

intensity on the structure factor is obscure, but if the observed intensities show a parallelism with the calculated structure factors when both are arranged in order of increasing glancing angle, the assigned structure must be correct. In comparing each plane with the next at a higher angle, a rise of structure factor should correspond with an increased intensity, and *vice versa*. In the discussion of the form of the law relating the intensity of scattered radiation I to the structure factor S, it is pointed out that an estimate of the extinction coefficient ϵ of rock salt (A., 1921, ii, 477) leads to the relation $I \propto S^2/(\sigma+\epsilon)$, where σ is the absorption coefficient. For a crystal in which ϵ is much larger than σ, this relationship becomes $I \propto S^2/(\sigma+\alpha I)$, where α is a constant. This assumes the form $I \propto S$, or $I \propto S^2$, according to whether I is large or small. The discrepancy between the observed and Hartree's calculated scattering coefficients for sodium, chlorine, and oxygen may be due in part or entirety to the heat motions of the atoms, for which no allowance has been made. F. G. T.

Diamagnetism and the Size of Ions. G. Joos (*Z. Physik*, 1925, **32**, 835—839).—The distance of the outer electrons from the nucleus is calculated from Langevin's theory and agrees remarkably well with the result obtained from the theory of the crystal lattice. E. B. L.

Formation of Band Spectra. R. Mecke (*Z. Physik*, 1925, **32**, 823—834).—The close relationship existing between the nuclear vibrational and rotational energy of sixteen band spectra is emphasised. For the complete development of a band spectrum the determining factor is probably the interaction between the nuclear oscillations and the electron motions, and not the strength of the non-harmonic bond. E. B. L.

Structure and Distribution of Band Spectra. H. Deslandres (*Compt. rend.*, 1925, **180**, 1980—1986; cf. *ibid.*, 1454).—The infra-red absorption of water vapour has been examined and the position of the absorption bands measured. Strong absorption is shown at 2·661μ, 6·26μ, and above 30·6μ, whilst other weaker bands are present. The frequencies of the bands agree fairly well with those deduced from the formula $\nu = q/r \times d_1/s$ (Deslandres, *loc. cit.*), where d_1 is a fundamental frequency of 1062·5, s is the number of atoms in the molecule which equals 3 for water, and q and r are whole numbers. Bands at 3·154μ and 6·26μ can be split up, by a suitable prism, into a number of secondary bands the frequencies of which differ by $d_1/24$ and $d_1/48$ in the two cases, respectively. The results can be explained on the assumption that the atomic nucleus is surrounded by a cubical zone of protection within which the attractive force on an electron becomes a repulsion. The cubes are perfectly elastic, of side $2a$, and emit a fundamental frequency d_1. Band spectra are produced by the elastic vibrations of the cubes without breaking the protective zone, but when the latter is broken down the ordinary line spectrum is emitted. W. H.-R.

Fulcher Hydrogen Bands. G. H. Dieke (*Phil. Mag.*, 1925, [vi], **50**, 173—179; cf. *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 490).—A comparison of the author's interpretation of the Fulcher bands with that of Curtis (this vol., ii, 351). The former interpretation gives a more satisfactory explanation of the vertical series, of the intensity of the lines, and of the variation of the intensities with temperature. On the other hand, Curtis' value for the moment of inertia of the hydrogen molecule is more acceptable than that based on the author's interpretation. F. G. T.

Extension of the Negative Band Spectrum of Nitrogen. T. R. Merton and J. G. Pilley (*Phil. Mag.*, 1925, [vi], **50**, 195—199; cf. this vol., ii, 333).—The negative band of the spectrum of nitrogen has been remeasured, and the heads of the bands have been arranged in five series. The results do not agree with those of Deslandres (*Compt. rend.*, 1904, **139**, 1174), but the constancy of the second differences in the wave-numbers is much closer than with the values of Deslandres. F. G. T.

Quantum Analysis of New Nitrogen Bands in the Ultra-violet. R. T. Birge and J. J. Hopfield (*Nature*, 1925, **116**, 15).—A group of strong bands in the predicted position (cf. A., 1924, ii, 803) has been analysed, but the progressions are unexpectedly not related to those of any other analysed group of nitrogen, or of any other substance. The equation for the new group is $\nu = 68{,}956{\cdot}6 + (1681{\cdot}45n' - 15{\cdot}25n'^2) - (2345{\cdot}16n'' - 14{\cdot}445n''^2)$, where n'' varies from 0 to 9 and n' from 0 to 3 only. A. A. E.

Infra-red Emission and Absorption of Potassium Vapour. A. L. Narayan and D. Gunnaya (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 1—14).—In potassium vapour at 500—700°, the existence of Moll's line at 3·65μ and Paschen's line at 2·72μ has been confirmed, and a new line at 1·2μ found. Below about 600°, the vapour exercises no selective absorption. W. A. C.

Absorption of Electrically Luminescent Potassium Vapour. A. L. Narayan and G. Subrahmanyam (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 15—18; cf. preceding abstract).—In potassium vapour at about 350° rendered feebly luminescent by an electrical discharge, the Bergmann line at 1·5μ shows distinct absorption. It is maintained that the energy of excitation of the spectral lines increases in the order: principal, diffuse, sharp, Bergmann. W. A. C.

Effect of Density on the Wave-length of the Absorption Bands of Iodine. A. Perot and M. Collinet (*Compt. rend.*, 1925, **180**, 2030—2032).—Known weights of iodine were vaporised in sealed glass tubes at 180° and the wave-lengths of six of the absorption bands were measured. The effect of density is given by the relation $d\lambda/\lambda = ad\rho$, where λ is the wave-length of the band, ρ the density, and $a = +12 \times 10^{-3}$ and is constant between the limits $\rho = 0{\cdot}16 \times 10^{-4}$ and $\rho = 1{\cdot}96 \times 10^{-4}$ C.G.S. Results of the same order were obtained when the iodine was vaporised in open tubes, indicating that it is the density of the vapour and not the total pressure that is effective. W. H. R.

Luminous Vapour from the Mercury Arc and the Progressive Changes in its Spectrum. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1925, **A**, **108**, 262—279).—When mercury distils away from the arc in a vacuum, the stream of vapour is luminous. An examination of the light shows that the spectrum lines of the arc which are members of known series are in general strongly developed in the vapour stream. An exception is $1p-1s$, 1850 Å. The arc lines not hitherto classified into series are faint or absent. The higher members of the various series appear in greater relative intensity in the vapour than in the arc. Their absolute intensity, even, may be greater in the vapour. At greater distances from the arc, the light from the arc changes in many ways. The higher series members lose in intensity, 2537 steadily becomes stronger, and the continuous spectrum of mercury appears. The effect of an electric field is to cause the rapid disappearance of the line spectrum of the vapour. 2537 is more persistent than the other lines, and the continuous spectrum passes on. The observations are discussed in relation to estimates of the life-period of an excited atom etc., and are difficult to reconcile with present views on the origin of spectra. S. B.

Ultra-violet Absorption Spectra of Dichloroethylenes. J. ERRERA and V. HENRI (*Compt. rend.*, 1925, **180**, 2049—2050).—The ultra-violet absorption of the *cis*- and *trans*-isomerides of dichloroethylene has been studied, using the pure liquids and also solutions of them in hexane and alcohol. Both isomerides begin to absorb at about 2600 Å., and the absorption increases with diminishing wave-length. The *trans*-isomeride has a higher coefficient of absorption than the *cis*-. The ratio of the two coefficients is the same in both solutions and in the pure liquids, and increases from 1·3 for 2595 Å. to 3·9 for 2200 Å. W. H.-R.

Fluorescence of Fisetin in the Ultra-violet Light of the Wood Lamp. L. MEUNIER and A. BONNET (*Compt. rend.*, 1925, **180**, 2038—2040).—Sections of ordinary wood barks used for tanning show no fluorescence, but woods from Quebracho in Colorado, and Tizerah of Morocco, show a brilliant fluorescence on freshly-cut sections. Solutions show a feeble fluorescence only, but if a substance with a large surface such as filter-paper, or, better, cellulose acetate silk, is added to the solution, a brilliant fluorescence is obtained in ultra-violet light, owing to the presence of fisetin in the bark (cf. Perkin, T., 1896, **69**, 1303), whilst the fluorescence is also observed if powdered leather, which has been tanned with extracts from either of these two barks, is treated similarly. The method enables extracts from these woods to be detected in tanning mixtures, and also enables slowly tanned leather to be distinguished from products rapidly tanned with Quebracho extract. W. H.-R.

Theory of Diminution of Fluorescence. A. PREDWODITELEW (*Z. Physik*, 1925, **32**, 861—871).—The energy absorbed by a fluorescent substance is partly transformed into heat and partly

radiated as fluorescence. A relationship is exhibited between the amount of fluorescence and the specific heat at constant volume of the active molecules. A method of calculating the mean energy of the resonators is given and its relation to the amount of fluorescence is deduced. E. B. L.

Polarised Fluorescence of Dyes. V. S. J. Vavilov (*Z. Physik*, 1925, **32**, 721—729; cf. Lewschin, this vol., ii, 629).—The König-Martens spectrophotometer was used to measure the intensity of the polarised fluorescent light from fluorescein in methyl alcohol, water, and glycerol, and of erythrosin in glycerol. At high concentrations, fluorescein in methyl alcohol and in water shows no polarisation. The amount of polarisation is independent of wave-length. E. B. L.

Opalescence of Binary Liquid Mixtures. J. C. K. Rao (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 19—60).—The intensity and polarisation of light scattered by dust-free mixtures of toluene and acetic acid at the ordinary temperature and of methyl alcohol and carbon disulphide over a range of temperatures has been measured. Intensities show maximum values at definite concentrations and temperatures; these maxima are steepest at the critical temperature and very steep indeed at the critical concentration. The degree of polarisation follows a similar course, and at the critical temperature and concentration the scattered light is almost completely polarised. A formula based on Lorentz's electromagnetic theory is developed to express the amount of scattering at right angles to the primary beam. W. A. C.

Spectrophotometric Studies of the Glow Discharge. R. Seeliger and W. Lindow (*Physikal. Z.*, 1925, **26**, 393—403).—The distribution of light intensity at various positions along discharge tubes containing (*a*) oxygen, (*b*) hydrogen has been measured for various individual lines in the spectra of the two gases. Graphs are given showing the variation in intensity of the lines 4650 Å. (spark), 4520 (band), 4268 (doublet) for oxygen, and the lines 4634, 4177, 4461 for hydrogen with distance in mm. from the cathode. The curve, distance from cathode–intensity, is plotted for single lines at various gas pressures. The relations between distance, intensity, and pressure are also given for the negative glow. The sharp beginning of the negative glow is clearly shown for single lines, but the distance of the intensity maximum as well as the shape of the curve differs widely for different lines. Hence visual recognition of a sharp edge to the glow loses in theoretical significance unless observations are carried out with suitable light-filters. Generally, the intensity–distance curve is flat for higher excitation potentials and shows a sharp maximum for lower excitation potentials. The work may provide a means of classifying the many-lined spectra.

Quantitative data for the absolute intensity gradient at the edge of the dark space are given, and a close approximation to the mean free path of electrons can be made at different pressures.

A theory is advanced which appears to account for many of the phenomena observed in the discharge tube. The authors consider that the primary electrons ionise the gas in the glow and excite the light; the positively and negatively charged entities then fill the space and by their recombination contribute to the light emission. Diffusion plays an important part, since the swift (and slower) primary electrons travelling in a straight line intersect the paths of the secondary electrons and scattering effects occur. Experiments designed to test this mechanism gave results in accord with the theory. R. A. M.

Spectroscopic Study of the Combustion of Phosphorus Trioxide and of Hydrogen Phosphide. H. J. Emeléus (*J. Chem. Soc.*, 1925, **127**, 1362—1368).—A modification of Thorpe and Tutton's method for the preparation of phosphorus trioxide is described. The glow of the trioxide appears as a luminous pulse starting at a considerable distance from the surface. Water vapour is essential to the glow and the pulses occur more readily in the presence of a little liquid water. The spectrum of the light from the glow of the trioxide is identical with that obtained in the case of glowing phosphorus by Emeléus and Downey (this vol., ii, 89). The burning of hydrogen phosphide in air shows the same ultra-violet bands, with that at about $\lambda=3270$ Å. relatively more intense. Ether and acetone inhibit the glowing of phosphorus and of its trioxide, and also prevent the ignition of an hydrogen phosphide–air mixture when the pressure is reduced; benzene, chloroform, coal gas, and ammonia act less effectively. It is suggested that the low-temperature combustions of phosphorus, phosphorus trioxide, and hydrogen phosphide involve some common stage responsible for the chemical anomalies and intimately associated with the characteristic light emission. W. T.

Generalisation of the Townsend Theory of Spark Potentials. W. Dällenbach (*Physikal. Z.*, 1925, **26**, 407—410).—Mathematical. An attempt to formulate more accurately the interdependence of spark-potential and glow discharge. R. A. M.

Electrification of Gases by Surface Combustion. J. Dickinson (*Phil. Mag.*, 1925, [vi], **50**, 225—241).—The extent of ionisation accompanying gaseous combustion has been determined by measuring the sign, and the rate of growth, of the charge on an iron chamber in which surface combustion is occurring, and on a metal vessel, acting as an electrode, into which the products of combustion were led. When the gas–air mixture is burnt by surface combustion alone, the charge on the burnt gases (flue gases) is negative for mixtures containing originally less than 16% gas. When that percentage is reached, all electrification disappears. For gas percentages above 16%, the products are positively charged. The 16% gas mixture is that corresponding with complete combustion. In the combustion chamber itself, the above electrification signs are reversed. The burning gases in mixtures with less than 16% gas carry positive charges and impart these charges to the

walls of the combustion chamber. When the gas percentage is above 16%, unburnt gas predominates, and imparts a negative charge.

When there is perfect combustion, there is no electrification either on the chamber or on the flue-box, showing definitely that there is then complete equilibrium between the gases and the heated surfaces, all the surplus electrical discharge being wholly taken up by the gases in the combustion chamber, so that there are no ions in the products of combustion. When the gas mixture burns as a flame, the charge on the combustion products is wholly positive for mixtures between 2·6% and 18·5% gas. On the other hand, the sign on the combustion chamber depends on the temperature, changing from negative to positive with increasing temperature in the neighbourhood of red heat. Evidence that the added heat of combustion during surface combustion is not due to currents in the metal tube is found in the fact that the conductivity of the gases in the chamber during flame combustion is approximately seventy times that of the gases during surface combustion in the cases of optimum gas mixtures. F. G. T.

Variation of Dielectric Constants of Organic Liquids with Pressure. M. GRENACHER (*Ann. Physik*, 1925, [iv], **77**, 138—158).—A new technique has been devised for investigating at intervals of 10 atm. the variation of dielectric constant with pressures up to 60 atm. for organic liquids. Accurate results were obtained for toluene, ether, chloroform, carbon tetrachloride, nitrobenzene, nitrotoluene, and bromobenzene. Waibel's results on benzene (*ibid.*, 1922, **72**, 161) were used to standardise the apparatus. Nitrobenzene, nitrotoluene, bromobenzene, ether, and chloroform show definitely greater variations of dielectric constant with pressure than is the case for toluene, benzene, and carbon tetrachloride. They correspond with Meyer's dipolar liquids (A., 1924, ii, 515). The difference is most marked with ether and chloroform. For the other liquids, there is some uncertainty because data on the compressibility are lacking.

An improved needle-vibration galvanometer has been devised which is prompt in action and much more convenient than other types in use. R. A. M.

Variation of Dielectric Constant with Pressure for Organic Liquids at Pressures up to 800 Atmospheres. (FR.) C. FRANCKE (*Ann. Physik*, 1925, [iv], **77**, 159—181).—A method for producing high pressures in a condenser is described and a complicated circuit has been devised which enables very accurate measurements of dielectric constant to be made at pressure intervals of 50 atm. up to 800 atm. maximum pressure. The following data were obtained: for benzene at 18° $\epsilon=2\cdot2765$ at 50 atm. and 2·3412 at 700 atm.; the pressure coefficient varies from $4\cdot96\cdot10^{5}$ to $3\cdot34\cdot10^{5}$; the Clausius-Mosotti expression $\epsilon-1/(\epsilon+2)\cdot1/d$, leads to extreme values of 0·3373 and 0·3297; for hexane, $\epsilon=1\cdot8905$ at 50 atm. and 1·9736 at 800 atm.; the coefficient varies from $7\cdot25\cdot10^{5}$ to $4\cdot42\cdot10^{5}$; for heptane, $\epsilon=1\cdot9468$ at 50 atm. and 2·0224 at 800 atm.; the

coefficient varies from $6{\cdot}53 \cdot 10^5$ to $3{\cdot}55 \cdot 10^5$; for carbon tetrachloride, $\epsilon = 2{\cdot}2311$ at 50 atm. and 2·3222 at 800 atm.; the pressure coefficient varies from $6{\cdot}26 \cdot 10^5$ to $4{\cdot}26 \cdot 10^5$. The temperature coefficients employed were those of Isnardi (*Z. Physik*, 1922, **9**, 153) and Graffunder (*Ann. Physik*, 1923, [iv], **70**, 225). R. A. M.

Influence of Solvents on Rotatory Power. R. Lucas (*Compt. rend.*, 1925, **181**, 45—47).—Investigations on the variation with the wave-length of the specific rotatory power of camphor in benzene, *cyclo*hexane, and in a mixture of these two liquids show that over the range studied, 6708—4358, the value of the expression $[\alpha]_C - [\alpha]_M / [\alpha]_C - [\alpha]_B$, is constant, $[\alpha]_C$, $[\alpha]_B$, and $[\alpha]_M$ being, respectively, the specific rotatory powers in *cyclo*hexane, benzene, and the mixed solvent. A theory is developed in which the dissolved substance exists in two forms, each characterised by a definite dispersion and rotatory power, the equilibrium between the two forms being determined by concentration, temperature, and the nature of the solvent. J. S. C.

Rotatory Power of certain Camphor Derivatives. A. Haller and R. Lucas (*Compt. rend.*, 1925, **180**, 1803—1806).—The rotatory power of alcohol and benzene solutions has been measured at seven wave-lengths between 4358 and 6708 Å. for the following compounds: benzylidenecamphor, *o*-chlorobenzylidenecamphor, anisylidenecamphor, and piperonylidenecamphor. For the second compound, $[\alpha]$ is a little higher in benzene than in alcohol; for the other compounds, $[\alpha]$ is about 5—6% lower in benzene than in alcohol. The following show much larger differences: benzylcamphor, anisylcamphor, piperonylcamphor. Measurements of $[\alpha]$ are given in alcohol, benzene, carbon disulphide, and *cyclo*hexane. The rotatory power varies greatly with the solvent. The quantity $\delta/\Delta = [\alpha]_{C_6H_{12}} - [\alpha]_{C_6H_6} / [\alpha]_{C_6H_{12}} - [\alpha]_{CS_2}$ is practically constant for a given solute, and varies little with wave-length. The constancy of δ/Δ follows from Biot's law for a mixture of two active bodies. Hence it is inferred that two different active forms exist in these solutions. R. A. M.

Rotatory Power and Dispersion in the Terpene Series. —Pariselle (*Compt. rend.*, 1925, **180**, 1832—1833).—The rotatory dispersions of *d*- and *l*-camphene are identical. The author's method (A., 1923, i, 813) for preparing camphene from pinene hydrochloride has resulted in specimens in which $[\alpha]_D = -79{\cdot}90°$ and $[\alpha]_D = +77{\cdot}10°$. The additive compounds of camphene always exhibit rotatory power of the opposite sign to that of the original camphene; the rotatory dispersion is always near to that of α-pinene and is definitely less than that of camphene and therefore of camphor. The camphene nucleus has thus been modified, an observation which confirms the work of Langlois, who has shown that camphene easily gives rise to abnormal compounds by intramolecular migrations. Ninety-eight % formic acid reacts with camphene in the presence of phthalic anhydride to give *isobornyl formate*, b. p. 95° (14 mm.), d_4^{20} 1·01, n_D^{15} 1·470, $[\alpha]_D$ −3·14°. R. A. M.

Rotatory Dispersive Power of Organic Compounds. XVI. Halogen Derivatives of Camphor. Optical Superposition in the Camphor Series. J. O. CUTTER, H. BURGESS, and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 1260—1274).—Measurements have been made of the optical rotations over a range of wave-lengths of α- and α′-chlorocamphor, of β-bromocamphor, and of five isomeric dibromocamphors. The basis of the principle of optical superposition is illustrated by α- and α′-chlorocamphor, the rotatory power of which can be represented by $[\alpha]_{5461}=65{\cdot}5°\pm24{\cdot}6°$; by α- and α′-bromocamphor, $[\alpha]_{5461}=51{\cdot}8°\pm98{\cdot}9°$, and by αβ- and α′β-dibromocamphor, $[\alpha]_{5461}=8{\cdot}8°\pm91{\cdot}9°$, whereas the means of the rotatory powers of the pairs camphor αα′-dichlorocamphor, camphor αα′-dibromocamphor, and β-bromocamphor and αα′β-tribromocamphor are $[\alpha]_{5461}=62{\cdot}1°$, 51·3°, and about 12°, respectively. No such regularities were observed with the π-compounds. In nine cases out of ten, the curves of rotatory dispersion are complex, but normal. The rotation increases progressively as the wave-length diminishes, giving rise to quasi-hyperbolic dispersion curves, which do not exhibit any obvious anomalies; the dispersion is not simple, since it cannot be represented by a single term of Drude's equation. The dispersion can be represented satisfactorily by two terms of Drude's equation, except for α′β-dibromocamphor. The dispersions of this substance are more complex, giving imaginary values for the constants of the two-term equation.

In the constants for the Drude equation, the low-frequency term, representing the contribution of the ketonic group to the optical activity of the molecule, is always positive, as in camphor. The high-frequency term, representing the sum of the partial rotations of the fixed asymmetric centres, is negative in camphor, and remains so in β-bromocamphor and in αα′-dibromocamphor, where no new centre of asymmetry is introduced, and the dispersion is quasi-anomalous. In compounds containing a halogen atom in the α-position, the large partial rotation of the new asymmetric carbon atom makes the high-frequency term positive, and the dispersion is complex but normal.

In the two α′-derivatives the fixed negative rotation of the camphor molecule is reinforced by the negative partial rotation of the new asymmetric carbon atom. For α′-bromocamphor the negative term of the Drude equation predominates over the positive in the visible region, but a reversal of sign is observed in the early ultra-violet region. The dispersion curve becomes totally anomalous, and an inflection at 5455, maximum at 4710, and a reversal of sign at 3890 Å. have been experimentally observed. F. G. T.

Variation of Rotatory Power of Solutions of Asparagine as a Function of Hydrogen-ion Concentration. (MLLE.) J. LIQUIER (*Compt. rend.*, 1925, **180**, 1917—1919).—The rotatory power of asparagine between p_H 1·29 and p_H 9·91 is measured by adding varying amounts of strong and weak acids or bases. The dispersion is normal at extreme p_H values, but anomalous at the intermediate value of $p_H=3$. The rotation at a given p_H is constant

whether the added acid is weak or strong, showing that a close connexion exists between dissociation and rotatory power. On the basis of a mixture of undissociated molecules and ions, a three-term expression gives quantitatively the rotatory power as a function of hydrogen-ion concentrations and of the two dissociation constants of the amphoteric asparagine. R. A. M.

Influence of Hydrogen-ion Concentration on the Optical Rotation of Gelatin. R. H. Bogue and M. T. O'Connell (*J. Amer. Chem. Soc.*, 1925, **47**, 1694—1697).—The specific rotation of 2% solutions of isoelectric and ash-free gelatin at 30° varies with the hydrogen-ion concentration. Within the range examined, p_H 0·3 to p_H 13·4, in which hydrolysis is improbable under the conditions employed (cf. Northrop, A., 1921, ii, 541), the specific rotation exhibits a minimum at the isoelectric point, p_H 4·7, and then rises as the acidity or alkalinity is increased, subsequently decreasing in high concentrations of acid or alkali. There is no indication of a second isoelectric point at p_H 7·7. At p_H 4·7, the specific rotation of pure ash-free isoelectric gelatin in 2% solution at 30° is $-104°$ ($\pm 4°$). R. B.

Colours Shown by Nobili's Rings. B. N. Chuckubutti (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 83—91).—Nobili's rings may be obtained with a variety of cathodes and electrolytes, but the finest display results when a brass plate is used in lead sulphate or manganous sulphate solution. The rings consist of granular particles of metal or oxide and are largest ($d=500\mu\mu$) near the centre and smallest ($d=275\mu\mu$) at the periphery. It is suggested that the colours are due to diffraction by these granules, and the similarity to metal colours produced by heat is pointed out. W. A. C.

The Significance of Atomic Constants in Additive Properties. F. Swarts (*Bull. Soc. chim. Belg.*, 1925, **34**, 161—182).—The existing tendency to ascribe definite values to various groups or atoms in respect of additive properties such as atomic and molecular volumes, magnetic rotation, refractivity, etc., and the establishment of general formulæ which are only verified to a very large degree of approximation is keenly criticised. Such functions, due to the fundamental properties of the electrons within the atom, are profoundly affected, not only by the structure of the molecule, but vary with the proximity of different atoms and the strength of the electromagnetic field within the molecule, and an approximate calculation shows that the latter may be of the order of 10^2 gauss, *i.e.*, that of the most powerful field employed in the study of magnetic rotatory power. Real progress can best be made by greater precision in the physical measurements and a determination of the atomic variations rather than the atomic "constants" in relation to compounds the structure of which has been firmly established by chemical means. The author's investigations show that fluorine exhibits the most regular behaviour in organic compounds and often establishes interesting relationships which are masked when the other halogens are used as substituents. The effect of fluorine on molecular dispersion is extremely small, its

spectrum shows the absence of rays in the near ultra-violet, and fluorine derivatives show much less absorption in that region than do the corresponding hydrocarbons themselves, and hence the frequency of the electrons must be very great. J. W. B.

Heat of Formation of Formaldehyde. H. VON WARTENBERG and LERNER-STEINBERG (*Z. angew. Chem.*, 1925, **38**, 591—592).—The experimental value of the heat of formation of formaldehyde, 158·8 cal. per mol. CH_2O, is not in accordance with theory; the experimental work has therefore been repeated. No error had arisen from incomplete combustion, but a slight tendency to polymerisation of the formaldehyde on the walls of the containing apparatus was detected. Whilst this error is considered to have been slight, a series of repetitions of the determination gave a final corrected value of 134·1 cal./mol. at constant volume, and this value, which is in fair agreement with that given by calculation (126·7 cal.), is to be substituted for the previous one. C. I.

X-Ray Crystal Analysis as an Auxiliary in Organic Chemical Research. R. ROBINSON (*Nature*, 1925, **116**, 45).—A brief account of the successful application, by Shearer, of X-ray analysis to the determination of the length of carbon chains and the position of a carbonyl group. Similar investigations indicate that the acetylenic linking of stearolic acid is hydrated in each of the theoretically possible directions, *i.e.*, $CH_3{\cdot}[CH_2]_7{\cdot}CO{\cdot}[CH_2]_8{\cdot}CO_2H$ and $CH_3{\cdot}[CH_2]_8{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H$, when the substance is treated successively with sulphuric acid and water. A. A. E.

X-Ray Analysis of Solid Solutions of Potassium Chloride and Potassium Bromide. T. SASAHARA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 277—286).—Powder photographs of fusion-mixtures ranging from 22 mol. % to 88 mol. % of potassium bromide indicate complete additivity in the lattice constant; the density also is additive. Although the mean lattice constant is thus a linear function of the concentration, it is probable that the spacing is a little smaller in the neighbourhood of chlorine atoms and a little larger in that of bromine atoms. W. A. C.

X-Ray Examination of the Inner Structure of Various Calcium Carbonates. A. ÔSAWA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 33—41).—X-Ray examination of various forms of calcium carbonate derived from animal and vegetable sources showed that most varieties consisted of the calcite modification, but calcium carbonate from an *Acropora*, a *Favia*, *Septifer bilocularis*, and *Trubo cornutus* consisted of the aragonite variety. The author's aragonite model agrees with that of Bragg (A., 1924, ii, 109). A. R. P.

X-Ray Analysis of Electrolytic Brass. H. NAKAMURA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 287—292).—Electrolytically deposited brass of 82·48% of copper and cast brass of 82·85% of copper have been examined by the powder method and the lattice constant 3·62 Å. has been found in both cases. In spite of com-

siderable differences in the microscopic structure of the two brasses, their atomic structures must be regarded as identical. After annealing, however, the constant of the electrolytic brass was 3·62 Å. and that of the cast brass 3·61 Å. W. A. C.

X-Ray Analysis of Copper–Zinc, Silver–Zinc, and Gold–Zinc Alloys. A. WESTGREN and G. PHRAGMEN (*Phil. Mag.*, 1925, [vi], **50**, 311—341).—It is suggested that the fundamental difference between solid chemical compounds and solid solutions lies in their structure. In an ideal chemical compound, structurally equivalent atoms are chemically identical. In an ideal solid solution all atoms are structurally equivalent. Most metallic phases represent intermediate stages between these two extreme types of structure. *X*-Ray analysis of the above alloys has shown that five different types of structure are common to all three systems, two additional phases occurring in the gold–zinc system. The β and γ phases of the copper–zinc system were investigated in the form of single crystals, the analyses in the other cases being made by the powder method alone. The five structures common to the systems, arranged in order of increasing zinc content, are: α, face-centred cubic; β, cubic of the cæsium chloride type; γ, cubic, with 52 atoms in the elementary cube; ε and η, close-packed hexagonal with axial ratios of 1·55—1·60 and 1·80—1·90, respectively. A gold–zinc phase, γ_1, stable at the ordinary temperature, and containing about 50% zinc, was cubic, with about 32 atoms in the elementary cube; another phase, γ_2, stable only at higher temperatures and obtained by quenching gold–zinc alloys containing 53—54% zinc, was apparently cubic with about 90 atoms in its elementary cube. The α, η, and very probably the ε phases represent ideal solid solutions as above defined, the first having copper, silver, or gold, and the others zinc as solvent. The other phases are regarded as solid solutions in chemical compounds, the solvents of the β phases being CuZn, AgZn, and AuZn. The formulæ Cu_4Zn_9, Ag_4Zn_9, and Au_4Zn_9 are proposed for the bases of the γ phases, and it is most likely that the γ phase of the gold–zinc system corresponds with $AuZn_3$.

F. G. T.

X-Ray Examination of Inner Structure of Strained Metals. III. Copper and Aluminium under Extension, Compression, and Torsion. A. ONO (*Mem. Coll. Eng. Kyushu*, 1925, **3**, 195—224).—An *X*-ray analysis of copper and aluminium, under strain due to extension, compression, or torsion, has been made. The effect of annealing strained aluminium has also been determined. The crystal rearrangement due to slip and rotation is discussed from the point of view of the behaviour of single crystals under distortion observed by previous investigators. [Cf. *B.*, 1925, 594]. M. S. B.

X-Ray Examination of Iodosuccinimide. (MISS) K. YARDLEY (*Proc. Roy. Soc.*, 1925, **A**, **108**, 542—547).—There are 4 mols. per unit cell of this substance. It does not belong to the ditetragonal pyramidal class, as stated by Groth, but to the tetragonal pyramidal polar class (cf. following abstract). L. F. G.

Crystallographic and Optical Properties of Iodosuccinimide. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 548—552; cf. preceding abstract).—The results of a detailed examination of these properties are given. Density determinations have also been made. The substance is optically active, but it was not possible to determine the angle of rotation. Miss Yardley's conclusion as to the crystallographic class is confirmed. L. F. G.

Quantum Theory of the Intensity of the Modified Band in the Compton Effect. G. E. M. JAUNCEY (*Physical Rev.*, 1925, [ii], **25**, 723—736).—The theory already developed (this vol., ii, 368) is extended to scattering by L and M electrons and by electrons in elliptical orbits. Experiments are in qualitative agreement with the required increase of the intensity of the modified band relative to that of the unmodified band as the angle of scattering is increased, and (for a given angle of scattering) with its required decrease as the atomic number of the scatterer increases. Curves show the intensity of the modified bands when molybdenum $K\alpha$ X-rays are scattered by carbon and sulphur at 30° and 90°.

A. A. E.

Dependence of the Intensity of the Compton Effect on the Atomic Number. B. DAVIS (*Physical Rev.*, 1925, [ii], **25**, 737—739).—The integrated intensity of the scattered radiation is proportional to $b/z^3\lambda^3$, where z is the atomic number and b the fraction of orbital electrons taking part in the scattering. All the orbital electrons appear to take part equally in the scattering effect. The relative intensities for molybdenum $K\alpha$ radiation for paraffin, aluminium, sulphur, and calcium, respectively, are 8, 1·25, 0·7, and 0·35. A. A. E.

Lattice Constants of Metals. W. P. DAVEY (*Physical Rev.*, 1925, [ii], **25**, 753—761).—Precision measurements of the lattice constants $a\times10^{-8}$ cm., by comparison with sodium chloride (a= 2·814 Å.) and the corresponding calculated densities are tabulated respectively as follows: aluminium, 4·046±0·004, 2·688±0·008; iron, 2·855±0·003, 7·93±0·03; nickel, 3·499±0·003, 9·04±0·03; copper, 3·597±0·004, 9·01±0·03; molybdenum, 3·142±0·003, 10·21±0·03; palladium, 3·859±0·004, 12·25±0·04; silver, 4·079±0·004, 10·49±0·03; tungsten, 3·155±0·001, 19·32±0·02; platinum, 3·912±0·004, 21·51±0·06; gold, 4·065±0·004, 19·37±0·06; lead, 4·920±0·005, 11·48±0·03; bismuth, 4·539±0·005 (hexagonal axes, axial ratio 2·606), 9·80±0·03. A. A. E.

Atomic Structure of Palladium and Platinum Black containing Adsorbed Gases. A. OSAWA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 43—45).—X-Ray examination of platinum and palladium blacks prepared by different processes show that the metal is crystalline and not amorphous as stated by Kirchner (*Ann. Physik*, 1922, [iv], **69**, 59). When the metals adsorb gases a true solid solution is formed, the gases entering into the interspace of the lattice. A. R. P.

Crystal Structures of Cæsium Tri-iodide and Cæsium Dibromoiodide. R. M. BOZORTH and L. PAULING (*J. Amer. Chem. Soc.*, 1925, **47**, 1561—1571).—The dimensions of the units of structure of cæsium tri-iodide and cæsium dibromoiodide as determined from considerations of spectral and Laue photographs are respectively: d_{100}=6·83 Å., d_{010}=9·89 Å., d_{001}=11·00 Å., and d_{100}=6·57 Å., d_{010}=9·18 Å., d_{001}=10·66 Å. In the crystalline substances there are four molecules in the unit. The structures are based on the simple orthorhombic lattice Γ_0 and the crystals belong to the space group V_h^{16}. The results of these investigations differ from those of Clark and Duane (*J. Opt. Soc. Amer.*, 1923, **7**, 455). J. S. C.

Crystal Structure of Mercurous Halides. R. J. HAVIGHURST (*Amer. J. Sci.*, 1925, [v], **10**, 15—28).—*X*-Ray analysis of powdered and of single crystals of mercurous halides (cf. this vol., ii, 502) shows that the cell units are tetragonal and contain 2 mols. of Hg_2X_2. The dimensions (in Å.) are: X=Cl: a=4·47, c=10·89; X=Br: a=4·65, c=11·10; X=I: a=4·92, c=11·61. Mauguin's cell unit for calomel is unnecessarily large (cf. A., 1924, ii, 588). The atomic arrangement may be derived from the space group D_4^5, or others; four mercury atoms are at (0, 0, u), (0, 0, $\bar{u}$), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$—u), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$+u) and four halogen atoms at (0, 0, v), (0, 0, $\bar{v}$), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$—v), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$+v). u and v are slightly lower than $\frac{1}{8}$ and $\frac{3}{8}$, respectively. The results indicate the existence of the chain molecule XHgHgX; strong positive double refraction is to be expected from crystals of this structure and has been observed. S. K. T.

Structure of Stearic and Stearolic Acids. A. MULLER (*Nature*, 1925, **116**, 45).—Stearic acid crystals, obtained from a saturated solution in carbon disulphide, are monoclinic. The dimensions of the unit cell are: a 5·60, b 7·38, c 50·9 Å., β 59·7°; d slightly above 1·05, indicating four molecules to the unit cell. A crystal of stearolic acid appeared to be triclinic. A. A. E.

Crystalline Structure of Pentaerythritol Tetranitrate. I. E. KNAGGS (*Min. Mag.*, 1925, **20**, 346—352).—Pentaerythritol tetranitrate (T., 1923, **123**, 77), examined by the *X*-ray spectrometer method, was found to be built on the simple tetragonal lattice Γ_t, to belong to the space-group D_{4h}^7, and to have 4 mols. of $C(CH_2O{\cdot}NO_2)_4$ per unit cell of dimensions a=13·2, c=6·66 Å. The arrangement of the atoms in the nitro group is thought to be $-N<^{O}_{O}$ or $-N\ll^{O}_{O}$, and not $-N=O=O$. The angles between the linkings from the central carbon atom show a considerable departure from the angle of the regular tetrahedron, and this perhaps causes a strain which contributes to the explosive nature of the compound. L. J. S.

Isomorphism of Zirconium Sulphate and Quadrivalent Cerium Sulphate. L. FERNANDES (*Gazzetta*, 1925, **55**, 290—293).—The compounds, $Ce(SO_4)_2,4H_2O$ and $Zr(SO_4)_2,4H_2O$ are

completely miscible and hence able, in all proportions, to form mixed crystals. T. H. P.

Monoclinic Double Sulphates containing Thallium. Thallium Nickel and Thallium Cobalt Sulphates. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 240—261).—A full crystallographic description is given of these two salts. The results confirm the conclusion previously reached from an examination of thallium zinc sulphate and selenate, that these double salts containing thallium are true members of the isomorphous series of monoclinic hexahydrated double sulphates and selenates $R_2M(SO_4)_2,6H_2O$. These all crystallise in the holohedral class of the monoclinic system. The small angular changes, which occur on substituting either thallium or rubidium for potassium in the salt, are about equal. S. B.

Regular Growth of Crystals of Different Species. L. ROYER (*Compt. rend.*, 1925, **180**, 2050—2052).—Regular growth of crystals of one substance on crystals of another requires an approximate identity of form and dimensions of the two lattices. The growth of crystals of alkali and silver halides on cleavage faces of potassium chloride, galena, and sodium chloride has been studied. Regular growths occur if the differences in the dimensions of the two lattices do not differ by more than 12, 10, and 16% in the three cases, respectively, but if these limits are exceeded the crystals are deposited quite irregularly. No formation of mixed crystals occurs when potassium and sodium chloride are deposited simultaneously. W. H.-R.

Crystal Structure and Physical Properties. A. E. VAN ARKEL (*Physica*, 1924, **4**, 286—301).—By passing the corresponding chlorides, together with hydrogen, and nitrogen or carbon monoxide, over a heated tungsten wire, titanium, zirconium, and tantalum nitrides and carbides have been prepared. In the regular system, values of d_{100} are: titanium carbide, 4·29 Å., nitride, 4·23 Å.; zirconium carbide, 4·71 Å., nitride, 4·59 Å.; tantalum carbide, 4·56 Å. For tantalum nitride (hexagonal, with 2 mols. per unit cell) Ta $(\frac{1}{3}\ \frac{2}{3}\ u)(\frac{2}{3}\ \frac{1}{3}\ \bar{u})$; u=0·25, axial ratio 1·62, edge of basal hexagon 3·05 Å. Combination of the metal with two oxygen or fluorine atoms still produces the ionic type of lattice, sulphides and selenides being intermediate between ionic and molecular lattices. In the regular system, values of d_{100} are: zirconium dioxide, 5·08 Å., thorium dioxide, 5·26 Å., uranium dioxide, 5·48 Å., strontium fluoride, 5·86 Å. Zirconium sulphide and selenide crystallise in the rhombohedric hexagonal system, with respective axial ratios 1·59, 1·63; edge of hexagon, 3·68, 3·79 Å.; (1 mol. per unit cell) Zr (000); S (Se) $(\frac{2}{3}\ \frac{1}{3}\ u)(\frac{1}{3}\ \frac{2}{3}\ \bar{u})$ with u 0·25, analogous to cadmium iodide. Ferrous and manganous sulphides form ionic space lattices. CHEMICAL ABSTRACTS.

Electrical Conductivity of Mixed Crystal Alloys. G. BORELIUS (*Ann. Physik*, 1925, [iv], **77**, 109—137).—The specific

conductivity of a metal is given according to Drude by the expression (1) $\chi=\epsilon^2/2m\,.\,NL/\mu$, where ϵ is the charge, m the mass, μ the velocity, N the number per c.c., and L the mean free path of the conducting electron. Wein regarded μ as a constant independent of temperature and characteristic of an atomic movement, and N as also constant, so that the temperature variation of χ would be due to the direct proportionality between energy content and L. Højendahl (A., 1924, ii, 647) sought an explanation on the basis of the Bohr atom and the independence of the translation velocity of the valency electron with temperature. He considered that the mean free path is constant from atom to atom of the same element, but that atoms of the second component interfere. N and μ were assumed to be constant throughout a series of alloys. The expression $\chi=$constant$\,.\,(1/pq-1)$ (p and q are concentrations of components) was deduced and found to be in agreement with experiment for Cu–Ni alloys. The author, however, finds that the agreement is fortuitous, since other series of alloys do not confirm Højendahl's reasoning. The discrepancy is due to the simplicity of the assumptions. N and μ are now assumed to differ for the two components of a mixture, and (1) is rewritten as (2) $\chi=\epsilon^2/2m(N_1L_1/\mu_1+N_2L_2/\mu_2)$ and simplified to (3) $\chi=A'pL_1+B'qL_2$, where A' and B' are constants characteristic of the two components.

On this basis, it is deduced that the conductivity at absolute zero is given by (4) $\chi_0=Ap/q+ap+Bq/p+bq$, where A, B, a, b are constants. This assumes random distribution of atoms and a straight line free path (a). To test the theory, it is necessary to investigate theoretically the variation of the resistance of alloys with temperature. It is then shown that the resistance ρ' of an alloy is given by $\rho'=p\rho_1+q\rho_2+\rho_0$, where ρ_1 and ρ_2 are the specific resistances of the components at the temperature of the alloy, $p\rho_1$ and $q\rho_2$ are interpolated linearly, and ρ_0 is a quantity independent of temperature. At the absolute zero, ρ_1 and ρ_2 vanish, so that $\chi_0=\frac{1}{\rho_0}=1/\rho'-p\rho_1-q\rho_2$. Thus χ_0 may be obtained from the experimental data and compared with the value obtained by the use of (4). The theoretical treatment is confirmed by the following systems: Au–Ag, Au–Cu, Pd–Pt, In–Pb, K–Rb. For example, in Au–Ag $\chi_0=27p/q+80p+27q/p+45q$ ohm^{-1} cm.$^{-1}$. 10^3. The data for the systems Cu–Ni, Au–P, Ag–Pd, Cu–Pd are also considered. The range of validity of assumptions (a) is discussed. Further, the results are used to calculate values for the mean free path and for the electron velocity in various elements. Regularities in the values of the constant A are pointed out which may prove significant when the theory can be tested more rigidly. (Cf. Cuy, this vol., ii, 378.) R. A. M.

Electric and Magnetic Spectroscopy. W. Arkadiev (*Phil. Mag.*, 1925, [vi], 50, 157—163). It is pointed out that since thermal waves have the same relation to magnetic centres in dielectrics as X-rays to electric centres, somewhere in the intermediate region between thermal oscillations and slow electric

vibrations the disappearance of magnetic behaviour must occur, accompanied by magnetic absorption of the passing rays and strong alteration of the magnetic permeability. This is illustrated by the magnetic spectra of iron and nickel wires in the wave-length region 1 cm. to 1 km. The apparent permeabilities of these substances, calculated from the absorption of waves in ferromagnetic wires, agree with the assumption that the elementary magnets in ferromagnetic metals, under the influence of weak magnetic fields, rotate according to the same laws of viscous-elastic motion adopted for the displacement of electric centres in dielectric bodies.

F. G. T.

Weiss's Theory of Ferromagnetism. R. H. DE WAARD (*Z. Physik*, 1925, **32**, 789—793).—The theory fails to account even approximately for the small coercive force necessary to remove residual magnetism in iron and nickel. E. B. L.

Magnetisation of Ferro-nickel: Saturation and Atomic Moments. M. PESCHARD (*Compt. rend.*, 1925, **180**, 1836—1838).—The specific magnetisation of iron and nickel mixtures has been plotted against percentage composition for the three temperatures +16°, −79°, −188°. The compound Fe_2Ni is very definitely indicated. The value at 0° Abs. for each saturation is extrapolated by means of the expression $\sigma=\sigma_0-KT^2$. The atomic moments (expressed in magnetons) are plotted against percentage composition and the curve is closely similar to that obtained for specific saturations at absolute zero. Both curves provide evidence for the existence of Fe_2Ni, Fe_3Ni_2, and $FeNi_2$. The first two have 9 magnetons per atom and the third has a total of 20 magnetons. The magnetisation to saturation point of solid solutions in equilibrium obeys the mixture rule. At each temperature, a hyperbolic function $\sigma=\sigma_\infty(1-a/H)$ represents the degree of saturation and the coefficient a varies from one alloy to another from 1 to 40. Ferro-nickel may exist in the β or γ state and the bearing of this fact on the results is worked out. R. A. M.

Optical Constants of Crystals of Selenium and Tellurium between 3000 and 5000 Å. R. F. MILLER (*J. Opt. Soc. Amer.*, 1925, **10**, 621—634).—When plane polarised light is reflected from the surface of an absorbing medium it becomes in general elliptically polarised, and if the form of the elliptical vibration is determined for some angle of incidence, the optical constants of the medium may be calculated. Such determinations have been made with crystals of selenium and tellurium, with the crystal axis parallel and perpendicular to the plane of incidence, and the corresponding values for the refractive indices and reflecting powers are given. In the parallel position μ for selenium is 3·4—4·4, and for tellurium 1·9—2·9, and in the perpendicular position, for selenium 2·3—3·1, and for tellurium 1·7—2·7, over the given range of wave-length. The analysis of the reflected light was made by a photographic method described by Voigt (*Physikal. Z.*, 1901, **2**, 203). S. B.

Polymorphic Transformations of Silica. L. LONGCHAMBON (*Compt. rend.*, 1925, **180**, 1855—1858; cf. A., 1913, ii, 133; 1919, ii, 420).—In the presence of a solvent (tungstate, molybdate, silicate, etc.) between 870° and 1470°, precipitated silica dissolves rapidly and after a few minutes hexagonal tridymite and β-cristobalite appear. The latter is slowly converted into tridymite, the stable form under these conditions. Quartz is converted into tridymite at 870—1470°. Cristobalite is not normally an intermediate product. The condition for its appearance is supersaturation of the solvent. Above 1470°, quartz, tridymite, silica, glass, and precipitated silica all form cristobalite (octahedra). With the precipitated silica numerous droplets of fused silica occur at 1500°, d (cold) 2·2. Below 870°, precipitated silica dissolves rapidly, giving tridymite and cristobalite, quartz being formed only very slowly. New determinations of n and d of cristobalite and tridymite give 1·487, 2·347 and 1·477, 2·266, respectively.

R. A. M.

Increase of Tensile Strength and Recovery of Zinc Crystals. E. SCHMID (*Z. Physik*, 1925, **32**, 918—921).—The tensile strength increases with plastic deformation, but this action is partly reversed if the crystal is allowed time to recover. E. B. L.

Strengthening and Weakening of Tin Crystals. M. POLANYI and E. SCHMID (*Z. Physik*, 1925, **32**, 684—712).—Single crystals of tin were subjected to slight tension and the rate of increase of length was measured; the results show increased resistance with deformation. When the stress was removed the crystals recovered, rise of temperature hastening the recovery greatly. Consequently the rate of stretching and the temperature influence the extent to which the crystals gain in strength. The recrystallisation of tin crystals was investigated by etching and by the X-ray spectrograph. Crystals were examined which had been stretched, quickly pulled apart, and compressed. Crystals both with and without cleavage lines were tested, the position at which the nucleus of the new crystal formed and the rate of formation were noted. Crystals which have been slowly and carefully drawn out and their internal energy increased are much less liable to crystallise than such as have been rapidly torn apart. E. B. L.

X-Ray Study of Soaps and Fats. J. J. TRILLAT (*Compt. rend.*, 1925, **180**, 1838—1840; cf. this vol., ii, 640).—When an alcoholic solution of a fatty acid is allowed to evaporate on glass, the crystals are oriented. Metal plates have been substituted for glass. With some metals, the X-ray spectra are the same as with glass; with others, a second spectrum, traced to a film of soap in which the molecules are also oriented, is superimposed. It is intense with plates of lead, tin, and antimony, fairly intense with iron, copper, and bismuth, feeble with nickel, zinc, and molybdenum, and absent with aluminium, palladium, platinum, and gold. All the soaps of palmitic acid have the same maximum distance of 46·3 Å. (except copper, 43·5 Å.). The lead soaps of a series of fatty

acids have been examined. The maximum distances for the stearate (51·3), palmitate (46·3), and myristate (41·2) exhibit constant differences $\Delta(C_{n+2}-C_n)=5$ Å., or $\Delta d/\Delta N$ (N is number of carbon atoms)=1·25 Å. This value increases to about 1·3 Å. when N is smaller. It is smaller than that observed with the fatty acids (1 Å.) and nearer to that of the ethers (1·22 Å.). Most simple fats and waxes are oriented by simple fusion on glass, *e.g.*, glyceryl margarate has d=48 Å. Even a compound like lecithin is oriented, d=47 Å. R. A. M.

Determination of Avogadro's Number from the Light Diffused by Ethyl Chloride. P. Daure (*Compt. rend.*, 1925, **180**, 2032—2034).—Avogadro's number (N) is calculated by the equation of Einstein from new measurements of the ratio R for ethyl chloride, where R is the ratio between the intensity I of light diffused at right angles to the primary beam of intensity E for 1 c.c. of gas. As the light used was not monochromatic, an approximate method of graphical integration was used. The method gives the values $N=(6{\cdot}5\pm0{\cdot}65)10^{23}$, and $R=(1{\cdot}06\pm0{\cdot}1)10^{-7}$ for green light. W. H.-R.

Revision of Weight of Normal Litre of Methyl Chloride Vapour. T. Batuecas (*Compt. rend.*, 1925, **180**, 1929—1932).—Methyl chloride vapour obeys the law of limiting densities. The vapour was prepared by two methods (*a*) the reaction between phosphorus trichloride and methyl alcohol (cf. T., 1905, **87**, 1592) and (*b*) by thermal decomposition of tetramethylammonium chloride. The highest and lowest values of seventeen determinations made with suitable precautions were 2·3099 and 2·3072. The final value, $2{\cdot}3084\pm0{\cdot}0001$, is definitely higher than the only other precise measurement 2·3045 (Baume, A., 1908, ii, 372). R. A. M.

Revision of the Compressibility of Methyl Chloride and the Molecular Weight of this Gas. T. Batuecas (*Compt. rend.*, 1925, **181**, 40—42).—Employing the method previously outlined (A., 1924, i, 1280), the value of the factor $(1+\lambda)$ for methyl chloride has been determined from measurements of compressibility. As with dimethyl ether, the compressibility decreases in a characteristic manner with decreasing pressure. The value for the weight of a litre of gaseous methyl chloride under standard conditions is 2·3084 g. This leads to a value for the atomic weight of chlorine, Cl=35·47. J. S. C.

Effect of a Magnetic Field on the Electrical Resistance of Liquid Metals and Alloys. E. J. Williams (*Phil. Mag.*, 1925, [vi], **50**, 27—46).—Theoretical. The change in the electrical resistance of a liquid conductor due to the action of a magnetic field is attributed to the sum of a true resistance change, and a change consequent on energy expended in maintaining hydrodynamic currents in the liquid conductor. These currents are set up because the magnetic field and electric current in the conductor are independent, whereas, for the liquid to remain at rest,

it is necessary for the force per unit volume acting on the liquid to be derivable from a single-valued potential function. An expression is obtained by means of dimensional analysis for the resistance change due to this cause. An analysis of the results of Rossi (*Nuovo Cim.*, 1911, [vi], **2**, 337) reveals evidence for the existence of a true resistance change in a magnetic field in bismuth amalgams, a 1% amalgam showing a resistance increase of 0·0001% in a field of 4000 gauss. The similar change in molten bismuth (Berndt, *Ann. Physik*, 1907, [iv], **23**, 805) is estimated as approximately 0·002% at 420° for a field of 3000 gauss. In other cases, the hydrodynamical effect certainly predominates, and, in most cases, a true change, if present at all, is negligible. The variation of the resistance change with the current traversing the liquid metal conductor, which has been observed in some cases, is explained by supposing that the motion of the liquid in these instances is turbulent. The further theoretical consequences of this supposition are substantiated by the experiments of Jones (cf. following abstract), from which it is shown that in the turbulent motion of liquids in an enclosed space, due to the action of external volume forces, the average stream-lines maintain a constant shape as these forces are varied proportionately at all points. In this respect the average stream-lines of turbulent motion resemble the stream-lines in steady motion. The resistance to the motion is in all cases proportional to (velocity)$^{1\cdot70}$, which is in agreement with the law of resistance in turbulent motion obtained by Osborne Reynolds for the flow of water through straight pipes. F. G. T.

Electrical Resistance of Mercury in Magnetic Fields. T. J. Jones (*Phil. Mag.*, 1925, [vi], **50**, 46—60).—In a column of mercury of about 5 cm. diameter, to which a magnetic field varying between 2 and 10 kilo-gauss is applied perpendicular to the direction of the current, the magneto-resistance change for currents between 0·5 and 5 amp. is given by $\delta R \propto H^{1\cdot58}d/i^{0\cdot40}b^{0\cdot41}$, where H, d, i, and b are respectively the field, the diameter of the column, the current in the column, and the distance apart of the poles of the magnet. It was found that the change of resistance is independent of the field resistance, but depends on the temperature, increasing by 12·5% for a rise of 273°. When the magneto-resistance change is measured in wide tubes and with comparatively large fields and currents, the effect is of a different nature from that exhibited by solid metals, with which the resistance change is proportional to the resistance in the field and independent of the current in the conductor. The theory of Williams (cf. preceding abstract) explains all the phenomena observed and gives for the resistance change a relation which is in good agreement with that obtained in the experiments. F. G. T.

Thermal Variation of Magnetism of Water and of Some Paramagnetic Solutions. B. Cabrera and A. Duperier (*J. Phys. Radium*, 1925, [vi], **6**, 121—138).—The Curie-Weiss equation $\chi(T+\Delta)=C$ for the variation of paramagnetism with temperature is valid over a wide range of temperatures (χ is the susceptibility,

T absolute temperature, Δ and C are constants characteristic of the substance). Langevin's expression $\mu_0=\sqrt{3RC}$ (μ_0 is magnetic moment, R the gas constant) is in accord with experiment and has been justified theoretically by Ehrenfest (*Comm. Phys. Labor. Leiden*, Supp. 44*b*). Weiss ascribes the origin of Δ to a molecular field varying directly as the density of the paramagnetic atoms (A., 1915, ii, 737), but Foex (*Diss., Strasburg*, 1921) has recently investigated certain solutions in which Δ appears, but mutual actions of paramagnetic atoms seem unlikely. The authors have measured by a couple the attraction in a non-uniform field and have determined the variation with temperature of the susceptibility of water and of certain solutions. The susceptibility of water between 20° and 80° is given by $-\delta\chi/\chi=[1{\cdot}67+0{\cdot}0016(t-20°)](t-20°)\,.\,10^{-4}$. The variation is due to depolymerisation of water molecules, so that addition of a diamagnetic salt like magnesium chloride increases the effect until $\delta\chi/\chi$ approaches zero. Solutions of manganese chloride, manganese nitrate, and nickel nitrate have been studied at various concentrations. The Curie-Weiss law is borne out by values of Δ ($Mn^{\cdot\cdot}$, −25; $Ni^{\cdot\cdot}$, −2), which are approximately independent of the concentration or the nature of the anion. These values of Δ have been used to calculate the number of magnetons of the two cations and the results $Mn^{\cdot\cdot}$ $28{\cdot}06\pm0{\cdot}08$, $Ni^{\cdot\cdot}$ $15{\cdot}96\pm0{\cdot}05$ are in the case of nickel identical with the number 16 already known, and in the case of manganese smaller by one than the number found for solid manganese salts. The constant Δ is due to a deformation of the surface of the paramagnetic atom by the influence of other atoms in chemical combination with it. The view that in solutions water exerts such a deformation effect is in harmony with the theory of Ehrenfest. R. A. M.

Diamagnetism of Nematic Substances. G. Foex and L. Royer (*Compt. rend.*, 1925, **180**, 1912—1913).—The magnetisation coefficient of *p*-azoxyanisole in the solid state is independent of temperature. At 116°, the nematic phase appears and the magnetisation diminishes abruptly by about 17%, owing to orientation of molecules by the magnetic field. The nematic phase (116—134°) shows great variations of the magnetisation coefficient with temperature; the value approaches the original value as the temperature increases and remains constant when the liquid phase is attained. The curve, magnetisation coefficient–temperature may be produced to 95° for the nematic phase and the maximum difference observed between two magnetisations in the liquid and nematic phases is greater than 18%. Whenever the substance solidifies, a different value is observed for the coefficient owing to imperfect distribution of the tiny crystals making up the solid. Anisaldazine gave similar results. R. A. M.

Dispersion of Electrical Double Refraction of Some Organic Liquids. G. Becker (*Ann. Physik*, 1925, [iv], 76, 849—862).—The dispersion of the electrical double refraction has been measured by Lyon and Wolfram's method (A., 1921, ii, 6) for the following

liquids at 20° : anisole, *m*-xylene, phenetole, ethylbenzene, acetal, ethyl butyrate, toluene, and ethyl ether. The behaviour of the first four is represented satisfactorily by the Havelock formula (A., 1911, ii, 165) $Bn\lambda/(n^2-1)^2=$const., where B and n are respectively the Kerr constant and the refractive index of the liquid for the wave-length λ. The mean values of the Havelock constant for these four liquids are $C\times10^{11}=0{\cdot}596$, 0·485, 0·643, and 0·425, respectively. The deviations from the above formula are most marked with ethyl ether and acetal. Owing to the ambiguous behaviour of toluene and ethyl butyrate, the conclusion that the Havelock formula does not hold for substances with low optical dispersions cannot be confirmed. F. G. T.

Black Body for Optical Pyrometer Calibration. H. S. ROBERTS (*J. Opt. Soc. Amer.*, 1925, **10**, 723—724).—Details are given for the construction of a black body for use in the calibration of optical pyrometers from the fusion point of a metal. A small piece of the metal is heated to fusion at the bottom of a graphite or porcelain tube of suitable shape, and the "matching" is done as the metal is observed to melt. The advantages of the procedure are that it gives a direct determination of the temperature of the black body and that very little of the standard metal is required. S. B.

Latent Heat Determinations. A. W. SMITH (*J. Opt. Soc. Amer.*, 1925, **10**, 711—722).—A summary of the methods proposed for determinations of the latent heats of fusion and evaporation. S. B.

Automatic Control of Low Temperatures. T. S. SLIGH (*J. Opt. Soc. Amer.*, 1925, **10**, 691—693).—A short review, with references, of the methods used for attaining constant low temperatures. S. B.

Thermal Conductivity of Wires and Rods. T. BARRATT and R. M. WINTER (*Ann. Physik*, 1925, [iv], **77**, 1—15).—The expression $K=H^2/pqhV^2\coth^2\alpha l$ gives the conductivity of a wire or thin rod, and is simplified to $K=H^2/pqhV^2$ when the length l is great (K is the thermal conductivity of the wire, p the circumference of the rod, q the cross-sectional area, h the emissivity of the surface, V the temperature of the hot end, and $\alpha=\sqrt{hp/qk}$. Of these quantities, h is the most difficult to measure. Accordingly, the experimental methods are designed to secure accurate values for H (the heat supplied in calories per sec. to the hot end of the wire) and V, and the theoretical treatment is designed so that h may be eliminated entirely from the calculations. The technique is based on earlier work (*Proc. Phys. Soc.*, 1914, **26**, 347). Values of K are given for platinum, iridium, rhodium, gold, tantalum, molybdenum, various alloys, and for glass, ebonite, graphite, and various woods.

The mathematical treatment includes a solution of the equation for the fall of temperature along a rod enabling K to be evaluated

from H, V, q, and the temperature at any point along the rod. Various cases are discussed and simple formulæ deduced so that the result of the work is to place on a sound theoretical basis the experimental methods developed by the authors for the measurement of K, using very small samples of material. R. A. M.

Specific Heats. S. WIESNER (*Ann. Physik*, 1925, [iv], **76**, 802; cf. this vol., ii, 275).—A correction. The refractivities previously used were the Gladstone and Dale values; thus u signifies the specific refraction and not the specific atomic volume. When the Lorenz and Lorentz values are used $r\sqrt{d}$ is in the neighbourhood of 1·5, instead of 3, as previously given. The elements silver, potassium, phosphorus, mercury, and sodium which gave abnormal results, now give values of $r\sqrt{d}$ between 0·87 and 0·68. F. G. T.

Molecular Heats of Gases at Low Temperatures. F. A. GIACOMINI (*Phil. Mag.*, 1925, [vi], **50**, 146—156).—The molecular heats at constant volume of ammonia, methane, and hydrogen were determined at temperatures down to 83° Abs. by observing the pressure increase on heating the gases in a closed vessel by an inductive electrical impulse in a small piece of constantin foil placed near the centre of the gas-container. The pressure was recorded by a sensitive membrane manometer. The determination of C_v by this principle presupposes a non-uniform temperature distribution in the gas. The validity of this type of measurement was supported by the direct observation of development and evolution of heat clouds in the gas, of the rate of heat evolution from, and the temperature attained by, the foil, and by the pressure–increase curves for various gases for varying heat changes, and under different pressures and temperatures. A theoretical consideration of the principle assumes the pressure development to occur in two idealised stages, an isochoric heating of a small volume of the gas round the foil, followed by the adiabatic compression of the rest of the gas. From these assumptions the condition for obtaining trustworthy results is $[RQ/V_0C_vP_0]^2 \leqslant 1$, where Q, V_0, and P_0 are, respectively, the heat supplied, and the initial volume and pressure of the gas. The pressure maxima for carbon dioxide were constant over a range of from 1 to 0·1 atm., the duration of the maximum decreasing with decrease of pressure. The molecular heats of methane and ammonia sink with falling temperature below the value corresponding with rigid molecules, the fall with ammonia being especially rapid. C_v=5·30 cals. for methane at 83° Abs., and =5·55 cals. for ammonia at 229° Abs. F. G. T.

Microscopic Study of the αβ-Transformation of Natural Cristobalite. R. WEIL (*Compt. rend.*, 1925, **180**, 1949—1951).—Cristobalites from different places have been examined. From San Cristobal the transformation begins at 180—195° and ends at about 205—210°; from Tehema County: 175—210° or 230°; from Chaudefour: two regions exist, 175—190° and 217—245°; from Blaue Kuppen: 220—230° or 250—255°; from Cottenheim: 220—230°. Pseudomorphic tridymite–cristobalite crystals from

Chaudefour showed a transformation point at 180—200°; tridymite from Mt. Egmont shows points between 170—190° and 235—250°. R. A. M.

Heat of Sublimation of Carbon Dioxide. J. W. ANDREWS (*J. Amer. Chem. Soc.*, 1925, **47**, 1597—1602).—Experiments in which a definite quantity of carbon dioxide was sublimed by means of an electric current, the energy input and the volatilised substance being measured, lead to a value for the heat of sublimation of 6205 cals. There is a difference of 2·64 units between the entropies as calculated from thermal and equilibrium data on carbon, oxygen, and carbon dioxide, and from the thermal data for carbon dioxide itself. The possible sources of error are discussed. J. S. C.

Additive Properties of Boiling Points. A. E. VAN ARKEL and J. H. DE BOER (*Physica*, 1924, **4**, 392—399; cf. this vol., ii, 734).—From the general additivity of the b. p., it is found that $\Sigma\sqrt{a}/\Sigma b$, representing the cohesion pressure at the b. p. (a and b being the van der Waals' constants) has a constant value for all tetra-halogen derivatives of methane. The results lead to an atomic volume for hydrogen of 9·20% less than that of fluorine. For compounds containing hydrogen, the external action of the central atom is not entirely screened, and van Laar's rules no longer apply. Also, when the size of the central atom is increased, individual differences in the screening efficiency of the halogens appear, leading to the existence of co-ordination complexes, *e.g.*, K_2SiF_6 and K_2SnCl_6. CHEMICAL ABSTRACTS.

Influence of Hydrogen and Substituted Halogens on the Properties of Organic Compounds, especially on their Boiling Points. A. E. VAN ARKEL and J. H. DE BOER (*Rec. trav. chim.*, 1925, **44**, 675—692).—In each group of organic compounds, for each halogen the value of $\sqrt{\alpha}$ per halogen atom is proportional to the volume, α being the constant in van der Waals' equation of state. The values of $\sqrt{\alpha}$ are different in different groups, and are smaller the greater the number of other atoms in proximity to the halogen atom. In the paraffin series, the central atom is surrounded by halogen and hydrogen atoms, and exerts no influence beyond these, but in the ethylene, benzene, and silicon series this is not so. As the surrounding of the central atom by other atoms will obviously be more perfect the greater the volume of the latter, it follows that the ethylene and chloroethylene compounds readily form additive compounds, whilst ethylene tetraiodide is formed from carbon tetraiodide by removal of iodine, and compounds such as silicon tetrabromide show no tendency to complex formation. It is shown that fluorine falls into line with the other halogens. Hydrogen, however, has a variable value of $\sqrt{\alpha}$. It is smallest in the hydrocarbons, and is greater the more halogens there are attached with hydrogen to a carbon atom. The introduction of halogens into other carbon groups also exerts an influence (although smaller) on the value of $\sqrt{\alpha}$ for hydrogen. L. L. B.

Variation with Pressure of the Boiling Points of Naphthalene, Benzophenone, and Anthracene. J. L. FINCK and R. M. WILHELM (*J. Amer. Chem. Soc.*, 1925, **47**, 1577—1582).—The variation with pressure of the b. p. of naphthalene, benzophenone, and anthracene has been investigated over the range of pressure 700—800 mm. of mercury, the data for the first two substances being intended for use in thermometry. Two purified samples of anthracene differed in their normal b. p. by about 0·5°. The experimental data are satisfactorily represented by the equation $t_p=t_{760}+A(t_p+273{\cdot}1)\log(p/760)$, in which t_p represents the temperature corresponding with pressure p (mm. of mercury), t_{760} the normal b. p., and A a constant characteristic of the substance. The following are the respective values of t_{760} and A: naphthalene 217·95° and 0·2075, benzophenone 305·84° and 0·194, anthracene 340·36°, 339·87°, and 0·201. J. S. C.

Melting Point of Carbon. H. ALTERTHUM, W. FEHSE, and M. PIRANI (*Z. Elektrochem.*, 1925, **31**, 313—316).—The authors have applied their method for the determination of the m. p. of difficultly fusible metals (cf. Pirani and Alterthum, A., 1923, ii, 125) to the determination of the m. p. of graphite. The graphite, in the form of a rod 140 mm. long and 37 mm. diameter, broadened at each end and with a hole (18 mm. deep and 3 mm. diameter) bored at an angle to the axis of the rod, is surrounded by a water-cooled jacket through which hydrogen at 800 mm. pressure is passed, and is heated by an alternating current (8000 amp. and 9 volts). The m. p. is 3760° Abs.±65°, a value in good agreement with other determinations. J. W. B.

Temperature Scale and M. p. of Molybdenum. A. G. WORTHING (*Physical Rev.*, 1925, [ii], **25**, 846—857).—Values are tabulated and plotted for the spectral emissivities of molybdenum as a function of temperature from 300° Abs. to 2800° Abs., and the relations between true, brightness, and colour temperatures examined. Molybdenum has m. p. 2895±10° Abs. A. A. E.

Cryoscopy of Diphenyl Ether. J. T. DURAND and E. ROUGÉ (*Bull. Soc. chim.*, 1925, [iv], **37**, 697—700).—Discrepancies observed in the m. p. of samples of diphenyl ether obtained by Sabatier and Mailhe's method (A., 1910, i, 669) are due to the relatively high cryoscopic constant (80) of this substance, which renders its m. p. much more sensitive to traces of impurities. The purest diphenyl ether obtainable has m. p. 26·9° in the cryoscope, and experiments with *cyclo*hexane, benzene, toluene, and naphthalene give the values 78·8, 79·8, 79·7, and 80·0, respectively, for the cryoscopic constant. Naphthalene gives the most constant results, *cyclo*hexane the most erratic. From these results, the latent heat of fusion is calculated to be 22·65 cals. R. B.

Constitution of Aromatic Substances and their Physical and Chemical Properties. II. Melting Points of Benzene Derivatives. I. A. PASTAK (*J. Chim. Phys.*, 1925, **22**, 264—279; cf. this vol., i, 531).—A review of the m. p. of polysubstituted benzene

compounds containing two different groups, R and r, of which R occurs once only, and r once or more times. Substituent groups are divided into two main classes: (1) basic groups including H, CH_3, (Cl), (Br), OH, NH_2 . . ., and, (2), acidic groups including H, CO_2H, NO_2. . . . The fundamental principle is that in disubstituted compounds, C_6H_4Rr, if R and r belong to the same class (see above), the normal position possessing the lowest m. p. is the meta, and the m. p. are in the order para > ortho > meta. If, however, R and r belong to different classes, the normal positions are the ortho and para, and the m. p. order is para > meta > ortho, the para position always having an abnormally high value. Polysubstituted compounds can be divided into two classes: (1) "Alphabetical isomerides," for which no simple rules exist for m. p., and in which the different r groups are in the ortho or para positions relative to one another; and (2) the "ompa" isomerides, in which the r groups are relatively in the meta position. In the "ompa" isomerides, two r groups in the meta position to one another resemble one group in the position midway between the two. Thus the isomeride of the compound $C_6H_3Rr_2$ with the r groups in the 1 : 3 positions resembles the compound C_6H_4Rr' with the r' in the meta position, and in this way polysubstituted compounds can be reduced so as to correspond with the disubstituted compounds for which the fundamental principle (above) holds.

W. H.-R.

The Group of Volatile Hydrides. F. Paneth and E. Rabinovitsch (*Ber.*, 1925, **58**, [*B*], 1138—1163).—The hydrides are classified as volatile hydrides (*e.g.*, HCl), salt-like hydrides (*e.g.*, LiH), and metal-like hydrides (*e.g.*, CuH); the first group is mainly considered in the present communication. Simple volatile hydrides containing only one atom of the central element in the molecule are formed by elements occurring in one to four places before a rare gas in the periodic system. Many of these elements form also more complex hydrides which generally resemble closely the simpler compounds, so that they are readily considered in a somewhat broader group.

[With W. Haken.]—Older determinations of the b. p. and m. p. of germanium hydride have given values which are widely divergent from those predicted from its association with the tetrahydrides of carbon, silicon, and tin. Pure germanium hydride is conveniently prepared by the electrolysis of a solution of germanium dioxide in sulphuric acid between lead electrodes, condensation of the gaseous products by liquid air, and fractionation of the condensate in Stock's vacuum apparatus; it has b. p. −88·5°, m. p. −164·5°, mol. heat of evaporation 3·65 kg.-cal. The value for the b. p. is in good agreement with that found recently by Schenk and Imker (this vol., ii, 279; cf. A., 1922, ii, 855), with whose views on the instability of the hydride in the presence of mercury the authors do not concur. It is shown that the m. p. and b. p. of the hydrides rise with increase in the number of the period in all groups of the periodic system and that the rise is linear to a first approximation. All the graphs

are parallel to the graphs of the m. p. and b. p. of the rare gases placed at the end of the periods. A distinct departure from the linear nature is caused by neon; among hydrides of the corresponding period methane alone is suitable for comparison, since ammonia, water, and hydrogen fluoride are markedly associated. Between the constants of methane and monosilane, however, the same discrepancy is noticed as between those of neon and argon, whilst, also, a similar discrepancy is observed in the b. p. of the halogens. An exceptional position is taken also by radium emanation, the m. p. of which appears to require redetermination. In every period the hydrides of the fourth group resemble the rare gases most closely in volatility; the mono-, tri-, and di-hydrides are increasingly less volatile in the given order. It follows therefore that the constants of the hydrides can be deduced from the position of the central element in the periodic system whereby the b. p. of the hydrides of lead, bismuth, and polonium are calculated to be $-13°$, $+22°$, and $+37°$, respectively. The exceptional positions occupied by the hydrides of fluorine, oxygen, and nitrogen may be attributed to the established association of hydrogen fluoride and water, but this has not been placed beyond doubt for ammonia; in general, the adequacy of molecular association as an explanation of abnormal b. p. is open to question. Graphic representation of the heats of evaporation (at the b. p.) of the hydrides gives a picture similar to that derived when the b. p. is used, but in which the irregular exceptions are rather more sharply defined. In addition to the hydrides of fluorine, oxygen, and nitrogen, hydrogen chloride and sulphide give "high" values. The tendency towards association among volatile hydrides diminishes towards the left and downwards from fluorine, so that in the first period it extends to the third member, NH_3, whereas in the second only to the second member, SH_2. With m. p., the same departures from linearity are in general observed as with the b. p., but the "abnormally high" m. p. of methane and hydrogen iodide shows the anomaly to extend to the fourth member. The remaining constants of the volatile hydrides are not generally known with sufficient exactitude to permit accurate comparison, but the graphs for the molecular volume at the b. p. and for refractive index are generally similar to those just discussed. The thermostability decreases as the periodic number increases, the maximum instability being exhibited in the sixth group of the periodic system. In general, the volatile hydrides behave as a homogeneous family. As far as their properties can be numerically expressed, the data vary very regularly within the separate periods and groups of the natural system. Their physical constants present unmistakable similarity to those of the rare gases.

Comparison shows that those elements which form volatile hydrides give also volatile or readily melted halogen or alkyl compounds, provided that the central element functions with the same valency. The alkyl derivatives appear to fall into the same two classes as the hydrides, since the alkali alkyls are solids at the atmospheric temperature, whereas those of the elements which

yield volatile hydrides are liquids and volatilise readily. The power of yielding volatile alkyls is more widely distributed in the periodic system, extending as far as zinc and mercury. The same parallelism between conductivity and volatility is encountered among hydrides, halides, and alkyls, volatility and poor conductivity occurring simultaneously. In every period, the hydrides and halides of the fourth group have the lowest m. p. and b. p., whereas those of the sixth group have the highest constants. The m. p. and b. p. of the compounds of a given element with hydrogen, chlorine, bromine, and iodine vary parallel to the constants of the free halogens with which hydrogen must be reckoned in this connexion. According to their physical constants, the volatile hydrides must be regarded as the lightest of the volatile halides.

Physically the hydrides resemble closely the rare gases, and their physical properties are most clearly expressed by considering their molecules to have the hydrogen nuclei "buried" and to present a "rare-gas" surface. The possibility of assigning a similar molecular structure to the volatile halides is considered. It is obvious that the volatile hydrides and halides in the right groups of the periodic system belong to the same structural type and that in the left groups the salt-like hydrides are in all respects comparable with the typical salts. H. W.

Atomic Volume of Manganese. A. N. CAMPBELL (*J. Chem. Soc.*, 1925, **127**, 1487).—The curve of atomic volumes shows in the neighbourhood of manganese two minima, one at manganese and the other at cobalt. With the new value of the density of manganese (Campbell, T., 1923, **123**, 2323), the two minima persist, but the first minimum is shifted from manganese to chromium. W. T.

Density-changes of Tungsten with Working. W. GEISS and J. A. M. VAN LIEMPT (*Ann. Physik*, 1925, [iv], **77**, 105—108; cf. *B.*, 1925, 361).—Cold working of tungsten leads to a limiting value of 19·35 for the density. This agrees with the value deduced from *X*-ray measurements, so that there is no evidence of compression of the space lattice by hammering or rolling. R. A. M.

Expansion of Water while Freezing. A. P. LAURIE (*Trans. Faraday Soc.*, 1925, **20**, 509—510).—On the assumption that the tetrahedral structure of ice is formed from liquid triangular molecules of trihydrol, the triangles meeting at the centre of the tetrahedron, the increase in volume on crystallisation is calculated. The dimensions of the molecules of trihydrol are determined from the atomic diameters of oxygen and hydrogen in the solid state. The calculated specific gravity for ice is 0·918, the experimental value being 0·917. F. G. S.

Trouton's Rule as a Criterion of Association. C. WAGNER (*Z. Electrochem.*, 1925, **31**, 308—309).—A mathematical paper in which it is shown that by integrating the Clausius-Clapeyron equation and combining the result with the Nernst formula the value of the Trouton coefficient (λ/T) is approximately 28 for

liquids in which bimolecular association occurs. This value may therefore be employed as a criterion for such association. The cases of water, and ethyl and propyl alcohols (λ/T 26·0, 27·1, and 26·9, respectively) are cited as examples. J. W. B.

Surface Tension of Water, Benzene, Methyl Alcohol, and Ethyl Alcohol. B. Ali (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 155—178).—The capillary tube method of measuring surface tension is modified by determining, instead of the rise of liquid in the capillary, the pressure which must be applied to the surface of the meniscus in order to depress it to the level of the horizontal surface of the liquid outside the tube, or to an arbitrary mark at a known distance below the free surface of the liquid. The pressure was measured by a sensitive differential manometer. The values of the surface tension of the above four liquids at 29·5° were, respectively, 71·32, 28·10, 23·30, 21·32 dynes/cm. The advantages of the method are discussed, and the average error in measurement is estimated as 1 part in 9000 parts. F. G. T.

Compressibilities of Some Organic Liquids. J. Hebeisen (*Ann. Physik*, 1925, [iv], **77**, 206—224).—Röntgen's measurements (*ibid.*, 1888, **33**, 644) for the absolute compressibility of water are taken as standards and the compressibilities of various organic liquids have been determined relative to that of water by a differential method. The technique has been described by Schmidt (*ibid.*, 1925, **76**, 571). The variation of compressibility with temperature is given by $x \cdot 10^6 = a + bt + ct^2$ (a, b, and c are constants). The true compressibilities ($x \times 10^6$), mean error (e%), temperature coefficient $dx/dt \cdot 10^6$, and density d for the following liquids at temperatures $t°$ are as follows:

	$x \cdot 10^6$.	e%.	$dx/dt \cdot 10^6$.	$d_{18°}$.	$t°$.
Paraldehyde	82·144	2·30	+1·051	0·9988	12·13
Anisole	60·416	1·01	+0·365	0·9956	11·87
Benzyl alcohol	46·429	1·38	+0·13	1·0486	17·85
Ethyl benzene	82·364	0·99	+0·443	0·8721	17·89
m-Cresol	49·914	0·079	+0·154	1·0359	17·78
Aniline	44·714	2·23	+0·104	1·0236	17·95
Acetone	121·182	1·05	+0·540	0·7961	18·32
Nitromethane	69·440	1·90	0·327	1·1398	18·36

R. A. M.

Thermal Separation in Gaseous Mixtures. G. A. Elliott and I. Massow (*Proc. Roy. Soc.*, 1925, **A**, **108**, 378—385).—If a gaseous mixture is kept in two communicating vessels maintained at different temperatures, the composition of the mixture will differ in the two vessels, owing to thermal separation. The amount of the separation with one vessel at 0° and the other at 500° has been measured for the gases hydrogen, helium, and carbon dioxide, taken in pairs. It was found that in each case the constituent of higher molecular weight becomes more concentrated in the colder part of the mixture. The greatest differences in composition observed exceed 10% in hydrogen–carbon dioxide mixtures, 12%

in helium–carbon dioxide mixtures, and approach 4% in helium–hydrogen mixtures. For each pair of gases there is an "optimum" mixture for which the separation is a maximum. The separations attained are about 0·7 of those predicted by Chapman for molecules behaving as rigid elastic spheres, and are higher than those previously recorded by Ibbs. S. B.

Physical Properties of Binary Liquid Mixtures in the Region of the Critical Miscibility Point. N. PERRAKIS (*J. Chim. Physique*, 1925, 22, 280—310; cf. Gay and Perrakis, this vol., ii, 669).—The results previously obtained (Gay and Perrakis, *loc. cit.*) for binary liquid mixtures near the critical point are tested by reference to new and older data. At constant temperature, the vapour tension of binary mixtures is independent of composition over the whole interval of non-miscibility. The freezing-point curves for binary mixtures of ethyl alcohol with phenol, *o*-cresol, and phenyl oxide have been determined, and also those of mixtures of benzene with methyl, ethyl, *iso*propyl, and *n*-butyl alcohols. If two liquid layers are formed, the freezing point remains constant over a range of concentrations, and if the freezing-point curve only falls slightly with change of concentration—as in the mixtures of benzene with alcohols, or of ethyl alcohol with phenyl oxide—it is an indication that the region of non-miscibility is being approached even although two liquid phases are not actually formed. In the mixtures of ethyl alcohol with phenol or *o*-cresol, the freezing-point curve falls very sharply, indicating good miscibility. In these cases, the liquid becomes highly viscous and tends to vitrify without crystallisation; theory shows that this abnormal increase in viscosity is characteristic of mixtures far removed from the zone of non-miscibility. Existing data confirm the deduction that, in the neighbourhood of and below the critical point, the surface tensions of each of the two liquid phases, in mutual equilibrium with air, are themselves equal.

Properties not common to the two liquid phases, such as specific heat, heat of mixing, and volume changes on mixing, are not independent of concentration over the region of non-miscibility, but vary directly with the concentration over this region. If the graph connecting these properties with concentration shows an approximately linear portion, it may be concluded that the region of non-miscibility is being approached. This is confirmed by new measurements of these properties for the above-mentioned systems, and the effect of the addition of water to mixtures of benzene with alcohols is also studied. W. H.-R.

Physical Chemical Properties of Mixtures of Ethyl and *iso*Propyl Alcohols. G. S. PARKS and K. K. KELLEY (*J. Physical Chem.*, 1925, 29, 727—732; cf. A., 1924, i, 930).—When ethyl and *iso*propyl alcohols are mixed there is an evolution of heat, which is never more than 13 cals. per mol., but is about 2½ times as great as the heat effect of mixing ethyl and propyl alcohols. The volume shrinkage is only 0·01%, and the vapour pressures and refractive indices agree closely with those calculated for perfect solutions.

Kendall's cube root equation for the viscosity of mixtures gives results which are, on an average, 0·4% too high, whilst the logarithmic equation gives values 0·9% too low. A. G.

Certain Physico-chemical Properties of Mixtures of Water and Acetone. C. SANDONNINI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 448—453).—The results of measurements for water–acetone mixtures of the specific heats at 14—20°, the heats of mixing at 15°, and the specific gravities, viscosities, and surface tensions at 25° render probable the existence of molecular complexes of water and acetone, although the maxima of viscosity and heat of mixing do not correspond with any stoicheiometric relation between the constituents. T. H. P.

Specific Heats of Binary Mixtures. J. W. WILLIAMS and F. DANIELS (*J. Amer. Chem. Soc.*, 1925, **47**, 1490—1503).—The variation of the specific heat with changes in composition of the binary liquid mixtures benzene–toluene, chloroform–carbon tetrachloride, chlorobenzene–bromobenzene, benzene–carbon tetrachloride, and chloroform–acetone has been investigated over the temperature range 20—60°. The first four pairs form solutions which are almost ideal. The partial molal heat capacities of the components have been calculated. The experimental data are critically discussed and the questions of "deassociation" and compound formation considered. The variations of the specific heats at constant pressure, C_p, with temperature, of acetone, bromobenzene, and chlorobenzene are represented by the equations: $C_p=0{\cdot}5042+0{\cdot}00030t+0{\cdot}0_419t^2$, $0{\cdot}3043+0{\cdot}000101t+0{\cdot}0_544t^2$, and $0{\cdot}2273+0{\cdot}000042t+0{\cdot}0_525t^2$, respectively, where t is the temperature. J. S. C.

Molecular Contraction in Solution. J. N. RAKSHIT (*Z. Electrochem.*, 1925, **31**, 320—323; cf. this vol., ii, 288).—Further measurements of the change in volume which occurs when various substances are dissolved in water and other solvents are made, the results of which are in agreement with the theory that association between solute and solvent occurs on dissolution and varies with dilution. J. W. B.

Viscosity of Solutions. N. DE KOLOSSOWSKY (*Bull. Soc. chim. Belg.*, 1925, **34**, 190—201).—A formula representing the specific heats of dilute solutions, based on kinetic considerations and particularly taking into account the work necessary to overcome the viscosity of the medium with rise of temperature, is given and tested by the determination of the viscosities of sodium chloride, trichloroacetic acid, oxalic acid, sodium carbonate, and lead acetate solutions. The specific heats of these solutions calculated from the formula are in every case in good agreement with the experimental values. J. W. B.

Molecular Compounds of the Phenols. V. Vapour Pressure Curves. G. WEISSENBERGER and F. SCHUSTER (*Monatsh.*, 1924, **45**, 437—448; cf. this vol., i, 538).—Where an equimolecular complex has been inferred from the position of maximum deviation

of the vapour pressure–composition curve of mixtures of two substances, it is shown that the vapour pressure, at a concentration c of one component should be given by $Pc/(c+1)+Pkc/(c+1)^2$, where k is a constant. If the complex formed is of the type 1 mol. : 2 mols. the second term of the expression becomes $Pkc/(c+1)^3$. These formulæ are in satisfactory agreement with the observed figures for mixtures of *cyclo*hexanol, *o*-, *m*-, and *p*-cresols, 2-, 3-, and 4-methyl*cyclo*hexanol with benzene, of *cyclo*hexanol with ethyl acetate, and of *o*-, *m*-, and *p*-cresols with ethyl alcohol. But with mixtures of *o*-, *m*-, and *p*-cresols with acetone or ethyl ether, respectively, second order differences are found, which are represented with satisfactory accuracy by the addition of a further term $k_2Pc^2/(c+1)^5$ to the above expression, and are interpreted as due to the formation of the two complexes 2 mol. : 1 mol. and 1 mol. : 1 mol. A similar second order deviation occurring in the case of mixtures of *cyclo*hexanol with acetone and methyl alcohol, respectively, is attributed to association in one of the components. The values obtained for the system *cyclo*hexanol–chloroform are too complex for interpretation. G. M. B.

Molecular Compounds of the Phenols. VI. Behaviour of the Naphthols, the *ar*-Tetrahydronaphthols, and Related Substances. G. Weissenberger, F. Schuster, and N. Mayer (*Monatsh.*, 1924, **45**, 449—455).—Measurements are recorded of the vapour pressure at 18° of solutions of various concentrations of α-naphthol in methyl alcohol, β-naphthol in acetone, *ar*-tetrahydro-β-naphthol in ethyl alcohol and in acetone, tetrahydronaphthalene in ethyl alcohol, acetone, ether, benzene, *n*-hexane, and chloroform, *cyclo*hexanone in ethyl alcohol, acetone, benzene, and chloroform, and of anethole in ethyl alcohol and chloroform, respectively, the figures being compared in each case with those calculated from the van't Hoff relation. The depression of vapour pressure caused by β-naphthol is less than that found with phenol, but the tetrahydro derivative gives depressions of the same order as phenol. In the solutions of tetrahydronaphthalene, the observed vapour pressures are higher than the calculated values in all cases with the exception of the solutions in chloroform, where experiment gives a lower value. *cyclo*Hexanone causes a depression of vapour pressure only in the solutions in chloroform where complex formation occurs, probably through the oxygen atom of the keto group just as it occurs through the oxygen atom of the phenols. Anethole, again, gives a depression of vapour pressure with chloroform only. Surface tension and viscosity measurements are also recorded for these mixtures. G. M. B.

Boiling Points of Mixtures of Water, Benzene, and Ethyl Alcohol under a Pressure of 760 Mm. of Mercury. J. Barbaudy (*Compt. rend.*, 1925, **180**, 1924—1926).—Young (T., 1902, **81**, 707) found a constant mixture boiling at 64·85° containing 18·5% alcohol, 74·1% benzene, and 7·4% water, and indicated the possibility of dehydrating alcohol by distillation in the presence of benzene. The author has worked out the ternary diagram at

760 mm. The critical point 39% alcohol, 42% benzene is ill-defined. The lowest b. p. is confirmed as 64·8—64·9°, at which temperature the distillate separates into two layers.

	$t°$.	% Alcohol.	Benzene.	Water.	% of layer in distillate.
Upper layer	65	16·3	81	2·7	90·6
Lower layer	65	39·6	5·9	54·5	9·4

On cooling, the lower layer increases in amount and in alcohol content at the expense of the upper layer. R. A. M.

Vapour Pressure of Aqueous Solutions of Nitric Acid. G. B. TAYLOR (*Ind. Eng. Chem.*, 1925, **17**, 633—635).—Previous data on the partial pressures of water and nitric acid vapours over solutions of nitric acid have been correlated by plotting log p against $1/T$. The best lines were drawn through the experimental values and the results are tabulated for 20—100% nitric acid and for temperatures of 0—125°. M. B. D.

Vapour Pressures of Glycerol–Water and Glycerol–Water–Sodium Chloride Solutions. A. R. CARR, R. E. TOWNSEND, and W. L. BADGER (*Ind. Eng. Chem.*, 1925, **17**, 643—646).—The vapour pressures of glycerol–water mixtures containing 10—96% of glycerol have been measured between 60° and 160°. Measurements were also made for similar mixtures when saturated with sodium chloride. M. B. D.

Some Physical Properties of Silicate Glasses and their Possible Bearing on the History of Igneous Rocks. W. E. S. TURNER (*Trans. Faraday Soc.*, 1925, **20**, 481—488).—A discussion of the density, thermal expansion, compressibility, viscosity, and the weathering of silicate glasses, and of the solubility of gases in the molten and hardened glass. Water is regarded as the chief cause of the weathering or corrosion of glass and figures are given showing that a rough proportionality exists between moisture absorption and corrosion. The corrosion increases with decrease of silica concentration and with increase of alkali oxide concentration. F. G. S.

Solid Solutions of Water and Oxygen. N. S. KURNAKOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 482).—Striking examples of series of compounds of continuously-changing composition are the iron compounds such as micas, tourmalines, phosphates, and borates. With such compounds, the gradual absorption of oxygen and the conversion of ferrous into ferric oxide do not affect the homogeneity of the crystals but result in continuous variation in the colour and optical properties. The mineral vivianite, consisting of a hydrated ferrous phosphate, may also be produced synthetically, and in the first stages of its formation is composed of almost colourless crystals, which retain their form and uniformity, but gradually become blue as absorption of oxygen proceeds. The proportion of water in vivianite crystals may also change continuously, owing to the formation of solid solutions of the mineral with water. T. H. P.

Dilatometric Anomaly of α-Solid Solutions of Copper and Aluminium. P. CHEVENARD (*Compt. rend.*, 1925, **180**, 1927—1929).—The dilatation curves of aluminium bronzes show a discontinuity at 265° (heating) and 250° (cooling) which is not due to phase changes. The temperature at which the anomaly occurs is independent of aluminium content, but the amplitude of the discontinuity reaches a maximum at 9·3% aluminium. This agrees with Stockdale's value 9·8% for the limit of α-solid solutions. The anomaly decreases on further increase in aluminium content and disappears at 16% when γ-solid solutions appear. R. A. M.

Inner Crystalline Structure of Ferrite and Cementite in Pearlite. N. T. BELAIEW (*Proc. Roy. Soc.*, **A**, 1925, **108**, 295—306).—The inner crystalline structure of ferrite and cementite in pearlite has been studied by examining sections under a magnification of 4000 diameters. The cementite lamellæ are petal-like in shape and curvature, but the edge is composed of rectangular steps. The ferrite lamellæ appear to be composed of a multitude of small cubes of uniform size and suitably oriented. The production of these peculiarities is attributed to the stresses imposed on the lamellæ during the change of the iron from the face-centred to the cube-centred lattice. S. B.

Volumetric Measurement of the Mutual Solubility of Liquids. Mutual Solubility of the Systems Ethyl Ether–Water and *iso*Amyl Alcohol–Water. I. A. KABLUKOV and V. T. MALISCHEVA (*J. Amer. Chem. Soc.*, 1925, **47**, 1553—1561; cf. Hill, A., 1923, ii, 467).—A method for the measurement of the mutual solubilities of liquid pairs is described, in which the quantity of each liquid and the volumes at equilibrium are measured. In cases of low solubility, *e.g.*, water in ether, the volumetric method fails to give accurate results due to the error in reading the volumes of the layers in the measuring tubes. The mutual solubilities of ether and water and of *iso*amyl alcohol and water were determined between 10° and 30°. Methods of increasing the accuracy of the determinations are discussed. The untrustworthiness of the refractometric method of solubility determination is emphasised. J. S. C.

The Solubility of Sulphur Dioxide in Water and in Aqueous Solutions of Potassium Chloride and Sodium Sulphate. J. C. HUDSON (*J. Chem. Soc.*, 1925, **127**, 1332—1347).—The solubility of sulphur dioxide has been determined in water (cf. Schonfeld, *Annalen*, 1855, **95**, 1; Sims, *J. Chem. Soc.*, 1862, **14**, 1; Lindner, A., 1912, ii, 825; Smith and Parkhurst, A., 1922, ii, 398) and in aqueous potassium chloride containing up to 30 g. of salt per 100 g. of water between 10° and 90°, and also, between 20° and 50°, in aqueous sodium sulphate containing up to 20 g. of salt per 100 g. of water. The solubility in aqueous potassium chloride increases linearly with the salt concentration. The curves for sulphur dioxide in sodium sulphate solutions exhibit distinct maxima. The increase of the solubility in salt solutions is probably due to

combination between the salt and the gas (cf. Péchard, A., 1900, ii, 398; Fox, A., 1902, ii, 645), whilst a decrease of the solubility is due to hydration of the salt. An improved method of iodometric titration of sulphur dioxide is described. F. G. S.

Miscibility of Mixtures of Water, Ethyl Alcohol, and *iso*-Butyl Alcohol. P. Brun (*Compt. rend.*, 1925, **180**, 1745—1747).—Mixtures of *iso*butyl alcohol and water containing less than 8% or more than 83% of the alcohol are not miscible at any temperature. When the percentage of *iso*butyl alcohol is 12—83%, the mixtures become homogeneous by use of temperature. From 8—12% the mixtures are homogeneous at the ordinary temperature, separate into layers by heating and on further heating again become miscible. The critical point is at 123·5° and 37·5%. The ternary system water–ethyl alcohol–*iso*butyl alcohol is characterised at 0° by a critical mixture of the composition: 31·6% *iso*butyl alcohol, 15·7% ethyl alcohol, 52·7% water. For *n*-butyl alcohol, the corresponding figures are 23%, 16%, and 61%. R. A. M.

Solubility of Sucrose. P. Mondain-Monval (*Compt. rend.*, 1925, **181**, 37—40; cf. A., 1923, ii, 131, 295; this vol., ii, 654).—The values of the limiting heat of solution, L, as determined by the direct and indirect methods are −1·84 and −1·76 Cal., respectively. The value of the coefficient i as obtained from vapour pressure measurements is 1·79. The solubility in water has been determined over the temperature range 0·9—30·5°, the solubilities at the two extremes being, respectively, 180·5 g. and 218·0 g. per 100 g. of water. The value of L as calculated from the solubility equation, $500LdT/T^2+idc/C=0$, is −1·77 Cal. at 18°. The eutectic mixture contains 166 g. of sucrose per 100 g. of water, the eutectic temperature being −13·9°. J. S. C.

Solubility of Bi-bivalent Salts in Solutions containing a Common Ion. O. J. Walker (*J. Chem. Soc.*, 1925, **127**, 61).—The solubilities of the succinates and malonates of calcium, strontium, and magnesium have been determined in water and in solutions containing a common ion at 25°. The solubilities in the mixed solutions are always greater than those calculated from the solubility product. They are, however, in qualitative agreement with the theories of Debye and Hückel and of Noyes, and magnesium oxalate shows a fairly satisfactory quantitative agreement. R. W. L.

Solubility of Oxygen in Silver. N. Parravano and G. Malquori (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 417—423).—The absorption of oxygen by silver depends in marked degree on the time of contact, so that the m. p. of silver determined in the ordinary way in air or oxygen cannot have a constant value. When the contact between oxygen and silver is prolonged, both at 875° and at 1050° constant values are obtained for the ratio between the concentration of the oxygen in the metal and the square root of the pressure of the gas, the oxygen dissolving even in the solid metal in the monatomic form. The view that the velocity of absorption

of the oxygen is a function of the velocity with which the gas diffuses into the interior of the metal is supported by the fact that the velocity of absorption increases with the surface of contact.

T. H. P.

Molecular Condition of Phenol in Benzene Solution. J. C. PHILIP and C. H. D. CLARK (*J. Chem. Soc.*, 1925, **127**, 1274—1277).—The distribution of phenol between benzene and water (cf. Rothmund and Wilsmore, A., 1902, ii, 447; Philip and Bramley, A., 1915, ii, 236) has been measured over the range 0·438—112·7 g. phenol per litre of the benzene phase. The distribution ratio ($=C_W/C_B$, where C_W and C_B represent the g. phenol per litre of the aqueous layer and the benzene layer, respectively) is constant up to $C_B=2·8$ and then departs from constancy at higher concentrations. Since the molecular weight of phenol in water is approximately normal, the condition of phenol in benzene corresponds with simple $C_6H_5·OH$ molecules so long as the distribution ratio is constant. The contradictory results obtained by the freezing-point method (Auwers, A., 1893, ii, 133) are due to the separation of a solid solution of phenol in benzene (Garelli, A., 1897, i, 26). It is probable that in a concentrated solution of phenol in benzene triple molecules as well as double molecules exist (cf. Herz and Fischer, A., 1905, ii, 304).

F. G. S.

Adsorption of Polonium by Various Substances and its Reversibility. J. H. BRENNEN (*Ann. Chim.*, 1925, [x], **3**, 390—418).—Polonium is adsorbed reversibly by silver and ferric hydroxide sols, the equilibrium attained being the same whether the polonium is added before or after precipitation. The same applies to certain substances insoluble in hydrochloric and acetic acids (*e.g.*, glass, charcoal) and to salts sparingly soluble in water; in these cases the adsorption increases with decreasing hydrogen-ion concentration, attaining a maximum in neutral solution. The polonium, which is adsorbed almost instantaneously, is liberated only with great difficulty. Freundlich's adsorption isotherm holds for the adsorption of polonium with an activity of 2·24—27 *E.S.U.*

S. K. T.

Adsorption Phenomena exhibited by Tricalcium Phosphate. P. JOLIBOIS and J. MAZE-SENCIER (*Compt. rend.*, 1925, **181**, 36—37).—Although immediate analysis shows that the precipitates obtained on treating solutions of phosphoric acid with an excess of lime water are practically pure tricalcium phosphate, on leaving them in contact with the solution for 48 hrs. a considerable adsorption of calcium oxide is observed. On agitating the liquid immediately after precipitation, a colloidal solution is obtained which deposits precipitates of the same composition as those obtained when the tricalcium phosphate is left in contact with the corresponding solutions without agitation for 48 hrs. Similar results are obtained when pure tricalcium phosphate, previously heated at 1000°, is agitated with lime water.

J. S. C.

Application of *X*-Ray Methods to the Problem of Imbibition. J. R. KATZ (*Physikal. Z.*, 1924, **25**, 659—666).—A general review of the possibilities of *X*-ray technique as a means of elucidating the problems associated with the phenomena of imbibition.

R. W. L.

Vapour Pressure–Water Content Diagrams and Adsorption Power of Aniline Black. G. STADNIKOFF (*Kolloid-Z.*, 1925, **36**, 352; cf. *ibid.*, 1922, **31**, 19, and 1924, **35**, 228).—A reply to the criticisms of Kosakewitsch (*ibid.*, 1925, **36**, 82). E. M. C.

Unimolecular Films between Liquids: Butyric Acid between Water and Hexane, and Acetic Acid between Water and Benzene. W. D. HARKINS and H. M. MCLAUGHLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 1610—1613).—The number of molecules in a unimolecular film of butyric acid between water and hexane is $2{\cdot}78\times10^{14}$/sq. cm. and the area per molecule 32 sq. Å. These are the quantities previously found for this acid between water and benzene and between water and water vapour (A., 1919, ii, 324). The films are tightly packed and the number of molecules in unit area depends on the dimensions of the molecules as they lie oriented in the film, the carboxyl groups being towards the aqueous phase and the hydrocarbon chains toward the air or organic phase. The expanded film of acetic acid on water, 50 sq. Å., is reduced to 38·7 sq. Å. with benzene as upper phase. Tables are given representing the partition of butyric acid between water and hexane and of acetic acid between water and benzene together with the interfacial tensions of the two systems. The partition data show that butyric acid forms double molecules in hexane.

J. S. C.

Foaming Power and Surface Tension, especially of Humus Sols. WO. OSTWALD and A. STEINER (*Kolloid-Z.*, 1925, **36**, 342—351).—There is no necessary relationship between foaming power and lowering of the surface tension. The independence of these properties is particularly striking in the case of humus sols, which foam strongly but have little surface activity. With sols of humus from peat, addition of alkali increased, and of acid decreased the foaming, but the surface tension remained unchanged. With sols prepared from *Acidum huminicum* (Merck) the foaming increased markedly in the order alkaline, slightly acid, strongly acid, whilst the surface tension also increased slightly. The alkaline humate sols have no structural viscosity, but the acid and especially the partly flocculated suspensions have a high structural viscosity which follows an exponential equation (this vol., ii, 392). No single fundamental property is associated with foaming power. The essential feature is the formation of a skin at the liquid–air surface. A simple apparatus is described for the quantitative measurement of skin formation by comparing the rates of movement within a graduated capillary tube of a freshly-formed and an aged meniscus. With an acid humus suspension which foams strongly the rate of movement with an aged meniscus is much

slower than that with an alkaline humate sol of much lower foaming power. E. M. C.

Superficial Solutions and the Law of Gay-Lussac. A. MARCELIN (*Compt. rend.*, 1925, **180**, 2022—2023; cf. A., 1924, ii, 594).—The equation $pS=KT$ is applicable to films of benzyl benzoate and oleic acid on the surface of water, where p and S are the pressure and surface area, and T is the absolute temperature. The value of the constant K depends on the particular liquid, and is from 20 to 60 times less than the constant R of the gas equation. Molecules in the surface film are probably partly dissolved and are polarised on the surface of the water. W. H.-R.

Extension of the Law of Gay-Lussac to Superficial Solutions. R. DELAPLACE (*Compt. rend.*, 1925, **180**, 2024—2026; cf. preceding abstract).—The value of the constant K of the equation $pS_M=KT$ (Marcelin, *loc. cit.*) has been determined at 15° and 27° for films of benzyl benzoate on water, alcohol, benzene, ether, and chloroform. K is independent both of the temperature and of the nature of the solvent, and equals $0{\cdot}126\times10^7$, or about 1/60 of the value of the gas constant R. The low value is not due to polymerisation, but a superficial colloid may be formed. In the evaporation of volatile liquids such as alcohol, benzene, ether, or chloroform from the surface of water, a superficial pressure is first produced, but this gradually dies away. W. H.-R.

Explanation of "Intertraction" Phenomena between Solutions, and Molecular Significance of Surface Tension. N. K. ADAM and G. JESSOP (*Proc. Roy. Soc.*, 1925, **A**, **108**, 324—331).—It has been suggested that the development of streamers at the interface of two liquids, during mixing, is due to a special force of "intertraction" which aids the mixing. The present experiments are entirely at variance with this view, and it has been found that the so-called "intertraction" phenomena only occur if the solutions are placed one above another, and not side by side, and if there is a difference in the rates of diffusion between the solutes in the two solutions. Quite different phenomena are observed when the faster replaces the slower as the uppermost solution, and regular streaming only occurs with the slower diffusing solution uppermost. It is concluded that the movements at the interface are due to the hydrostatic equilibrium of the layers being upset by the diffusion of the solutes across the interface at different rates. Negative surface tension means that those forces of cohesion perpendicular to the interface which act when there is positive surface tension, restraining the diffusion of molecules away from the interface, become negative. This state is manifested by the diffusion of one liquid into the other. S. B.

Freezing Points of Very Dilute Solutions of Electrolytes. F. HOVORKA and W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1925, **47**, 1614—1624).—The freezing-point depressions produced by the electrolytes of different valency types, viz., potassium chloride, cæsium nitrate, potassium sulphate, barium nitrate, magnesium

sulphate, cupric sulphate, and lanthanum sulphate, at concentrations between 0·01 and 0·001*M*, are in very close agreement with the values derived from the equations of Debye and Hückel (A., 1923, ii, 459; Rodebush, A., 1924, ii, 825). J. S. C.

Quantitative Absorption Measurements in the Ultra-violet in Very Dilute Solutions. R. SUHRMANN and P. HUPPERT (*Z. physikal. Chem.*, 1925, **116**, 319—331).—Dilute solutions of salicylic acid in alcohol ($8·57 \cdot 10^{-5}$—$8·57 \cdot 10^{-8}$ mol./litre) and potassium nitrate in water ($1·112 \cdot 10^{-2}$—$4·65 \cdot 10^{-4}$ mol./litre) exhibited marked deviations from Beer's law in the region 248·2—365·5 $\mu\mu$ (cf. Ghosh and Bisvas, A., 1924, ii, 523; Halban and Ebert, *ibid.*, 824). It is considered that the molecular extinction coefficient is subjected to two opposing influences which alter with the concentration. Beer's law holds only in the concentration range where these forces nearly compensate each other. The influence of the dielectric constant of the solvent on electrical forces conditioning absorption is discussed. L. F. G.

Measurement of the Viscosity of Solutions of Cotton in Aqueous Cuprammonium Hydroxide and its Significance as a Test of Textile Quality. F. D. FARROW and S. M. NEALE (*J. Text. Inst.*, 1924, **15**, T, 157—172).—A method for determining the viscosity of solutions of cotton materials in ammoniacal copper oxide solution is described. For comparative purposes 2% solutions are convenient, but equations which have been tested over the range 0—3% may be used to convert the viscosities for other concentrations into a 2% or other standard. These equations are $1+C/m = 11/\log(\eta_m/\eta_B)$ and $1+C/n=11/\log(\eta_n/\eta_B)$, where m is the weight of cotton in the solution used the viscosity of which is η_m, η_B is the viscosity of the solvent, and n is the weight of cotton in a solution of standard concentration the viscosity, η_n, of which is required. The falling sphere viscosimeter is recommended.

In the paper, the log viscosities for 2% solutions of a large range of cotton materials are reported. Whilst it does not yet seem possible to propose standards of viscosity with which cotton should conform at any normal stage of manufacture, comparisons of the viscosities of the material before and after a treatment afford an extremely sensitive indication of the inception of structural change in the cellulose. For example, such processes as boiling cotton with alkali in the presence of air, or boiling with extremely dilute acids, or immersion in oxidising solutions, produce distinct falls in viscosity which also run parallel with falls in tensile strength. Mercerisation, however, being merely a swelling phenomenon, does not cause any noteworthy diminution in viscosity. J. C. W.

Dielectric Constants of Solutions of Electrolytes. II. P. WALDEN, H. ULICH, and O. WERNER (*Z. physikal. Chem.*, 1925, **116**, 261—290; cf. this vol., ii, 512).—The dielectric constants, mostly at 20°, of the undermentioned solutions have been determined by an apparatus previously described, slight modifications being introduced when using solvents of higher dielectric constant

than 10 : tetrapropylammonium iodide in chloroform, ethylaniline, aniline, *o*-dichlorobenzene; *s*.-tetrachloroethane, pyridine, *m*-nitrotoluene, and water; diethylamine hydrochloride in chloroform, aniline, and pyridine; tetraethylammonium picrate in *o*-dichlorobenzene; potassium chloride, barium chloride, and cadmium bromide in water. Measurements in chlorobenzene, bromobenzene, and ethylene dichloride gave only qualitative results. Successive small additions of solute to solvent cause the dielectric constant to fall towards a minimum, beyond which it rises. This rise was not observed with the solution of tetrapropylammonium iodide in *m*-nitrotoluene, owing to the small solubility of the solute, nor in any of the aqueous solutions, as here the measurements could not be carried far enough. The results are discussed theoretically.

L. F. G.

Effect of Light on Settling of Suspensions. C. G. T. Morison (*Proc. Roy. Soc.*, 1925, **A**, **108**, 280—284).—It has been observed that the passage of a beam of light through soil or kaolin suspensions contained in a rectangular tank causes the suspensions to stratify, the layers running parallel to the surface. The distance between successive strata appears to vary with the wave-length of the light traversing the tank, but the strata produced by white light are quite sharp. The stratification persists while the illumination is continued, and slowly disappears when it is cut off. S. B.

Use of Scattered Light in the Determination of the Distribution of Size of Particles in Emulsions. A. J. Stamm and T. Svedberg (*J. Amer. Chem. Soc.*, 1925, **47**, 1582—1596).—A method for the determination of the distribution of size of particles using scattered light is developed and applied to benzene-in-water emulsions in presence of soaps. After a period of sedimentation the systems are illuminated from the two sides in a narrow cell with dark opaque background and the variation in the intensity of the scattered light with the height is recorded photographically, the densities on the plate being determined with a photometer. The theoretical and practical derivations of the distribution of the size of particles from the density–height relationship are developed. The ratio of the average sizes of the particles in disperse systems, the average diameters of the particles of which are not less than two or three times the wave-length of light, may be obtained from the slopes of intensity–concentration curves. Mass distribution curves obtained for emulsions in presence of sodium, potassium, and cæsium palmitates are in good agreement with those from microscopic measurements. The position of the mass maxima is not shifted by using different alkali soaps, although there is an increase in the number of small particles in passing from sodium to potassium to cæsium soaps. An exponential increase in the radius corresponding with the mass maxima is caused by increasing the benzene concentration, the concentration of stabiliser remaining constant. Increase of the concentrations of benzene and stabiliser, their ratio remaining constant, gives maxima corresponding with a larger size of particles.

J. S. C.

Method of Determination of the Granular Distribution of Disperse Systems. R. AUDUBERT and H. RABATÉ (*Compt. rend.*, 1925, **180**, 1663—1665).—A method is described for measuring the size and granular distribution of solid particles by observations of the rate of sedimentation. The intergranular liquid is placed in two vertical tubes which communicate near the lower ends and a small portion of the disperse phase is introduced at the top of one of the vertical tubes, causing a difference of pressure, which diminishes as the grains fall; this difference is measured at regular intervals. If the relation between the mass (m) of the grains and their diameter (r) is of the form $dm=F(r)dr$, application of the Stokes law leads to the relation $F(r)=K't^{3/2}dp/dt$, where p is the difference of pressure after time t, and K' is a constant depending on the form of the apparatus and on the Stokes constant A, where $r^2t=A$. $F(r)$ is thus calculated for each value of t, from which the number of grains can be obtained as a function of the diameter. W. H.-R.

Reduction Velocity and Growth of Particles in the Preparation of Colloidal Gold Solutions. R. ZSIGMONDY and E. HÜCKEL (*Z. physikal. Chem.*, 1925, **116**, 291—303).—An attempt to correlate the autocatalysis of the reduction of gold salts by formaldehyde with increase of size of the particles. Solutions of gold salts were reduced either alone or in the presence of definite quantities of a red gold hydrosol. The times taken to attain a standard colour were observed. Reduction is accelerated by rise of temperature, and, to a certain extent, by increase in the amounts of formaldehyde and of added hydrosol. In some cases, the phenomena suggest that the velocity of linear increase of the particles is constant; where growth is very rapid, however, there appears to be an acceleration of the linear increase. Reduction takes place in the immediate neighbourhood of the gold particles. The concentration of the reactants is increased in this region by adsorption; this enhanced concentration, and not the mean concentration of the solution, controls the course of the reaction. L. F. G.

Preparation of Well-defined Silicic Acid Sols. W. GRUNDMANN (*Kolloid-Z.*, 1925, **36**, 328—331).—Almost identical silicic acid sols can be prepared by attention to the following factors. The same quantities of hydrochloric acid and sodium silicate must be used and the mixture transferred at once to collodion membranes of the same thickness and freshly-prepared for each sample. Only distilled water is used for the dialysis and the rate of its addition must be the same in all cases. The sols should be protected during dialysis from atmospheric contamination. The difficulty of preparing concentrated sols in summer (cf. Lösenbech, A., 1922, ii, 695) and the readiness with which these flocculate especially after storms, are ascribed to the action of atmospheric impurities. E. M. C.

Preparation of Colloidal Silver by Reduction with Chloroform. V. MORÁVEK (*Chem. Listy*, 1925, **19**, 195—203).—To prepare colloidal silver, using gelatin as protective colloid, the

author employs 8 millimols. of silver nitrate, 435·2 millimols. of ammonia, 50 millimols. of chloroform water, and 20 millimols. of chloroform to give 12·5 c.c. of a mixture in which the silver : gelatin ratio is 0·11 : 1. The mixture is warmed for 15—20 mins. on a water-bath at 90°, dialysed, and evaporated in a vacuum, the colloidal silver being obtained in solid, cold water-soluble form. The reducing action is increased in the presence of sodium or potassium hydroxide. Measurements are recorded of the size of the colloid particles, and of the resistance of the solution towards coagulating electrolytes. B. F.

General Colloid Chemistry. XIV. Constitution and Stability of Iron Oxide Sols. IV. N. KÜHNL and W. PAULI (*Koll. Chem. Beihefte*, 1925, **20**, 319—337; cf. A., 1924, ii, 740).—Ferric hydroxide sols prepared by peptisation of precipitated hydroxide with ferric chloride contain on the average ten times as much iron and twenty times as much chlorine as those prepared by hydrolysis. The ratio of active to total chlorine is from 1 : 5 to 1 : 6 in hydrolysed sols and is little affected by dialysis; but it decreases from 1 : 3 to 1 : 17 on dialysis of peptised sols, whilst the total oxychloride per colloid equivalent increases more than sixfold. The extent to which chlorine is substituted by sulphate and oxalate anions on coagulation is throughout considerably higher for hydrolysed than for peptised sols. By dialysis, the oxychloride portion of the sol-substance is progressively diminished, more markedly so in hydrolysed sols. Transport numbers are much the same for both varieties. W. A. C.

General Colloid Chemistry. XIV. Structure of Heteropeptoids. I. Aluminium–Iron Oxide Sols. N. KÜHNL and W. PAULI (*Koll. Chem. Beihefte*, 1925, **20**, 338—355; cf. preceding abstract).—When precipitated aluminium hydroxide is peptised with ferric chloride, or ferric hydroxide with aluminium chloride, brown sols are obtained containing roughly equivalent amounts of aluminium and iron, the proportions varying with the mode of preparation. In the replacement of chlorine by coagulating anions, and in the relations exhibited by the transport numbers, and the size of particles, these sols resemble pure ferric hydroxide peptised sols. It is suggested that the sol particles have the same constitution as mixed crystals (solid solutions). W. A. C.

Viscosity of Reversible Emulsions. S. S. JOSHI (*Trans. Faraday Soc.*, 1925, **20**, 512—519; cf. A., 1924, ii, 529, 731).—The viscosities of water-in-oil emulsions prepared from castor oil, olive oil, and paraffin oil have been determined, using sodium oleate, potassium palmitate, oleate, and stearate as emulsifying agents. The viscosity, which is independent of the concentration and nature of the emulsifying agent, increases with increase of the disperse phase and falls suddenly on inversion of the emulsion to the oil-in-water type. The viscosities calculated from the equations of Arrhenius (A., 1888, 336), Hatschek (A., 1911, ii, 98), and Einstein (A., 1921, ii, 19) are compared with the experimentally determined

values. The suggestion is made that an increment in the size of the grains of the water-in-oil emulsions with increase in the proportion of the aqueous phase may be one of the factors causing deviation of the calculated from the observed values. F. G. S.

Alteration of Viscosity of Disperse Systems with the Velocity of Shear. A. DE WAELE (*Kolloid-Z.*, 1925, **36**, 332—333).—Herschel's equation (cf. Ostwald, *ibid.*, 249) for the viscosity of disperse systems under varied velocities of flow is discussed and a new equation suggested to include the dynamic and static behaviour both of peptised and flocculated substances. E. M. C.

Theory of the Colour of Colloidal Metal Suspensions. G. JOBST (*Ann. Physik*, 1925, [iv], **76**, 863—888).—Mathematical. The theory of Mie (*ibid.*, 1908, **25**, 378) is developed. A radiation formula is deduced for a disperse system of completely reflecting spheres suspended in a transparent medium, and applied to the case of gold suspensions. The absorption and emission spectra are calculated for a number of systems consisting of particles with diameters from 100—600$\mu\mu$. These curves are in very approximate agreement with those calculated by the original theory of Mie. As the diameter of the particles increases, the maxima in these curves flatten. This flattening in the absorption spectra curves illustrates the gradual change in colour of transmitted light from greenish-blue to green. The curves for the emission spectra indicate the change in colour of gold sols from yellow, through reddish-yellow, to the characteristic red, with increase of particle size. The latter colour occurs only with particles of considerable size. F. G. T.

Velocity of Ice Crystallisation through Supercooled Gelatin Gels. E. H. CALLOW (*Proc. Roy. Soc.*, 1925, **A**, **108**, 307—323).—The velocity has been followed by seeding a supercooled gel with ice, and measuring directly the movement of the crystal boundary. Experiments with the gels at $-3°$ showed that the presence of more than 1% of gelatin greatly reduces the velocity of crystallisation. Thus in a 1% gel of p_H 1·50, the velocity was half that through distilled water and in a 1·5% gel it was twenty-four times slower still. Smaller quantities of gelatin have not a proportionate effect. When the hydrogen-ion concentration of the gels is altered, the velocity of crystallisation shows a minimum at the isoelectric point of gelatin. The velocities were greater if the gel had been previously boiled for some hours, β-gelatin having apparently less influence on the rate than the normal gelatin.

Opaque gels offer less resistance to a falling body than do clear gels of equal concentration. It is suggested that the opaque gels owe their turbidity to the presence of fibrils, which take no part in the gel structure. S. B.

Relation between Swelling of Gelatin and Hydrogen-ion Concentration. WO. OSTWALD, A. KUHN, and E. BÖHME (*Koll. Chem. Beihefte*, 1925, **20**, 412—433; cf. Kuhn, A., 1922, i, 183).—The swelling produced by acids when added to gelatin which has been brought to the isoelectric condition (p_H=4·7) by repeated extraction with water diminishes in the order: hydriodic, gly-

cerophosphoric, sulphosalicylic, hydrochloric, sulphuric. The same order is observed in presence of salts of the respective acids. As a rule, at equal values of p_H, the swelling by pure acids is greater than that by mixtures of acids and salts. In certain cases, however, where the anion has a marked swelling action, buffer mixtures exert a much greater effect than the pure acids, although the salts alone tend to diminish swelling. Dibasic acids have a stronger swelling effect, within certain limits of p_H, than monobasic. W. A. C.

Influence of Very Small Quantities of Foreign Substances on the Stability of Colloidal Solutions. A. Boutaric and (Mme.) Y. Manière (*Compt. rend.*, 1925, **180**, 1841—1842; cf. this vol., ii, 394, 526).—The stability of colloidal solutions against a particular electrolyte may be increased or decreased by the addition of small amounts of other substances. If α is the maximum amount of an electrolyte which fails to bring about any flocculation and if the value is β after addition of another substance, the expression $\beta-\alpha/\alpha$ measures the new stability. The phenomenon has been studied in detail, using an arsenic sulphide sol. Small amounts of salts or of ammonia or potash increase the stability when the alkali chlorides are used as flocculating agents. If the salts of bivalent elements are used, the stability is increased if alkali chlorides were added first, but decreased if the preliminary addition consisted of chlorides of bi- or ter-valent elements, or of sodium silicate, ammonia, or potash. If aluminium chloride is used as coagulating agent, the previous addition of chlorides decreases the stability, but a preliminary treatment with a trace of silicate or of ammonia or potassium hydroxide makes the quantity $\beta-\alpha/\alpha$ positive, *i.e.*, protection occurs.

R. A. M.

Coagulation of Prussian Blue and Ferric Hydroxide Sols. S. Ghosh and N. R. Dhar (*J. Physical Chem.*, 1925, **29**, 659—678; cf. *ibid.*, 435).—Further evidence that there is a close relation between abnormal behaviour on dilution, abnormality towards mixed electrolytes, and acclimatisation has been obtained by studying the coagulation of sols of Prussian blue and of positively charged ferric hydroxide, both of which behave abnormally. These phenomena are believed to be due mainly to the adsorption of ions carrying the same charge as the sol. Ferric hydroxide behaves normally when coagulated by potassium chloride or bromate, and arsenic trisulphide is normal towards silver nitrate. The former is, however, abnormal when coagulated by ferric chloride or aluminium nitrate, because the positive ions of these salts are absorbed. Similarly, ferric hydroxide is abnormal towards mixtures containing ferric chloride or aluminium nitrate, but can be acclimatised to these salts. It is normal towards mixtures of potassium bromate and oxalate and of potassium chloride and sulphate.

Some experiments on the influence of non-electrolytes are included.

A. G.

Coagulation of Colloids by Electrolytes. I. Arsenic Trisulphide Sols and Barium Chloride. A. J. Rabinovitsch (*Z. physikal. Chem.*, 1925, **116**, 97—110).—The "total" and the

"free" hydrogen-ion concentrations in arsenic trisulphide sols were determined by the method of Pauli and Semler (A., 1924, ii, 333). The sols were then coagulated by barium chloride solutions. In the filtrate from each coagulum the total hydrogen-ion concentration was found to be unaltered, after correcting for dilution by the barium chloride solutions, but now equalled the free hydrogen-ion concentration, *i.e.*, the filtrate was more acid than the original sol. The increase of acidity rises with the concentration of the sols. Arsenic trisulphide sols are considered to be fairly strong complex acids, dissociating as follows: $(As_2S_3)_nSH_2 \rightleftarrows (As_2S_3)_nSH^- + H^+ \rightleftarrows (As_2S_3)_nS^= + 2H^+$; the second dissociation constant is less than the first. In the coagulum it was found that the hydrogen had been completely replaced by an equivalent amount of barium; there was no chlorine present. L. F. G.

Emulsions. III. Double Reversal of Oil Emulsions by the Same Electrolyte. W. SEIFRIZ (*J. Physical Chem.*, 1925, **29**, 738—749; cf. A., 1924, i, 127).—Petroleum distillates (*d* 0·828—0·857) are not emulsifiable with aqueous casein, but on the addition of sodium or barium hydroxides, water-in-oil emulsions are formed which are converted into oil-in-water emulsions by more of the reagent. Similarly, when sodium hydroxide is added to an oil-in-water emulsion of olive oil, stabilised with agar-agar, it is reversed to a water-in-oil emulsion, and further addition again reverses it to the oil-in-water type; if the stabiliser is gelatose, the first reversal is only partial, but the effect is then also produced by barium hydroxide. Readily reversible petroleum emulsions frequently consist of both oil-in-water and water-in-oil systems; these may exist side by side, or one within the other, in which the drops of the primary emulsion are emulsions of the opposite type. These latter systems may be termed "bimultiple," and more complex emulsions, up to quinquemultiple, have been observed. When an emulsion is stabilised by an organic substance, the films surrounding the drops are often microscopically visible, solid membranes. A. G.

Simple Kinetic Principle of Colloidal Processes. J. ALEXANDER (*Kolloid-Z.*, 1925, **36**, 334—337).—The behaviour of heated steel and iron illustrates the general principle that maximum colloidal properties are developed when both the specific surface and the kinetic activity have medium values. Absence of colloidal properties may be caused by either too low a specific surface or too high a kinetic activity. E. M. C.

Viscosities of Aqueous Solutions of Pure Soaps and their Variations with Temperature. N. A. JAJNIK and K. S. MALIK (*Kolloid-Z.*, 1925, **36**, 322—327).—The viscosities of solutions of pure sodium palmitate and sodium stearate have been measured at 60°, 70°, and 80° in a constant pressure viscosimeter of the type used by Scarpa (A., 1911, ii, 16) and Farrow (T., 1912, **101**, 347). The viscosity increases rapidly with the concentration. Sodium palmitate solutions have a lower viscosity than those of sodium stearate, but the differences become very small for solutions more dilute than $N/20$, especially at 60°. E. M. C.

Moisture Relations of Cotton. I. Taking up of Water by Raw and Soda-boiled Cotton at 20°. A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1924, **15**, T., 138—143).—Investigation of the absorption and desorption of water by cotton at 20±0·5°, in atmospheres of about 1% to 98% relative humidity has shown definitely that there are at least two possible values for the moisture content of a sample of cotton which has been exposed to an atmosphere at a fixed temperature and degree of humidity. A higher value is obtained when the cotton was initially wetter than the atmosphere, and a lower value if it was initially drier. Further experiments show that if cotton is previously heated at 110° it is less able to absorb water vapour, and that scouring the cotton also reduces its capacity for taking up moisture when placed dry in a wet atmosphere. Soda-boiled cotton shows a greater hysteresis than raw cotton. J. C. W.

Moisture Relations of Cotton. II. Absorption and Desorption of Water by Soda-boiled Cotton at 25°. A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1924, **15**, T., 433—442; cf preceding abstract).—An improved method has been devised for investigating the complete absorption–desorption curves for a sample of purified cotton at 25°. In the absorption experiments, a bulb containing the cotton was connected to a manometer readable to 0·01 mm. and to a pipette readable to 0·02 c.c., from which any desired quantity of water could be transferred to the cotton by evaporation. In the desorption experiments, the water pipette was replaced by a phosphorus pentoxide tube which could be detached and weighed. It is found that soda-boiled cotton absorbs 22·6% of water at 25° from a saturated atmosphere. The results again show that the absorption curve lies lower than the desorption curve. Contrary to previous statements, however, the curves do not meet at zero humidity, but at a point corresponding with 1·8% relative humidity. Nor do the curves meet at 100% R.H. A possible explanation of the phenomenon of hysteresis in cotton is advanced which is not inconsistent with botanical views of the structure of the cotton hair, and which leads to the figure 13×10^{-8} cm. as the dimension of the smallest pores. J. C. W.

Moisture Relations of Cotton. III. Effect of Temperature on the Absorption of Water by Soda-boiled Cotton. A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1924, **15**, T, 559—572).—Measurements of the absorption of water by cotton have been made up to 130°. The apparatus was that described in the preceding abstract, with small modifications in the means for reading the higher pressures, and the material was the same. The results show that when the relative humidity is constant at less than 80%, increase of temperature from 10° to 110° decreases the moisture content of the cotton. When, however, the relative humidity is constant at more than 80%, a similar decrease in moisture content only occurs from 10° to 50°, whilst above 60° the moisture content may actually increase with rise of temperature. Furthermore, the hysteresis also decreases with rise of temperature, and the isosteres are apparently con-

current near the critical temperature and pressure of water. The change which sets in at about 60° is explained as due to swelling and the consequent exposure of new surface. Processes which depend for their success on the swollen state of cotton will therefore become easier above 60° at high humidities, and the most suitable conditions for attaining maximum moisture content in cotton appear to be 100° and 100% R.H. J. C. W.

Moisture Relations of Cotton. IV. Absorption of Water by Cotton Mercerised without Tension. A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1925, **16**, T, 155—166; cf. preceding abstracts).—The variations in the water-fixing power of mercerised cotton with the concentration of the alkali hydroxide employed are found to bear a close resemblance to the variations in dimensions in the single cotton hairs. For example, when mercerised with 15% sodium hydroxide or 28% potassium hydroxide, which are known to cause maximum swelling, the cotton also has a maximum hygroscopicity. On the other hand, the ratio between the moisture contents of the mercerised and unmercerised, scoured cottons at the same atmospheric humidity is independent of the degree of humidity. When mercerised with 15% sodiun hydroxide, for example, the moisture content of cotton when absorbing moisture is 1·57 times and when losing moisture 1·46 times the corresponding values for the unmercerised cotton, no matter what the prevailing humidity may be. The results indicate that mercerisation increases the accessible surface of cotton in proportion to the ratio between the moisture contents (the " mercerisation ratio "). A determination of this ratio should afford a measure of the increased capacity of a mercerised cotton, not only for water, but also for dyes. It is calculated that the diameter of the smallest pores in mercerised cotton is equal to or less than 8×10^{-8} cm. as against 13×10^{-8} cm. for soda-boiled cotton. J. C. W.

Swelling of Cotton Cellulose. II. Cotton Hairs in Solutions of Potassium Hydroxide. G. E. COLLINS and A. M. WILLIAMS (*J. Text. Inst.*, 1924, **15**, T, 149—156).—In extension of work on the alteration in dimensions of cotton hairs in sodium hydroxide solutions (A., 1923, i, 1065), similar measurements are now recorded for potassium hydroxide. Although contractions in length are about the same for the two alkalis, increases in diameter are less than half in potassium hydroxide solutions of what they are in sodium hydroxide solutions of the same concentration. Maximum swelling occurs in 28% potassium hydroxide solution, which is the solution of maximum electrical conductivity. J. C. W.

Swelling of Cotton Cellulose. III. Cotton Hairs in Solutions of Lithium, Rubidium, and Cæsium Hydroxides. G. E. COLLINS (*J. Text. Inst.*, 1925, **16**, T, 123—126).—Previous results (cf. preceding abstract) suggested that the solution of alkali having the maximum swelling power might be that of maximum electrical conductivity (and in the case of sodium hydroxide of maximum heat of formation). The data for the other alkalis afford

no support for this connexion. On the other hand, there seems to be a correlation between the degree of hydration of the metal ion and maximum swelling power. For example, there is a maximum on the swelling curve at LiOH 6·6%, or LiOH : $17H_2O$,NaOH 15·5% ($12H_2O$), KOH 38% ($7H_2O$), RbOH 49% ($6H_2O$).

Changes in length produced by the rare alkalis are small; in cæsium hydroxide, cotton hairs are actually elongated, even in the most concentrated solutions. The increments in diameter are only about half those attained in solutions of sodium hydroxide.

New physical data are recorded for the rare alkalis, as follows: lithium hydroxide: solubility, 10·73% at 20°, d_4^{18} of saturated solution 1·115; rubidium hydroxide: solubility, 65% at 20°, d_4^{20} of saturated solution 2·022; cæsium hydroxide: solubility, 81·2% at 20°, d_4^{20} of saturated solution 2·939. Measurements of the electrical conductivities are also recorded. J. C. W.

Hygroscopic Capacity of Wool in Different Forms and its Dependence on Atmospheric Humidity and other Factors. S. A. Shorter and W. J. Hall (*J. Text. Inst.*, 1924, **15**, T, 305—327).—The moisture contents of various samples of wool have been measured by direct weighing after keeping them sufficiently long in a room at constant temperature, and with a controlled degree of humidity. The data are trustworthy to ±0·1%. Raw wools differ considerably in their absorption of moisture, owing to the grease and other foreign matter, but, after scouring, their behaviour is fairly uniform. The curves connecting moisture content with atmospheric humidity are sigmoid. The paper deals largely with the influence of various technical processes. J. C. W.

Mercerisation of Cellulose. K. Hess (*Z. Electrochem.*, 1925, **31**, 316—319).—Mainly a polemical review in which the author discusses his own results and conclusions (cf. Hess, Weltzien, and Messmer, A., 1924, i, 142; Hess and Wittelsbach, A., 1920, i, 584) with the opposing views of Herzog and his collaborators (cf. Herzog and Londberg, A., 1924, i, 373, 619) and Katz and Mark (this vol., i, 640). Increase in the accuracy of measurement of the Röntgen diagrams of natural cellulose and hydrocellulose (*loc. cit.*) has shown that the deviation is systematic, the diagrams being very similar, but not identical. The author believes that mercerisation is caused by the salt-forming ability of the amphoteric cellulose and not by a change in the chemical structure of the molecule. The original crystal lattice of the fibre is converted by salt formation into a kind of ion-lattice, the displacement of the $C_6H_{10}O_5$ groups caused by the inorganic component being irreversible. J. W. B.

Dispersion of Different Kinds of Cellulose by Mechanical Means and by the Action of Aqueous Salt Solutions. P. P. von Weimarn (*Kolloid-Z.*, 1925, **36**, 338—341; cf. A., 1921, i, 847).—The dispersion of cellulose in concentrated salt solutions is accompanied by hydrolysis with the production of substances in true solution. The rates of dispersion and hydrolysis depend on the form of cellulose used. The dispersion of resistant forms of cellulose

is greatly accelerated by a preliminary mechanical treatment such as grinding at the temperature of solid carbon dioxide or liquid air.
E. M. C.

Effect of Treatment with Sulphuric Acid on the Breaking Load of Cotton. P. D. VINCENT (*J. Text. Inst.*, 1924, **15**, T., 281—290).—When cotton is soaked in sulphuric acid it suffers loss of strength, which is generally ascribed to the formation of "hydrocellulose." It is now shown that with the single cotton hair this "tendering" is a linear function of the concentration of the acid, complete disruption occurring in a solution containing 77 g. per 100 c.c. J. C. W.

Elasticity and Tensile Strength of Starch. S. M. NEALE (*J. Text. Inst.*, 1925, **15**, T, 443—452).—Dried films of pure starch pastes, and pastes containing modified starch and other ingredients common to the practice of sizing have been tested at 20° and 34% or 66% relative humidity in a special apparatus which traced the load-extension diagrams. The general behaviour of starch films resembles that of a ductile metal. Maize, potato, and sago starch films have almost identical elastic properties, but weaker films are produced by oxidation or hydrolysis of the starch, or by the addition of acids, alkalis, or soap to the paste. J. C. W.

Ammonia Solutions. F. E. C. SCHEFFER and (MISS) H. J. DE WIJS (*Rec. trav. chim.*, 1925, **44**, 655—662).—The work of Moore (T., 1907, **91**, 1377) on the equilibrium $NH_3+H_2O \rightleftharpoons NH_4{\cdot}OH$ is criticised on the ground that certain values in his equation are contradictory. It is considered that the equilibrium constant can only be determined in terms of the total concentration of ammonia in the liquid, as the NH_3 and NH_4OH cannot be separately determined. The constant in the equilibrium $(NH_3)_{gas} \rightleftharpoons (NH_3)_{diss.}$ cannot be determined, but as $k_{mol.}=C_{NH_4OH}/C_{NH_3}$, then $C_{NH_3}/C_{am}=C_{NH_3}/(C_{NH_3}+C_{NH_4OH})=1/(k_{mol.}+1)$=constant. The equilibrium constant of $(NH_3)_{gas}+xH_2O \rightleftharpoons [xNH_4OH+(1-x)NH_3]_{diss.}$ is determinable by means of the ratio p_{NH_3}/C_{am}, where p_{NH_3} is the pressure of the gas above the liquid, and C_{am} is the total concentration of the ammonia (corrected for the small ionic concentration). Henry's law was found to hold for concentrations up to about $0{\cdot}2N$. The pressure of ammonia (gas) could be expressed as a function of the total concentration by the formula $p=12{\cdot}9C_{am}(1+0{\cdot}046C_{am})$. The addition of a constant small quantity (0·15 mol.) of ammonium nitrate to varying concentrations of ammonia was found to have no influence on the agreement of the ratio p/C_{am} with Henry's law or the above equation; but the addition of increasing quantities of the salt to small concentrations of ammonia was found to be represented by $p=12{\cdot}9C_{am}(1+0{\cdot}019C_n+0{\cdot}0085C_n^2)$, where C_n is the ammonium nitrate concentration. The thermodynamic potential of the ammonia molecules in the solution is discussed. L. L. B.

Hydrolysis of Alkali Cyanides in Aqueous Solution. R. W. HARMAN and F. P. WORLEY (*Trans. Faraday Soc.*, 1925, **20**, 502—507).—The degree of hydrolysis of sodium and potassium cyanides

in aqueous solution (cf. Worley and Browne, A., 1918, i, 60; Meyer, A., 1921, i, 501) has been determined by the method previously employed by Worley and Browne (*loc. cit.*). The molar concentration, C, of the cyanide was varied from 0·01 to 1·0 mol. per litre and the results obtained for the mass law expression $P^2C/100(100-P)$, where P is the percentage hydrolysis, are in satisfactory agreement. The mean hydrolysis constants found for sodium and potassium cyanides at 25° are $2{\cdot}51\times10^{-5}$ and $2{\cdot}54\times10^{-5}$, respectively, and the heat of hydrolysis of potassium cyanide, calculated from measurements at various temperatures is $2{\cdot}95\times10^3$ cal. F. G. S.

Homogeneous Equilibria in Magmatic Melts and their Bearing on the Processes of Igneous Rock Formation. P. Niggli (*Trans. Faraday Soc.*, 1925, **20**, 428—441).—The formation of igneous rocks of Pacific, Mediterranean, and Atlantic types is discussed with reference to equilibria in the magma and the processes of silicification and desilicification, complex decomposition reactions, substitution reactions with formation of new molecular types, formation of double salts, and polymerisation. The importance of the study of such homogeneous equilibria for the systematic classification of rock types is emphasised. F. G. S.

Kinetic and Electromagnetic Definition of the Thermodynamic Temperature of a Gas. E. Wertheimer (*Z. Physik*, 1925, **32**, 596—619).—The thermodynamic temperature of a gas may be defined by means of either the thermal agitation of the molecules or the electromagnetic energy of radiation. In the latter case, although the actual energy is quantitatively of no account, yet the temperature can be defined as that at which the medium is in equilibrium with black body radiation of temperature T.

E. B. L.

Kinetic Theory of Evaporation. D. B. Macleod (*Trans. Faraday Soc.*, 1925, **20**, 525—543).—On the assumption that the ratio of the densities of vapour and liquid in equilibrium is equal to the ratio of the number of the molecules with sufficient speed to escape from the liquid to the number with insufficient speed, the minimum escaping speeds of molecules of a number of liquids at various temperatures have been calculated. It is found that for unassociated substances the minimum kinetic energies of escape fall off linearly with the temperature to within 20° or 30° of the critical temperature. They then decrease rapidly to zero. The minimum energies of escape for acetic acid and the alcohols are not so simply related to the temperature. It is shown that for unassociated liquids the minimum energy of escape is practically directly proportional to the molecular surface energy as is required by the theory, whilst definitely associated liquids do not show this proportionality. The latent heats of evaporation of six unassociated liquids, calculated over a range of temperature by evaluation of the difference between the total kinetic energy of 1 g. of the escaping molecules and the total

kinetic energy of 1 g. of the general mass of molecules, are in very good agreement with the values determined experimentally.

F. G. S.

Dissociation of Several Metallic Oxides. F. BORN (*Z. Elektrochem.*, 1925, **31**, 309—311).—A theoretical paper in which by means of the Nernst heat theorem and existing data for the melting points, boiling points, latent heats of vaporisation, and heats of formation, the dissociation pressure of the oxygen and the degree of dissociation of several metallic oxides at 2000° and 3000° Abs. are calculated. Calcium oxide is practically completely dissociated at its b. p. (3120° Abs.), as are probably magnesium oxide and zirconium oxide which have b. p. above 3500° Abs. Silica and chromic oxide are largely dissociated, aluminium and thorium oxides only slightly. The dissociation pressures obtained respectively for aluminium, calcium, chromic, magnesium, silicon, thorium, titanium, tungsten, and zirconium oxides, are at 2000°, 25, 0·2, 3, 0·3, 2, about 3×10^{-3}, 3, 760, about 6×10^{-4} mm.; at 3000° >760, 700, >760, 750, >760, about 16, >760, >760, about 16 mm. J. W. B.

Vapour Pressure of the Volatile Constituents of Glass at the Ordinary Temperature. F. BORN (*Z. Elektrochem.*, 1925, **31**, 312).—By means of the Nernst vapour pressure formula and equilibrium equation the vapour pressures of the volatile constituents of glass (oxides and silicates of the alkali metals) at the ordinary temperature are calculated to be of the order of 10^{-16}—10^{-20} and 10^{-25}—10^{-30} mm., respectively; the calculated partial pressure of the oxygen is less than 10^{-40} mm., and the combined effects produce a vapour pressure of 10^{-16}—10^{-20} mm. J. W. B.

Relationships Existing between Hydrogen and Palladium. B. LAMBERT and S. F. GATES (*Proc. Roy. Soc.*, 1925, **A, 108**, 456—482).—Pressure–concentration equilibria were investigated at 75°, 103°, and 120°. Different equilibrium pressures, with the same concentrations of hydrogen in the solid phase, were obtained when the method of approaching equilibrium was varied. There is some evidence, however, in each series of experiments, for the existence of the compound Pd_2H. The contention that metallic palladium exists in at least two allotropic forms is supported. L. F. G.

Equilibrium Conditions of Magnesium Carbonate in Ammoniacal Solutions. G. H. LAFONTAINE (*Compt. rend.*, 1925, **180**, 2045—2047).—Solutions of magnesium hydrogen carbonate were treated with known quantities of ammonia and ammonium hydrogen carbonate, and the composition of the solid phase determined after prolonged stirring at 30°. The solid phases consist of the following compounds: (1) the neutral hydrated carbonate $MgCO_3,3H_2O$, (2) a double carbonate, $MgCO_3,(NH_4)_2CO_3,4H_2O$, (3) a basic carbonate, $MgCO_3,Mg(OH)_2,4H_2O$, and (4) a second basic carbonate, $4MgCO_3,Mg(OH)_2,4H_2O+5(MgCO_3,3H_2O)$, which is not a mixture, but a definite compound forming minute spheroids which are optically inert. The approximate limits of concentration in which these

compounds are precipitated, either singly or in pairs, have been determined. W. H.-R.

System Sodium Nitrate–Sodium Sulphate–Water and the Minerals Darapskite and Nitroglauberite. H. W. Foote (*Amer. J. Sci.*, 1925, [v], **9**, 441—447).—Solubility data for the system have been determined at 0°, 25°, and 35°. No evidence in favour of the existence of double salts other than darapskite, $NaNO_3,Na_2SO_4,H_2O$, was obtained (cf. Massink, *Z. physikal. Chem.*, 1918, **92**, 364). The mineral nitroglauberite is shown to be essentially a mixture of sodium nitrate and darapskite. The quintuple point temperatures, at which the three solid phases are sodium nitrate, sodium sulphate decahydrate, darapskite, and anhydrous sodium sulphate, sodium sulphate decahydrate, and darapskite, respectively, are 13·5° and 24·5°. The double salt is formed above 13·5° and still exists at the highest temperature investigated, although evidence was obtained of another quintuple point in the region of 50°, above which darapskite does not form. J. S. C.

Equilibria in the Systems: Ammonium Chromate–Ammonium Sulphate–Water, and Ammonium Chromate–Potassium Chromate–Water at 25°. S. Araki (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 213—222).—The solubility curves for each pair of salts consist of two branches and show that two series of solid solutions are formed in each case. No solid solutions exist when the molar percentage of ammonium chromate is between 2·90% and 21·50% in the former system, and between 16·75% and 55·50% in the latter. The molar percentages of ammonium chromate in the total dissolved salts in the liquid solutions which are in equilibrium with these two series of solid solutions are 8·56% and 61·66%, respectively. J. W. B.

Equilibrium in the Ternary System Bismuth Oxide, Hydrochloric Acid, Water. G. Waris (*J. Indian Chem. Soc.*, 1925, **1**, 307—310).—Analyses of the liquid and solid phases of the ternary system at 25° show that no hydrate of bismuth oxychloride exists at this temperature; the solid phase which separates out from solutions containing 25—33·67% of hydrogen chloride is normal bismuth oxychloride. J. W. B.

Nature of Aluminium-Magnesium Alloys. G. G. Urazov (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 480—481).—Investigation of the m. p. diagram and microstructure of alloys of magnesium with aluminium shows that these two metals form three series of solid solutions. In the first aluminium dissolves up to 11 at.-% Mg; in the second magnesium dissolves up to 7 at.-% Al; whilst the third contains between 37 and 59 at.-% Mg. The m. p. diagram consists of three branches, corresponding with the temperatures at which the first crystals of the three series of solid solutions appear. T. H. P.

Equilibrium Diagram of the Aluminium-Zinc System. T. Isihara (*Science Rep. Tôhoku Imp. Univ.*, 1925, **13**, 427—442).—The equilibrium diagram of the aluminium–zinc system was

redetermined by the electrical resistance method, in conjunction with microscopic, dilatometric, and *X*-ray measurements. The form of the liquidus agrees with the results of previous investigations. For the γ-phase the solidus occurs at a higher temperature than that previously obtained, but for the β-phase Hanson's result (*Engineering*, 1922, **113**, 538) is confirmed. The eutectic at 380° contains 5% Al. The solubility of aluminium in the α-phase varies from 1% at 380° to 0·3% at the ordinary temperature. A transformation in the β-phase is found at 340—350°, corresponding with the A_2 transformation in iron. There is no change in the Laue diagram taken above and below this range. The solubility of zinc in aluminium at the ordinary temperature is found to be 32·5%, showing a large divergence from previous results. The diagram generally confirms that of Hanson. C. S.

Copper–Antimony Alloys. N. S. KURNAKOV and K. F. BELOGLAZOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 490—492).—Reimann's observation that the maximum m. p. for copper–antimony alloys occurs at 71 at.-% of Cu is in moderately good agreement with the authors' result, namely, 72 at.-% Cu (*Z. Metallkunde*, 1920, **12**, 321), but does not justify the conclusion that the β_2-phase consists of a definite compound Cu : Sb = 5 : 2. Within the limits of stable existence of the β_2-phase, no evidence for this is afforded by the m. p. diagram, the electrical conductivity isotherms, or the curve of temperature coefficient of conductivity. Between 400° and 600° these curves are continuous and show no singularity at Cu : Sb = either 3 : 1 or 5 : 2. Analogous relations are observed for the electrical conductivity and hardness diagrams of the β_1-phase (74—80 at.-% Cu), which is the product of the polymorphous transformation of β_2 below 410° and is stable at the ordinary temperature. The β_1- and β_2-phases must therefore be regarded as of variable composition. T. H. P.

Constitution of Aluminium–Copper Alloys. G. MASING and L. KOCH (*Wiss. Veroff. Siemens-Konzern*, 1925, **4**, [1], 109—112).—By diffusion experiments with $CuAl_2$ and an alloy in the α region the existence of the two crystalline phases δ and η has been confirmed. Since *X*-ray investigation failed to detect these phases, it would seem that they have the same lattice structure. A. R. P.

Equilibrium Diagram of the System Iron–Carbon–Titanium. K. TAMARU (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 25—32).—In ternary alloys of iron, carbon, and titanium containing less than 4% Ti the whole of the titanium is retained in solid solution in the ferrite. Titanium decreases the carbon content of the iron–carbon eutectic and the solubility of graphite in austenite at high temperatures. [Cf. *B.*, 1925, 593.] A. R. P.

Ternary System, Lead–Cadmium–Thallium. C. DI CAPUA (*Gazzetta*, 1925, **55**, 280—290).—The solidification phenomena observed with the alloys Cd–$PbTl_2$ indicate that the alloy corre-

sponding with the maximum in the m. p. curve of lead–thallium alloys behaves as a compound and with cadmium gives mixtures which may be regarded as a series of binary alloys, $PbTl_2$–Cd. Thus the ternary system may be divided into two regions, Cd–$PbTl_2$–Tl and Pb–Cd–$PbTl_2$, the alloys of each region constituting a separate ternary system. In neither of these partial ternary systems do solids appear other than those of the three limited binary systems. The possible solids in the system $PbTl_2$–Pb–Cd are, therefore, mixed crystals $PbTl_2$Pb and Cd, the ternary diagram showing two surfaces of primary separation meeting along a curve of secondary separation stretching from the eutectic Pb–Cd to the eutectic $PbTl_2$–Cd. The diagram for the other partial system, $PbTl_2$–Cd–Tl, is more complex, since $PbTl_2$–Cd and Cd–Tl exhibit a eutectic without mixed crystals in appreciable amount, and $PbTl_2$–Tl gives a diagram resembling Roozeboom's type IV, except that the concentration of the mixed crystals rich in thallium which are formed at 312° from those poorer in thallium virtually coincides with that of the liquid which at 312° is in equilibrium with the two solids. Three solids are possible in this case, namely, two species of binary mixed crystals and cadmium; there should, therefore, be a point of invariant equilibrium in which three univariant curves meet, but one of these is a curve of transformation and does not correspond with deposition of two solids and the invariant point becomes a transformation point and not a eutectic point. T. H. P.

Theory of Crystallisation in Rock Magmas. C. H. Desch (*Trans. Faraday Soc.*, 1925, **20**, 469—473).—The difference in behaviour of molten metallic and silicate systems is ascribed to the high viscosity of the latter. This high viscosity probably accounts for the comparative rarity of eutectic structures in igneous rocks. Bowen's views (*J. Geol.*, 1922, **30**, 177), which involve reaction between solid and liquid phases and exclude the eutectic conception, are criticised and similarities in the structure of certain igneous rocks and alloys are pointed out. F. G. S.

Graphic Methods of Representing Equilibria in Systems of Three Components. G. G. Urazov (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 482—483).—The author develops methods for the graphic analysis of the equilibrium in systems of three components characterised by the existence either of a stable chemical compound or of a compound melting with decomposition, the formation of solid solutions between the components being excluded in both cases. Application of the method of "crystallisation paths" permits of the determination of the composition of any point within the projected triangular system, and of the order in which solid phases are deposited; it is also possible to foretell the number of breaks in the cooling curve for a mixture of any composition. T. H. P.

A Property of van't Hoff's Plane Diagram. K. F. Belogolazov (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 502—504).—It is shown that van't Hoff's diagram (*Vorlesungen über theor.*

u. phys. Chemie, **1**, 161) representing the isothermal crystallisation of solutions of two salts may be adapted to crystallisation at variable temperature, the saturation isotherms for different temperatures being brought into relation to one set of axes. Crystallisation and the inverse process of dissolution correspond in the diagram with curves combining the isotherms for the initial and final temperatures of the process. For such curves, in conformity with Kurnakov's terminology, the name " crystallisation paths " is suggested.

T. H. P.

Thermodynamics of the Capillary Layer. G. BAKKER (*Ann. Physik*, 1924, [iv], **75**, 685—710; cf. A., 1924, ii, 23).—Mathematical. The formation of the capillary layer is imagined to occur in two steps: homogeneous phases of liquid and of vapour are first formed, and interaction between these leads to the formation of the stable capillary layer. The energy change in the first step is $\frac{1}{2}(\rho_1-\rho_2)r_i/(\rho_1+\rho_2)$ and in the second $\epsilon-\frac{1}{2}(\epsilon_1+\epsilon_2)$, where ρ_1, ρ_2 are the densities and ϵ_1, ϵ_2 the energies of the liquid and vapour, respectively, ϵ is the energy of the capillary layer, and r_i the internal heat of evaporation. A discussion of the energy relations leads to the equation $\left(H-T\frac{dH}{dt}\right)S=\epsilon-\frac{1}{2}(\epsilon_1+\epsilon_2)+\frac{1}{2}(\rho_1-\rho_2)/r_i(\rho_1+\rho_2)$, where H is the surface tension and S the surface of the capillary layer. From this is derived the expression $d\epsilon-Td\eta+p_Tdv=Hv(\delta s/v/\delta t-1/R\,.\,\delta w/v/\delta t)dt$, where η is the entropy, R the radius of curvature, v the volume per unit mass of the capillary layer, p_T the average pressure along the capillary layer, and w a function of the volumes of the liquid and vapour phases. For isothermal changes this expression reduces to one derived earlier (*loc. cit.*): $Td\eta=d\epsilon+p_Tdv$.

A calculation is made of the thickness of the capillary layer of two drops of liquid and of a vapour bubble of carbon dioxide at 20°. Experiment and theory agree fairly well.

A. S. R.

Thermodynamics of Water Absorption by Textile Materials. S. A. SHORTER (*J. Text. Inst.*, 1924, **15**, T, 328—336).—The Clapeyron–Clausius equation is applied to the absorption of moisture by textile materials, giving a connexion between the heat change and the mode of variation with temperature of the humidity–regain relationship. The heat changes are calculated for cotton, silk, and wool at various regains, from Schlœsing's data. The calculated values vary in accordance with theory, becoming large in the neighbourhood of zero regain, and approaching zero in the neighbourhood of saturation. The values of the " heat of wetting " are calculated by integrating the heat of absorption. The calculated value for cotton at a regain of 5·1% is found to be in close agreement with the experimental value obtained by Barratt and Lewis (A., 1922, i, 526). The theory is applied to a critical consideration of the results obtained by Hartshorne (*Trans. Nat. Assoc. Cotton Manuf.*, 1905, **79**, 194; 1911, **90**, 281) for the influence of temperature on the regain of cotton and wool. Values of the heat of absorption calculated from Hartshorne's data

do not show a rapid increase in the neighbourhood of zero regain, although this is to be expected on theoretical grounds and is shown to be so by the values calculated from Schlœsing's data. Hartshorne's conclusions are therefore not acceptable; the invalidity would seem to be due to the neglect of the influence of temperature on the relative humidity given by his control solutions of sulphuric acid. J. C. W.

Calculation of Specific Affinity. T. DE DONDER (*Compt. rend.*, 1925, **180**, 1922—1924).—Mathematical. R. A. M.

Activity Coefficients. E. WILKE and O. KIENIGER (*Z. physikal. Chem.*, 1925, **116**, 215—226).—The influence of high concentrations of hydrochloric acid and of sodium chloride on hydrogen and chlorine electrodes has been examined. Whilst the *E.M.F.* of hydrogen cells, in the presence of hydrochloric acid alone, are in approximate agreement with the Nernst formula, the chlorine cells do not obey this formula, the *E.M.F.* with 5*N*-hydrochloric acid in the variable half cell being about four times as great as the calculated value. The *E.M.F.* of hydrogen–chlorine cells were measured as a check, and found to be the same as those calculated from the single potentials of their electrodes. The effect of applied currents on the individual electrode potentials in hydrogen–chlorine cells was measured; with the same current, the potential shift of the hydrogen electrode increases with dilution of acid or neutral salt, the reverse occurring with the chlorine electrode. This is ascribed to the superior mobility of the hydrogen ion. The heats of solution of chlorine in water, hydrochloric acid solutions, sodium chloride solutions, and mixed hydrochloric acid–sodium chloride solutions were measured. L. F. G.

Heats of Solution and Heats of Incomplete Reactions. (MLLE.) BÉRENGER and A. TIAN (*Compt. rend.*, 1925, **180**, 1907—1910).—If a chemical reaction occurs in the presence of a solvent the heat effect is given by $X=Q+Q_1-Q_2$, where Q is the heat released in the thermochemical experiment, Q_1 is the heat of solution of reactants (1), and Q_2 the heat of solution of resultants (2), and X is the required heat of reaction. For completed reactions Q_1 and Q_2 are easily measured. They are also measurable for incomplete reactions which can be studied calorimetrically in dilute solutions, for Q_1 and Q_2 are given by the algebraic sum of the heats of solution of all the components of (1) and (2) in a large volume of solvent S. The problem is quite different if the reaction has to be carried out in concentrated solutions. Many organic reactions, *e.g.*, esterification, can only be carried out slowly in concentrated solutions, and are incomplete. Whilst the equation is still theoretically valid, practically the measurement of Q_1 and Q_2 is possible only when the reaction is either (*a*) purely catalytic and the catalyst is not in concentrated solution, or (*b*) the reaction is very slow. Methods are indicated whereby approximate values for Q_1 and Q_2 can be obtained under these conditions. R. A. M.

Heats of Solution and Dilution of Salts. I. J. WÜST and E. LANGE (*Z. physikal. Chem.*, 1925, **116**, 161—214; cf. Richards and Rowe, A., 1921, ii, 380).—An electrical adiabatic calorimeter is described by means of which the heats of solution and dilution of the chlorides, bromides, and iodides of sodium and potassium were determined at 25°. The concentrations of the solutions were varied over a wide range. L. F. G.

Theory of Specific Heats of Solutions. N. DE KOLOSSOWSKY (*J. Chim. physique*, 1925, **22**, 225—252).—Assuming, (*a*), that the specific heat (*k*) of a solution is an additive property of the specific heats of all the constituents, and, (*b*), that the specific heats of dissolved molecules or ions are given, as in the gaseous state, by the relation $C_p=2N+3$, where N is the number of atoms in the molecule, the following equation is deduced:

$$k=\{\mu mc+2n+3(1-\gamma+i\gamma)-(mc-2x)v\}/(M+\mu m) \quad . \quad . \quad (1)$$

Here m and M are the molecular weights of the solvent and solute, respectively, μ is the number of molecules of the solvent containing 1 mol. of the solute, c the specific heat of the solute, n and x are the numbers of atoms contained in the molecules of the solute and the solvent, respectively, γ is the degree of dissociation, i the number of ions given by the dissociation of one solute molecule, and v the number of solvent molecules combined with one solute molecule as, *e.g.*, hydrate. By placing γ equal to zero or unity, the equation is applicable to cases where dissociation is either entirely absent or complete. Existing data are in general agreement with the equation for both electrolytes and non-electrolytes except when n is greater than 10, in which case assumption (*b*), above, is unjustified, but the error is only slight. The specific heat of an equimolecular solution increases with increase of n, but diminishes with increase of M. The effects of dissociation of the solute or of association of the solvent are usually insignificant. By a suitable transposition, the equation enables v to be calculated from the specific heat of a solution, and in this way the numbers of water molecules associated with 1 mol. of a large number of salts, acids, and bases in aqueous solution have been calculated. They are usually not whole numbers, but the nearest integer often agrees with a known hydrate, although the method gives no indication of how the water molecules are distributed among the different ions. W. H.-R.

Electrical Conductivity of Potassium Iodide in Bromine–Iodine Solutions. W. PLOTNIKOV (*Z. physikal. Chem.*, 1925, **116**, 111—118).—The conductivities of potassium iodide in mixtures of bromine and iodine have been determined at 25°. The solubility of potassium iodide in bromine is greatly increased by the addition of iodine. In spite of the low dielectric constant of bromine, the solutions have a considerable conductivity. The specific conductance increases very rapidly on the addition of iodine or of potassium iodide to solutions of medium concentration, but only slowly on the addition of potassium iodide to solutions already nearly saturated with that substance. These effects are explained by the formation

of polyiodides which dissociate to form complex ions. The calculated molecular conductivities of the substances KI_9 and KI_{11} decrease rapidly on dilution. L. F. G.

Ionisation of Aromatic Nitro Compounds in Liquid Ammonia. I. (Miss) M. J. Field, W. E. Garner, and C. C. Smith (*J. Chem. Soc.*, 1925, **127**, 1227—1237).—From observations of the electrolysis of solutions of *m*-dinitrobenzene in liquid ammonia it is concluded that ionisation occurs through the formation of organic anions, and cations consisting of ammonia molecules carrying one, or possibly two, positive charges. The equations $R(NO_2)_2+xNH_3 \rightleftharpoons R(NO_2)_2,xNH_3 \rightleftharpoons R(NO_2^{--})_2+xNH_3^{+}$ are suggested for this process, the nitro compound possibly behaving as a colloidal particle of high mobility. Similar solutions of isomeric nitrobenzenes and -toluenes were found to exhibit slow increases of conductivity, due to the ionisation of an additive compound with ammonia. For *m*-dinitrobenzene, 2 : 4- and 2 : 6 : dinitrotoluenes the conductivity increases from zero with a velocity which corresponds with a unimolecular charge. For *o*- and *p*-dinitrobenzenes, and for 2 : 5-, 3 : 4-, and 2 : 3-dinitrotoluenes, the small initial conductivity increases linearly with time, at a rate independent of the concentration, the solution becoming yellow. The above changes occur simultaneously with 3 : 5-dinitrotoluene. The first type of change is characteristic of compounds with two nitro groups in the *m*-position to one another, the additive compounds being blue or purple. The second type, which is probably due to the production of a pseudo-acid, is characteristic of compounds with two nitro groups in the *o*- or *p*-position. The maximum conductivity of these compounds is regarded as a measure of the electronegative character of the nitro groups, and, except for 2 : 6-dinitrotoluene, the nitro groups in the *m*- are much more electronegative than those in the *o*- and *p*-derivatives. The methyl group in *m*-position lowers, and in the *o*- and *p*-positions raises, the negative character of the nitro groups. F. G. T.

Displacement of Some Organic Acids from their Sodium Salts as shown by Electrical Conductivity. J. Bureau (*Compt. rend.*, 1925, **181**, 42—44).—On titration of aqueous solutions of sodium salts of monobasic acids, $K \leq 10^{-5}$, with hydrochloric acid, the electrical conductivity being determined after each addition, 1% accuracy is obtained provided the dilution be not greater than *N*/400. Greater accuracy is attained if the salt solution be added to the acid. Using salts of dibasic acids, $K_1=10^{-2}$—10^{-3}, K_2 being much smaller (10^{-5}), the formation of acid salts is indicated with an error varying from 2 to 4%. More exact results are obtained by adding the salt solution to the acid. On titration of salts of dibasic acids for which the *K* values do not differ greatly, the total displacement of the organic acid is indicated with an error of 5—6%, the accuracy being not much improved by adding the salt to the acid. J. S. C.

Electrical Transport in a Ferric Oxide Hydrosol. H. Puiggari (*1st. S. Amer. Congress Chem.*, 1924).—Ferric oxide

hydrosol (p_H 3·8) was prepared by gradually adding ammonia solution (90 g. of 28% ammonia solution in 180 c.c. of water) to 1000 g. of ferric chloride hexahydrate in 2000 c.c. of water, and dialysing for 264 hrs. For 0·003 amp., the *E.M.F.* across the electrodes was about 23 volts at 17°. The amount of spongy, dark-orange coloured coagulum which separated on the platinum cathode was directly proportional to the current, averaging 304×10^{-5} g. per amp. sec. for currents of 0·003—0·01 amp., irregularly and progressively smaller for 0·036—0·065 amp., and invisible for less than 0·0003 amp. The electrical transport is increased by rise of temperature. A new similarity between electrolytic and colloidal solutions is thus exhibited. CHEMICAL ABSTRACTS.

Dissociation of Weak Electrolytes in Water–Alcohol Solutions. L. MICHAELIS and M. MIZUTANI (*Z. physikal. Chem.*, 1925, **116**, 135—159).—The dissociation of the following substances in mixtures of ethyl alcohol and water has been investigated by a potentiometric method: acetic acid, phosphoric acid, lactic acid, salicylic acid, benzoic acid, carbonic acid, aminoacetic acid, *o*-, *m*-, and *p*-aminobenzoic acids, and ammonia. L. F. G.

Physical Significance of Electrolytic Solution Tension. J. HEYROVSKÝ (*Compt. rend.*, 1925, **180**, 1655—1658).—By means of a reversible cycle of operations the following equation is deduced for the reversible electrode potential (π), of a univalent metal in contact with a solution containing its ions; (1) $\pi=RT/F$. log $P_M+I+H/F+RT/F$ log $[M^+]$. Here R, T, and F have their usual significance, P_M is the vapour pressure of the metal at temperature T, H is the free energy of hydration of the ions, and $[M^+]$ the concentration of the ions in the solution, whilst the affinity of electrons for the metallic ions is given by the relation $IF=\log P_M/P_{M+}.P_e$, where P_{M+} is the partial pressure of the ions in the vapour, and P_e the pressure of the electrons in the solid metal. The first three terms in equation (1) thus replace the single term for the Nernst electrolytic solution pressure and give a physical significance to the latter. In the few cases in which the terms in equation (1) are known, the calculated and experimental values of π agree as well as can be expected. W. H.-R.

Method of Studying Electrode Potentials and Polarisation. H. D. HOLLER (*Bureau of Standards Sci. Paper*, No. 504).—A resistance-coupled thermionic valve amplifier is used to operate an oscillograph under conditions which permit of observations of the variations in the potential when no current is taken from the electrode under investigation. The electrode is put in series with the grid battery, variations in the anode current, as recorded by the oscillograph, being proportional to variations in the electrode potential over the range employed. The electrode is used in conjunction with a standard electrode to form a cell through which direct current is passed, and changes in potential whilst opening and closing the circuit are recorded. When the polarisation disappears slowly, the *E.M.F.* of polarisation and the potential difference due to

resistance can be distinguished. By superposing alternating current on the cell, and using a separately excited wattmeter, the true resistance of the electrode can be determined. The results show that the electrode potential as measured by the potentiometer method may be more than 0·2 volt too high because of the potential drop due to resistance. Preliminary results indicate that the so-called transfer resistance between electrode and electrolyte may be due to gas. C. S.

Standard Values in the Calculation of the Hydrogen Exponent from Measurements with the Hydrogen and Quinhydrone Electrodes. I. M. KOLTHOFF (*Chem. Weekblad*, 1925, **22**, 332—339).—Recent work on the calculation of the hydrogen-ion concentration from the potentials of the hydrogen, calomel, and quinhydrone electrodes in various solutions is reviewed and discussed, and formulæ for the calculation of p_H values from measurements made with the hydrogen and quinhydrone electrodes in conjunction with the various forms of calomel electrode are put forward. S. I. L.

Electrometric Behaviour of Aluminium. A. SMITS and H. GERDING (*Z. Elektrochem.*, 1925, **31**, 304—308; cf. *ibid.*, 1924, **30**, 423).—The potentials of aluminium amalgams of varying composition in saturated acetylacetone solution were measured against the normal calomel electrode. An increase in the atomic percentage of mercury from 0 to 0·35% causes a continual increase in the negative potential, the mercury being a positive catalyst for the establishment of internal equilibrium in the aluminium, which is not attained until the latter concentration of mercury is reached. Further increase in the mercury concentration up to 0·78 atomic % causes a straight line decrease in the negative potential; at the latter concentration, separation of a liquid phase occurs, and the potential remains constant up to 99·97 atomic % of mercury. Extrapolation of the straight line curve obtained between 0·35 and 0·78 atomic % of mercury back to the axis gives the true potential of pure aluminium when it is in internal equilibrium, this value being 1·520 volts, which is 0·130 volt more negative than the two-phase system aluminium+mercury. The potential of the latter system in a normal solution of aluminium chloride relative to the normal hydrogen electrode has a value 1·30 volts (Müller and Hölzl, A., 1922, ii, 341) and therefore the potential of pure aluminium in internal equilibrium in a *N* aqueous solution of aluminium chloride must have a minimum value of −1·430 volt relative to the normal hydrogen electrode. A correction is applied to the *E.M.F.* diagrams in the earlier communication (*loc. cit.*), and the results confirm the conclusion that no compound of aluminium and mercury is formed. J. W. B.

Electronegative Potential Series in Liquid Ammonia. F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1925, **47**, 1503—1507).—Kraus (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 175) has shown that the elements may be arranged in two electro-affinity series depending

on whether the element functions as an anion or as a cation. Replacement reactions in liquid ammonia solutions show that in the following series an element will in general replace any previous element when this is present as a homo-atomic anion: lead, bismuth, tin, antimony, arsenic, phosphorus, tellurium, selenium, sulphur, iodine. J. S. C.

Potentials of Metals against Pure Water. A. SMITS, H. GERDING, and (MISS) R. KROON (*Rec. trav. chim.*, 1925, **44**, 638—642).—From theoretical considerations, the expression $E=-0{\cdot}058/\nu F \cdot \log L_M/M_L{}^{\nu}-2{\cdot}784$ is obtained for the potential of a metal in pure water, assuming that the metal exists in equilibrium with a hydrogen phase at 1 atm. pressure. L_M is the solubility product of the metal and $M_L{}^{\nu}$ is the ionic concentration. For silver, this gives $E=-0{\cdot}406$ volt. The potential of a hydrogen film on a metal electrode which is not developing hydrogen is equal to that outside the electrode, and can be calculated from the electron concentration outside the surface layer, or from the hydrogen ion concentration of the liquid. From an ion–electron equation which is derived theoretically, E for the hydrogen potential in pure water is found to be $-0{\cdot}406$ volt. Measurements of the electrode potential of silver and copper in pure water gave equilibrium potentials of $-0{\cdot}411$ and $-0{\cdot}410$, respectively. The potential of silver was found to be influenced by light. A study of the influence of temperature showed that an increase rendered the silver more negative and the copper more positive. L. L. B.

Electrical Charges Arising at a Liquid–Gas Interface. H. W. GILBERT and P. E. SHAW (*Proc. Physical Soc.*, 1925, **37**, 195—214).—The various methods of studying electrification produced when a liquid is in contact with a gas are discussed under nine headings: one or both at rest, cataphoresis of gas bubbles. passage of gas over a liquid, fall of a liquid in an unbroken column through a gas, liquid jets, waterfall electricity, bubbling, shattering of drops in an air stream, and spraying. Explanations are given in terms of the modern theory of orientation and polarisation at the surface, but emphasis is laid on the discrepancies between the results of different observers. A summary is given of established results in regard to the three properties of a gas–liquid interface: potential difference, surface tension, and balloactivity.

E. B. L.

Surface Potential in Solutions of Inorganic Electrolytes. W. WESSEL (*Ann. Physik*, 1925, [iv], **77**, 21—43).—Theoretical. The equilibria of inorganic ions in the surface layers of liquids have been investigated statistically. A formula is deduced showing the connexion between surface potential and concentration. Complete dissociation is assumed and the theory leads to correct values for the magnitude and sign of the surface potential of various acids and salts. Differences in behaviour are traced to differences in ionic volumes. R. A. M.

Contact *E.M.F.* between the Solid and Liquid Phases of the same Metal and between the Outgassed Surfaces of two Dissimilar Metals. P. H. DOWLING (*Physical Rev.*, 1925, [ii], **25**, 812—825).—No definite change in contact *E.M.F.* at the m. p. of tin, Wood's metal, or a tin–lead alloy (25% Pb) could be observed. Any such change, if it exists, is at most of the order of 0·005 volt, and may possibly have been masked by the gas-effect. After removal of gas, the contact potential between copper and nickel reaches a limiting value of 0·25 volt (nickel positive to copper). When tin cools in a glass vessel, audible clicks are observed, accompanied by large electrical effects; this is apparently a tribo-electric phenomenon. A. A. E.

Electromotive Force of Filtration. L. RIETY (*Compt. rend.*, 1925, **180**, 2026—2027; cf. A., 1924, ii, 528).—Solutions of ferrous, ferric, and copper salts were forced through glass tubes, and the potential difference between the entering and issuing solution was measured. For salts of monobasic acids the issuing solution has a negative charge, whilst for salts of di- and tri-basic acids the charge is positive; iron lactate is an exception. The results are due to the dissolving of alkali silicate from the glass with resulting hydrolysis of the iron or copper salts. Mercuric cyanide and chloride resist hydrolysis and with these salts high positive potentials are produced. W. H.-R.

Specific Electro-kinetic Effects between Solid Phases and Dissolved Electrolytes. R. LABES (*Z. physikal. Chem.*, 1925, **116**, 1—64).—The conditions for electro-kinetic phenomena are reviewed and discussed mathematically (cf. Stern, *Z. Elektrochem.*, 1924, **30**, 508). Electro-kinetic phenomena are influenced by the solubility products for the anion components of the solid phase and the cations of the electrolyte on the one hand, and the cation components of the solid phase and the anions of the electrolyte on the other. The smaller the solubility products, the greater is the effect. Endosmotic experiments with barium sulphate, zinc oxalate, and silver chloride, in contact with various solutions, confirmed the above conclusions. L. F. G.

Decomposition Potentials of Solutions of Metallic Bromides in Molten Aluminium Bromide. W. ISBEKOV (*Z. physikal. Chem.*, 1925, **116**, 304—312).—Current–voltage data have been obtained for solutions of zinc, cadmium, silver, mercuric, antimony, and bismuth bromides in molten aluminium bromide. The decomposition potentials of the salts are in the above order, the nobility increasing from left to right. This order is different from that in aqueous solutions (zinc, cadmium, antimony, bismuth, mercuric, silver), but is the same as that of the equivalent heats of formation. Also, any metal in this series will precipitate any subsequent member from the bromide solution. Data were also obtained for sodium and potassium bromides. Their decomposition potentials are the same, and indicate that aluminium is here the primary product of electrolysis. L. F. G.

Potentials of the Alkali Metals Determined by the Measurement of Decomposition Voltages of Molten Alkali Chlorides, Bromides, and Iodides. B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1925, **31**, 287—296).—The authors have determined or redetermined the decomposition voltages of a large number of molten alkali halides at various temperatures by a slightly improved modification of the method previously employed (cf. Neumann and Bergve, A., 1915, ii, 817) and hence calculated the temperature coefficients and the absolute potentials of the alkali metals. Mixtures of the halides of two alkali metals show two points of inflection on the curve corresponding with the decomposition potentials of the two salts and hence small quantities of other alkali metal halides present in the cæsium, rubidium, and lithium salts employed do not affect the accuracy of the values obtained. The temperature coefficients for all halides of a metal (with the possible exception of fluorides) have the same value, as also have all the alkali metal halides with the exception of lithium. The following values are obtained as the mean of a large number of concordant determinations with different halides and with mixtures of halides at different temperatures: absolute potentials, cæsium 2·909, rubidium 2·744, potassium 2·614, sodium 2·454 (cf. Trümpler, A., 1924, ii, 526 gives 2·72), lithium 2·091 volts. The discrepancy between these values compared and those obtained by other investigators working in aqueous solution is due to the untrustworthy absolute potential of the hydroxyl and sulphate ions. Temperature coefficients for sodium halides, $1{\cdot}487\times10^{-3}$, potassium halides $1{\cdot}500\times10^{-3}$, rubidium halides $1{\cdot}50\times10^{-3}$, cæsium halides $1{\cdot}544\times10^{-3}$ (mean $1{\cdot}501\times10^{-3}$), and for lithium halides, $1{\cdot}347\times10^{-3}$. The decomposition voltages for rubidium and cæsium salts, not determined in the earlier work (*loc. cit.*) are: rubidium chloride 2·93 at 783°, bromide 2·67 at 738°, iodide 2·29 at 675°, cæsium chloride 3·28 at 647°, iodide 2·56 at 595° (volts). J. W. B.

Potentials of Metals of the Alkaline Earths and the Rare Earths Determined by Measurement of the Decomposition Potentials of the Molten Chlorides, Bromides, and Iodides. B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1925, **31**, 296—304).—The method previously employed with the halides of the alkali metals (cf. preceding abstract) has been extended to the measurement of the decomposition voltages of the fused halides of the alkaline-earth and rare-earth metals and of aluminium chloride. Measurements were made at various temperatures in each case with a mixture of the pure anhydrous halide with either potassium or sodium chlorides, and the temperature coefficient and the absolute potential of the metal calculated as previously. As with the alkali halides, the temperature coefficient of the group is practically constant with the exception of the first member, *i.e.*, beryllium and aluminium, respectively. The following values were obtained for the decomposition voltage: beryllium chloride 1·47 at 737°, temperature coefficient $0{\cdot}965\times10^{-3}$; magnesium chloride 2·23 at 783°, t. c. $0{\cdot}712\times10^{-3}$; calcium chloride 2·82 at 638°, t.c. $0{\cdot}704\times10^{-3}$;

strontium chloride 2·99 at 633°, t. c. $0·7143\times10^{-3}$; barium chloride 3·06 at 647°, t. c. $0·7143\times10^{-3}$; the absolute potentials for the metals beryllium, magnesium, calcium, strontium, and barium being, $0·811\pm0·003$, $1·422\pm0·001$, $1·903\pm0·002$, $2·075\pm0·002$, $2·154\pm0·005$ volts. Further decomposition voltages are: thorium chloride 1·70 at 765°, t. c. $1·875\times10^{-3}$; cerium chloride 2·10 at 738°, t. c. $1·875\times10^{-3}$; lanthanum chloride 1·65 at 783°, t. c. $1·882\times10^{-3}$; neodymium chloride 1·55 at 800°, t. c. $1·852\times10^{-3}$; praseodymium chloride 1·45 at 737°, t. c. $1·862\times10^{-3}$; aluminium chloride 1·49 at 640°, t. c. $1·132\times10^{-3}$; the absolute potentials for the metals cerium, thorium, lanthanum, neodymium, praseodymium, and aluminium being $2·097\pm0$, $1·747\pm0$, $1·748\pm0·002$, $1·645\pm0$, $1·436\pm0·002$, $0·845\pm0·006$ volts. J. W. B.

Concentration and Polarisation at the Cathode during Electrolysis of Solutions of Copper Salts. W. L. Miller (*J. Franklin Inst.*, 1925, **199**, 773—783).—The overvoltage obtained when a solution of a copper salt is electrolysed between copper electrodes has been determined by subtracting from the total potential difference between the electrodes, measured by means of an oscillograph element, the internal resistance drop through the cell and the concentration voltage. The internal resistance drop, or instantaneous fall in potential difference when the current is stopped, was equal, in the experiments under consideration, to the product of the current into the resistance of the leads, electrodes, and electrolytes, indicating the absence of any "transport resistance" or of a non-conducting film on the electrodes. The concentrations at the electrodes during electrolysis were calculated from the equations developed by Rosebrugh and Miller (A., 1911, ii, 181) on the basis of Weber's diffusion theory. Measurements of the time required to liberate hydrogen from acid solutions of copper salts by constant, interrupted, successive, and sinusoidal currents have all confirmed the validity of these equations. Concentration changes at the anode were found to be trifling compared with those at the cathode, and measurements with auxiliary electrodes showed that the overvoltage was almost exclusively cathodic. An expression for the overvoltage, $A+(B-0·03)\log z_0/z$, where z_0 is the copper concentration in the body of the electrolyte and z that at the cathode, has been deduced. A, the "instantaneous overvoltage," has hitherto been considered as the true overvoltage. It is independent of the copper concentration, but increases with increasing acidity. It falls to zero with the current density and reaches a constant maximum value in 7·5 N-sulphuric acid at 0·7 amp. per sq. dm. A depends on the previous history of the cathode, and not on some reaction in solution such as dehydration of ions. It has less than its normal value for a measurable time after the electrode has been the anode, so that lower values of A are obtained with alternating than with direct or interrupted currents. The rapidity with which the overvoltage falls when the current is interrupted shows that it cannot be studied successfully by the com-

mutator method. *B* is independent of the copper concentration, current density, and sulphuric acid concentration. M. S. B.

Dissolution of Nickel in Sulphuric Acid under the Influence of an Alternating Current. A. P. Rollet (*Compt. rend.*, 1925, **180**, 2047—2049).—An alternating current of 50 periods was passed through two nickel electrodes immersed in sulphuric acid. The solution was stirred and large volumes used to minimise the effects of the products of electrolysis. The hydrogen evolved corresponds exactly with the weight of nickel dissolved. The yield increases with increasing speed of stirring. As the temperature is raised from 0°, the yield rises to a maximum at 30° and then falls, until at 70° it is less than at 0°. With low current densities the yield increases rapidly with the concentration of the sulphuric acid and then becomes constant, but with high current densities concentration has a more gradual effect, and the yield only reaches a constant value in very concentrated solutions. The yield rises with the current density up to a value between 0·7 and 1·5 amp. per sq. cm.; under these conditions hydrogen only is evolved. Above this limiting current density the yield falls rapidly and both oxygen and hydrogen are given off. W. H.-R.

Theory of Reaction Rate. G. N. Lewis and D. F. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 1508—1520).—Theoretical and mathematical. The theory that the rate of a chemical reaction is governed by the concentration of activated molecules, the latter being defined as all those molecules possessing more than a minimum energy, is discussed. The classical Arrhenius equation is exactly true in certain simple cases and is in all cases a very close approximation. Observed reaction velocities can be satisfactorily accounted for both by collision and by radiant energy. An equation representing the number of encounters between molecules and the quanta of light necessary for activation is developed. Whilst there is no serious drawback to the general radiation theory, the simple theory assuming activation by nearly monochromatic light is untenable. A subsequent paper will give reasons for believing that radiation, and not collision, is the important factor in the promotion of chemical processes. J. S. C.

Mechanism of Chemical Reaction. R. C. Tolman (*J. Amer. Chem. Soc.*, 1925, **47**, 1524—1553).—A theoretical and mathematical paper in which the various suggested mechanisms of activation of molecules prior to their participation in chemical processes are discussed. As typical examples of homogeneous reactions proceeding entirely in the gaseous phase the unimolecular decomposition of nitrogen pentoxide (Daniels and Johnston, A., 1921, ii, 249) and the bimolecular reaction, decomposition of nitrous oxide (Hinshelwood and Burk, A., 1924, ii, 751) are considered in an attempt to find out whether the various proposed mechanisms are sufficiently rapid to account for the observed rates of reaction and whether they lead to a velocity expression of the proper order. Activation by collision cannot take place fast enough to account for the unimole-

cular process, but might be a possibility for bimolecular processes if each of the molecules of the reacting species brings an appreciable fraction of the total energy of activation, or if both activation and immediate reaction are a result of the same collision. Activation by collision with a molecule which is itself in an activated state, resulting in a transfer of energy, although of importance in certain types of reactions is not the primary method of activation for reactions of constant order. The simple radiation theory cannot satisfactorily explain unimolecular reactions and leads to incorrect predictions of the active frequency. In the case of bimolecular reactions activation may occur sufficiently rapidly to account for the observed rates provided that each of the reacting molecules brings an appreciable fraction of the energy of activation. Activation by the simultaneous absorption of more than one frequency is not a probable mechanism. An elaborated form of the radiation theory involving the existence of a series of activated states of nearly the same energy content rather than a single activated state, probably provides a satisfactory mechanism for unimolecular and bimolecular reactions and also explains why absorption lines are not found in the positions calculated from the simple theory. The simultaneous absorption and emission of quanta may be a definite step in a chemical process but there is no evidence that such stages are of primary importance in accounting for known rates of reaction. A large number of references to the published work of various authorities are given.

J. S. C.

Gaseous Combustion at High Pressures. V. Explosion of Hydrogen–Air and Carbon Monoxide–Air Mixtures at Varying Initial Pressures up to 175 Atmospheres. W. A. Bone, D. M. Newitt, and D. T. A. Townend (*Proc. Roy. Soc.*, 1925, **A**, **108**, 393—418; cf. A., 1924, ii, 398).—Hydrogen–air mixtures ($2H_2+O_2+4N_2$) and carbon monoxide–oxygen–diluent mixtures ($2CO+O_2+4R$, where R=CO, A, or N_2) were studied at higher initial pressures (75—175 atm.) than those previously employed. The time taken for the attainment of maximum pressure in the explosions diminished as the initial pressure increased, except in the case of the mixture $2CO+O_2+4N_2$, where the reverse occurred; this exceptional behaviour gives further confirmation of the activation of nitrogen on the explosion of carbon monoxide–air mixtures, the activation increasing with initial pressure. The ratio, maximum pressure attained during explosion : initial pressure, increased with the initial pressure; this is possibly due to the increasing opacity of the gaseous medium to the radiation emitted during the explosion. No evidence of "after-burning" was observed with this initial pressure range. Previous views on carbon dioxide dissociation are revised. The degree of carbon dioxide dissociation at the maximum temperature attained was probably 15—25% with $2CO+O_2+4A$ mixtures, and about 5% with $2CO+O_2+4N_2$ mixtures. When carbon monoxide is the diluent, it suppresses such dissociation. Secondary formation of nitric oxide in the carbon monoxide–air explosions was inconsiderable except when excess of air was present;

in this connexion, mixtures containing 25, 50, and 60% of excess air were studied. With excess of air, and 125 atm. initial pressure, amounts of nitrogen peroxide largely in excess of those predicted on thermodynamical grounds were obtained, thus confirming the view that the primary nitrogen activation is more a pressure than a temperature phenomenon. In the explosion of the hydrogen–air mixtures, the amount of water dissociation at the maximum temperatures attained never exceeded about 1%, nor could any nitrogen activation be detected. L. F. G.

Detonation Limits in Explosive Gas Mixtures. R. WENDLANDT (*Z. physikal. Chem.*, 1925, **116**, 227—260).—The conditions obtaining in and near the zone of pseudo detonation (cf. this vol., ii, 135) are investigated. It is assumed that, with progressive dilution of the explosive mixture, chemical reaction finally becomes so slow that it is not consistent with the high velocity of normal detonation, *i.e.*, a volume element would remain for too short a time in the normal wave zone for complete chemical change to take place. With greater dilution the change becomes still more incomplete, the retardation being accentuated by decrease in temperature and pressure in the wave zone. Data previously obtained are examined and shown to conform with this assumption, correlated with the equations of Riemann, Hugoniot, and Jouguet (cf. Becker, *Z. Physik.*, 1922, 8, 321). Reaction velocities at high temperatures can be calculated from experimental data obtained in this region. L. F. G.

Rate of Decomposition of Nitrogen Pentoxide at Low Concentrations. J. K. HUNT and F. DANIELS (*J. Amer. Chem. Soc.*, 1925, **47**, 1602—1609).—The various theories which have been put forward to explain unimolecular reactions are critically discussed. The decomposition of nitrogen pentoxide is shown to be unimolecular. The rate of decomposition has been determined at 35°, 45°, and 55° at pressures ranging from 280 to 0·01 mm. The specific rate of reaction is independent of concentration over the range investigated and is not influenced by nitrogen dioxide or by the presence of a large excess of nitrogen. J. S. C.

Chemical Deposits of a Regular Form. J. M. MULLALY (*Phil. Mag.*, 1925, [vi], **49**, 1222—1225).—Ammonia and hydrogen chloride were allowed to diffuse steadily from opposite ends of a tube of uniform bore. The distribution of ammonium chloride crystals along the tube was measured (by the thickness of the salt deposited along an axis of the tube) by means of a travelling microscope. The results may be represented by the combination of two error curves, with a common origin at the point on the axis where the deposit is thickest. If m_0 is the maximum thickness at $l=0$ and m the thickness at a point l distant from the origin the equations are: $m/m_0=e^{-kl^2}$ and $m/m_0=e^{-k_1 l^3}$, where k and k_1 are constants for a given tube. Within limits k and k_1 are independent of time and of the bore of the tube. R. A. M.

Velocity of the Synthesis of Hydrogen Bromide by Capacity Change. A. BRAMLEY (*Physical Rev.*, 1925, [ii], **25**, 858—864). —The dielectric constant of bromine vapour at 180° is 1·0128, evidently corresponding with the molecular aggregate $(Br_2)_6$. When investigated by the capacity method, the formation of hydrogen bromide from hydrogen and bromine is shown to be practically zero in the dark at 18°; activation by illumination is four times as effective with blue light as with red. At 58° the reaction proceeds in the dark, the thermal predominating over the photochemical effect. A. A. E.

Chemical Activity. P. PETRENKO-KRITSCHENKO, D. and B. TALMUD, W. BUTMY-DE-KATZMAN, and A. GANDELMAN (*Z. physikal. Chem.*, 1925, **116**, 313—318).—The velocities of reaction of halogen derivatives of methane and ethane with various reagents were measured. A periodicity in the reactivities was observed, minima occurring with compounds of the type $C_2H_5X,CH_3{\cdot}CHX_2$, and CX_4, and maxima with compounds of the type $CH_2X{\cdot}CH_2X$, and CHX_3. L. F. G.

Is the Hydrolysis of Esters Derived from Strong Acids Accelerated by Hydrogen Ions? S. C. J. OLIVIER and G. BERGER (*Rec. trav. chim.*, 1925, **44**, 643—651).—A reply to the criticism by Skrabal (this vol., ii, 139) of the views advanced by the authors that the hydrolysis of esters of the above type is not accelerated by hydrogen ions. Small quantities of trichloroacetic acid are not decomposed under the conditions of the experiment. L. L. B.

Reactions of Benzoic Acid at the Boundary of Two Liquid Phases. (MLLE.) A. KLEIN (*Roczniki Chemji*, 1925, **5**, [1—3], 101—109).—The mechanism of the reaction between benzoic acid dissolved in carbon tetrachloride and aqueous sodium hydroxide is shown to be in agreement with the diffusion theory. The velocity of the reaction is greatly accelerated by stirring and by rise in temperature, 10° increasing the velocity by 32%. Benzoic acid in carbon tetrachloride solutions of more than 0·04*N* exists in the form of double molecules. The partition coefficient of benzoic acid between the two solvents used is 0·00126. R. T.

Relation between Rapidity of Stirring and Velocity of Reaction in Heterogeneous Systems. (MLLE.) A. KLEIN (*Roczniki Chemji*, 1925, **5**, [1—3], 138—147; cf. preceding abstract). —For reactions in heterogeneous systems the following equation is shown to hold: $(K-a)/n$=const., where K is the velocity of reaction with stirring, a the velocity without stirring, and n the number of revolutions of the stirrer per minute. The value of K also depends on the shape and exact position of the stirrer, and is not constant for the same apparatus, but only for each experiment. R. T.

Reactions between Liquid Amalgams and Aqueous Solutions. (MLLE.) A. KLEIN (*Roczniki Chemji*, 1925, **5**, [1—3], 110—137).—The velocity of reaction of amalgams of sodium and

zinc with water, acids, alkalis, and salts is investigated. The results obtained are not constant if with sodium amalgam water, alkaline, or sodium chloride solutions are used; for other solutions, the velocity falls with increase in the sodium-ion concentration. With neutral or alkaline solutions a temperature rise of 10° increases the velocity by 46%, whilst the rate of stirring has no effect on the speed of reaction. The latter, for acid solutions, consists of the sum of two components, one of which is the velocity of reaction in neutral solution, the other being at any moment proportional to the concentration of acid, to the rate of stirring, and to the temperature (a 10° rise increasing the coefficient of proportionality by 7%), but not to the concentration of amalgam. In the case of zinc amalgam, the velocity of reaction with hydrochloric acid appears to be proportional to the 4·6th power of the concentration of the latter, and is doubled by a 10° rise in temperature. The presence of zinc ions in the supernatant liquid diminishes the velocity of reaction. R. T.

Thermal Decomposition of Silver Carbonate. M. Centnerszwer and B. Bružs (*J. Physical Chem.*, 1925, **29**, 733—737).—The velocity of decomposition of heated crystalline silver carbonate is normal, diminishing according to the unimolecular equation, but the amorphous carbonate, prepared from silver nitrate and potassium hydrogen carbonate, behaves abnormally. The velocity at first falls rapidly, then remains constant, and finally falls exponentially. This is explained by the formation of an unstable oxycarbonate as an intermediate product; the reaction velocity diminishes with rising temperature between 245° and 260°, and it is concluded that the oxycarbonate is a catalyst, but that above 260° no such intermediate product is formed. A. G.

Thermal Dissociation of Calcium Carbonate, and the Differential Method. II. L. Andrussov (*Z. physikal. Chem.*, 1925, **116**, 81—96; cf. this vol., ii, 538).—The above reaction was investigated by means of a slight modification of the differential method previously described. Reaction velocities were determined and were found to be affected considerably by moisture. The equation for the reaction isochore was constructed, and was in agreement with the Nernst equation. Extrapolated values for the dissociation pressures of calcium carbonate on each side of the experimental range (500—900°) were determined by means of the isochore. The chemical constant of carbon dioxide is $1·035 \pm 0·1$. Advantages of the differential method are discussed. L. F. G.

Nephelometry. Suggested Sensitive Test for the Stability of Explosives. A. F. C. Pollard (*Trans. Opt. Soc.*, 1924—25, **26**, 63—73).—Colloidal solutions of silver oxide, prepared by adding small quantities of 0·001*N*-sodium hydroxide to a great excess of 0·1*N*-silver nitrate solution, are exceedingly sensitive to traces of nitrogen peroxide, the colloidal particles disappearing. Purified air is drawn over finely-divided cordite or guncotton and through the solution contained in one tube of a nephelometer

similar to that described by Kingslake (this vol., ii, 821); the disappearance of the colloidal particles reduces the scattering of the light, the effect being measured by the movement of the standard tube necessary to restore photometric equality. The test is not sufficiently delicate to measure directly the time rate of evolution of nitrous gases, which is a measure of the stability of an explosive, but by carrying out two tests at an interval which need not exceed 10 hrs., the amount of nitrogen peroxide accumulated during the interval may be determined. The test is superior to the Abel test, since the explosive does not require to be heated. S. I. L.

Spark Photography as a Means of Measuring Rate of Explosion. J. E. SMITH (*Physical Rev.*, 1925, [ii], **25**, 870—876).—The explosive is placed in a cartridge having openings at definite intervals, additional charges being placed at the openings. Automatic spark illumination enables photographs to be obtained of the shadows of the sound waves associated with a particular opening. Rates of explosion for various charges of lead styphnate, mercury fulminate, and gunpowder were determined. [Cf. *B.*, 1925, Aug.] A. A. E.

Titanous Chloride and Nitric Acid. M. COBLENS and J. K. BERNSTEIN (*J. Physical Chem.*, 1925, **29**, 750—752; cf. A., 1924, ii, 605).—Like nitric acid, nitrous acid is reduced to nitric oxide by titanous chloride, whilst hyponitrous acid is reduced to nitrous oxide; stannous chloride reduces all three acids to hydroxylamine. The formation of the gaseous oxides is a catalytic effect of titanous chloride and they are reduced to ammonia when shaken with the reagent. A. G.

Catalytic Action. XIV. Comparative Study of the Catalytic Activity of Reduced Copper, Reduced Nickel, and Thoria. II. S. KOMATSU and C. TANAKA.—(See i, 905.)

Catalytic Action. XV. Catalytic Activity of Reduced Copper. II. S. KOMATSU and M. KURATA.—(See i, 942.)

Mechanism of Catalytic Decomposition. F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, **A**, **108**, 355—378).—The theory of the dehydrogenation of alcohols at a copper surface is discussed in the light of previous experimental results (A., 1924, ii, 843; this vol., ii, 311). It is concluded that the mechanism of the change is the loss of neutral hydrogen atoms, and that activation of the alcohol molecule by the copper consists in increasing the distance between the hydrogen atom and the oxygen atom of the hydroxyl group. The quantitative deductions from this point of view are not in agreement with experiment unless it is assumed that only a part of the copper surface is catalytically active, *i.e.*, that "reaction centres" exist.

These centres are treated as being some characteristic grouping of copper atoms, and the variation in the activity of the catalyst with its temperature of preparation is discussed from this point of view.

S. B.

Poisoning of Nickel Catalyst by Thiophen and Action of a Copper Catalyst. B. KUBOTA and K. YOSHIKAWA (*Sci. Papers Inst. Phys. Chem. Res.*, 1925, **3**, 33—50).—The toxic influence of thiophen on the catalytic reduction of benzene to *cyclo*hexane in presence of reduced nickel is investigated. It is considered that unstable nickel hydrides, $H(Ni)_nH$, coexist in the catalyst in proportions depending on the conditions under which the catalyst is prepared. The most active hydride, H'...HNiH...H', alone is capable of hydrogenating an aromatic nucleus and is the only one poisoned by thiophen. A nickel catalyst thus poisoned will still reduce phorone to valerone with yields equal to those obtained with the most active catalyst, because the unpoisoned $H(Ni)_2H$ is present. Copper catalysts will not catalyse the hydrogenation of aromatic nuclei and copper is not poisoned by thiophen, which supports the above theory. In the reaction studied, the thiophen nucleus is reduced and nickel sulphide is formed progressively throughout the catalyst. The percentage of active nickel formed decreases rapidly the higher the temperature at which the oxide is reduced; the temperature of preparation of the latter from the nitrate has little effect.

Valerone semicarbazide melts at 121°, higher than previously recorded. S. K. T.

Action of Promoters in Catalysis. M. C. BOSWELL and C. H. BAYLEY (*J. Physical Chem.*, 1925, **29**, 679—692).—When ferric oxide containing ceric oxide is reduced by hydrogen the volume of hydrogen retained by the oxides, compared with the amount of water removed, is greater than in the absence of ceric oxide, and the addition of potassium hydroxide has a similar effect on platinum. It is therefore concluded that the action of promoters is to increase the concentration of charged hydrogen and hydroxyl in the surface layer (cf. A., 1923, ii, 231; this vol., ii, 215; *Proc. Roy. Soc. Canada*, 1923, **17**, III). The promoter probably (1) enables the surface film to be formed more rapidly on reduction, (2) acts as particles throughout the reduced layer around which dissociated water can accumulate at higher concentrations, and (3) increases the stability of the catalytic film so that it is not lost, at high temperatures, as water. A. G.

Reciprocal Excitation and Inactivation of Catalysts. A. QUARTAROLI (*Gazzetta*, 1925, **55**, 252—264; cf. this vol., ii, 53).—The catalytic effect on the decomposition of hydrogen peroxide produced by copper hydroxide prepared from a copper salt and sodium hydroxide in presence of the peroxide increases enormously as the concentration of the hydrogen peroxide is diminished; under certain conditions, diminution of such concentration sixteenfold results in more rapid liberation of oxygen. Ferric hydroxide, precipitated with the copper hydroxide, greatly increases the catalytic activity of the latter, although alone its effect is negligible; a mixture of these two hydroxides in presence of alkali is far superior to colloidal platinum as a catalyst for the peroxide in very dilute solution. On the other hand, nickel and magnesium hydroxides,

similarly precipitated, weaken the action of copper hydroxide, whilst the effect of aluminium hydroxide may be in either direction according to the concentration of the copper in the solution.

T. H. P.

Positive and Negative Catalysts of the Dehydration of Cupric Hydroxide. A. QUARTAROLI (*Gazzetta*, 1925, **55**, 264—270).—Addition of as little as 1 part of hydrogen peroxide per 2×10^8 parts of solution appreciably increases the velocity with which cupric hydroxide, in presence of a small amount of alkali, changes colour at 50° to green and ultimately to black. The traces of the peroxide present in ordinary distilled water are possibly the cause of such change. Even in amounts very small compared with the quantity of cupric hydroxide itself, various electrolytes, particularly magnesium salts, markedly retard the alteration of the hydroxide. The blackening of copper hydroxide suspended in alkaline solution appears to be, not a simple dehydration, but a complex phenomenon composed of oxidations and reductions, with formation of saline hydrates containing copper atoms of different degrees of oxidation. T. H. P.

Low-temperature Oxidation at Charcoal Surfaces. I. Behaviour of Charcoal in the Absence of Promoters. E. K. RIDEAL and W. M. WRIGHT (*J. Chem. Soc.*, 1925, **127**, 1347—1357).—Oxygen may be adsorbed on a charcoal surface to form at least three types of surface compounds: (i) the autoxidisable fraction formed by the readily detachable atoms not in the regular space lattice; (ii) strong adsorbing surface from which carbon dioxide can be evolved only at high temperatures (non-catalytic surface); (iii) a fraction forming unstable oxygen complexes, which may in time pass over into the more stable form; the oxygen on this is activated. Attempts have been made to measure the areas of these different surfaces on the charcoal. The autoxidisable fraction was measured by determining the amounts of poison (potassium ferricyanide and amyl alcohol) adsorbed per 100 mg. of charcoal to arrest autoxidation; it was found to be 0·38% of the surface. Aqueous solutions of substances containing but one polar group (alcohol, formic, acetic, and the higher fatty acids) do not undergo oxidation at the surface of charcoal; substances containing two adjacent polar groups (one of which may be a mobile hydrogen atom) are readily oxidised. Reaction velocities of acid oxidation were much higher than the autoxidation, and $k_{50°}/k_{40°}$ was 2·0 against 1·8 for the latter. Hence oxidation is proceeding on another portion of the charcoal greater in extent than that undergoing autoxidation. The two reactions are not coupled reactions, and the autoxidisable areas can be poisoned without influencing catalytic oxidation. The velocity of oxidation increases with the concentration of the acid and then falls; the maximum rate corresponds with a higher concentration of acid if the oxygen pressure is increased, the optimum being independent of the temperature. This corresponds with a suitable stoicheiometric proportion of the reactants on the catalytic surface. From

the amount of amyl alcohol adsorbed to prevent oxidation it was concluded that 40·5% of the total area is active. W. T.

Decomposition of Hydrogen Peroxide by Cobaltic Hydroxide. F. G. TRYHORN and G. JESSOP (*J. Chem. Soc.*, 1925, **127**, 1320—1330).—The cobaltic hydroxide was prepared by the addition of ammonia to a mixture of hydrogen peroxide and cobalt chloride solution. Low concentrations gave a stable brown sol; higher concentrations gave unstable sols which soon coagulated. The catalyst activity kA has been calculated by means of the equation for a catalysed unimolecular reaction: $kA=1/(t_2-t_1)\log\{(a-x_1)/(a-x_2)\}$. The activity appears to be subject to a dual change: an irreversible fall, and a simultaneous reversible increase inversely dependent on the hydrogen peroxide concentration. The irreversible fall seems to be due to a change in the nature of the catalytic surface, resulting in an orientation of the molecules in a position of minimum potential energy, which orientation probably corresponds with a minimum activity. This fall is made negligible by previous treatment of the catalyst with excess of hydrogen peroxide or by allowing it to form slowly by the hydrolysis of a cobaltammine salt. The promoter effect of ammonia is attributed to hydroxyl ions. High concentrations of ammonia decrease the activity due to dissolution of the catalyst. The activity of the catalyst is at first proportional to its concentration; at higher concentrations, it increases more rapidly than catalyst concentration. The catalytic activity is an inverse linear function of the concentration of hydrogen peroxide. A mechanism is suggested for the reaction in which the decomposition of the peroxide occurs in a unimolecular film on the catalyst surface, a distortion of the intramolecular force field on adsorption rendering one hydrogen atom of the peroxide molecule removable by the impact of a hydroxyl ion. The peroxide ion thus formed decomposes to give oxygen and hydroxyl ions. An equation derived on this basis agrees with experimental data and is applicable to other cases of catalysis. W. T.

Electrolytic Preparation of Hydrogen Sulphide and Sulphides. P. FISCHER (*Z. Elektrochem.*, 1925, **31**, 285—286).—In order to obtain satisfactory yields of hydrogen sulphide and metallic sulphides by the electrolytic method, the cathode must (i) possess as large a conductivity as possible, (ii) have as large a sulphur content as possible, (iii) be of simple composition. The resistance of homogeneous mixtures of silver, arsenic, and copper sulphides, and copper pyrites, stibnite, and galena, with excess of sulphur were determined, but only in the case of copper sulphide was the mixture a conductor, the greatest specific conductivity being obtained with a 50% mixture of the two components. Using this electrode as the cathode, a pure cadmium anode, sodium sulphate solution as electrolyte, and a current density of 0·05 amp./cm.^{2}, the yield of cadmium sulphide is practically theoretical, both yellow and orange forms being produced. With a current density of 0·005 amp./cm.^{2}, only the yellow form is obtained.

Since the current–potential curve for a 0·1*N* solution of sodium hydroxide using this cathode and a platinised-platinum anode is a straight line showing no decomposition potential, no evolution of hydrogen occurs, but the sulphur passes directly into solution as an ion. J. W. B.

Electrolytic Preparation of Selenides and Iodides. P. Fischer (*Z. Elektrochem.*, 1925, **31**, 286—287).—Metallic selenides and iodides may be prepared electrolytically by methods similar to those employed for the preparation of sulphides (cf. preceding abstract). In the case of selenides the cathode consists either of a rod of selenium round which is wound a platinum wire, or, better, an alloy of zinc (5 parts) and selenium (1 part), since in the latter case no hydrogen is evolved and no disintegration of the cathode occurs, the anode being a zinc or copper plate, the electrolyte a solution of sodium sulphate, and the current density 0·1—0·2 amp./cm.^{2}. With a silver anode, mainly polyselenides were formed. The valency of the selenium in solution varies with the nature of the anode, the nature and concentration of the electrolyte, current density, etc. For the formation of iodides, the cathode may be either a rod of silver iodide or a platinum plate coated with a thick layer of solid iodine, the electrolyte a solution of potassium nitrate, and the anode a platinum or lead plate; with the latter, crystalline lead iodide separates during the hydrolysis. Lead iodide is also formed when a lead plate and an iodine-coated platinum plate dipping into a 5% solution of potassium nitrate are connected by a copper wire. Varying amounts of free iodine also pass into solution. J. W. B.

Electrodeposition of Zinc from Sulphate Solutions. A. L. Marshall (*Trans. Faraday Soc.*, July 1925, advance proof, 7 pp.).—The efficiency of deposition of zinc from pure sulphate solutions increases with rise in temperature more rapidly the lower the zinc and the higher the acid concentration. The potential of a zinc electrode against a 3·51*N*-solution of sulphuric acid increases with the current density rapidly at first, then slowly to a maximum of about −1·36 volt at 20° and −1·25 volt at 41—59°; these values are considerably reduced by the addition of zinc sulphate to the solution and still more so by the presence of even minute amounts of antimony. The current efficiency of zinc deposition is decreased very greatly by the presence of copper, ferrous, or manganese sulphates, especially at the higher temperatures, but antimony has the most marked effect of any impurity, even 1·0 mg. per litre reducing the efficiency by 10%. A. R. P.

Electrolytic Oxidation of Alcohols. II. Electrolytic Chlorination of Ethyl Alcohol. S. Koidzumi (*Mem. Coll. Sci. Kyōto*, 1925, **8**, 155—166).—The electrolytic chlorination of ethyl alcohol in potassium chloride solution is studied. A special electrolytic cell is described, and the effects of temperature, current density, and electrolyte are determined. Using a carbon plate

anode and a copper cathode, both anolyte and catholyte being a solution of potassium chloride, saturated at 70°, at a temperature of 70—80° and a current density of 0·08 amp./cm.^{2}, the main products are chloral hydrate and alcoholate, monochloroacetic acid, ethyl acetate, monochloroacetaldehyde hydrate and alcoholate, and chloroether, the last three products representing intermediate stages in the production of chloral. In the formation of monochloroacetic acid, the alcohol is first oxidised to aldehyde, which is then chlorinated, and the chlorinated aldehyde then undergoes further oxidation to the acid. By limiting the time of passage of the current, corresponding dichlorinated products are isolated. The yield of monochloroacetic acid is increased and that of chloral decreased by interruption of the electrolysis, the best yield (61·2%) of the latter being obtained by addition of the alcohol drop by drop to the potassium chloride electrolyte, the concentration of which is maintained as high as possible, the electrolysis being carried out at 70—80°. In no case was chloroacetal produced. J. W. B.

Life Period of Activated Molecules in Thermal and Photochemical Reactions. N. R. Dhar and B. K. Mukerji (*Z. Elektrochem.*, 1925, **31**, 283—285).—The authors have applied Turner's formula for the calculation of the average life of an activated molecule (A., 1924, ii, 362) to a number of thermal and photochemical reactions in dilute solutions, the concentration of the reacting substances being substituted for the gaseous pressure in the original equation. The value of τ is found to be of the same order (10^{-8}—10^{-9} sec.) in each type of reaction, thus confirming the authors' opinion that there is no fundamental distinction between thermal and photochemical reactions. J. W. B.

Experimental Technique of Photochemistry. II. Determination of Energy Distribution and Total Energy in Radiation from Quartz Mercury Lamps. R. G. Franklin, R. E. W. Maddison, and L. Reeve (*J. Physical Chem.*, 1925, **29**, 713—726; cf. this vol., ii, 234).—Details are given of the apparatus used for the determination of energy distribution. It is shown in detail that, whatever the widths of the telescope and collimator slits, and whatever the nature of the line, whether simple or complex, its relative energy is obtained by dividing the area of its energy distribution diagram by $d\lambda$; the energy distribution diagram is obtained by plotting the galvanometer deflection against the wave-length and $d\lambda$ is the wave-length range embraced by the telescope slit. Total energy is measured by comparison with a Hefner lamp; care must be taken that the mercury lamp is in the position in which it is to be used subsequently, and the field illuminated by the lamp must be explored by the thermopile in order to obtain a correct mean value. Corrections are applied for reflection at the surfaces of lenses etc. and for the infra-red radiation passing through the water-cell. The radiant energy of any wave-length is calculated from the total energy and the energy distribution. A. G.

Change of Mass of Silver Halides on Intense Illumination. P. P. Koch and B. Kreiss (*Z. Physik*, 1925, **32**, 384—396).—Grains of silver halides prepared in a variety of ways were suspended by means of an electrical field between the plates of a condenser and the light from a "pointolite" lamp focussed on them. Silver bromide lost about 25% of its weight, and silver chloride rather less. The loss with silver iodide was doubtful. E. B. L.

Ripening of Photographic Emulsions from the Point of View of Ionic Deformation. H. Schmidt (*Z. wiss. Phot.*, 1925, **23**, 201—216).—"First-ripening" (*i.e.*, during emulsification) and "after-ripening" (*i.e.*, after washing) are considered. The former results in increase of grain size and no increase in sensitiveness, and it determines the lattice-form of the grains. In "after-ripening" there is no apparent change in grain size, but the individual lattice-forms are made more sensitive to light by the elimination of adsorbed bromide ions, which leads to a change in the deforming forces in the silver halide grains. The quantum jumps are then no longer reversible, but become irreversible and form atomic bromine and silver. The adsorption forces vary in magnitude, and are dependent on the structure and size of the grains, and therefore on the "first-ripening." The extent of "after-ripening" is determined by the "first-ripening" and the resulting lattice form. In "after-ripening" the forces holding the adsorbed bromide ions are overcome by the adsorption of the gelatin, which can be assisted by addition of certain salts, *e.g.*, nitrates, by heating, or by dehydrating with alcohol. "After-ripening" is accelerated catalytically by hydroxyl ions, and ripening-agents act by forming hydroxyl ions by hydrolysis or dissociation, or else by reacting chemically with bromine. The bromide ions removed during ripening are taken up by the gelatin, and the degree of "first" and "after-ripening" depends on the gelatin used. Chemical fog is due to excessive displacement of adsorbed bromide, and is identical in nature with the latent image. With emulsions prepared with excess of silver instead of excess of bromide, silver ions are adsorbed to the lattice bromine ions and increase their deformation, thus giving enhanced sensitivity. On "after-ripening" or keeping, these emulsions fog, owing to reduction by the developer of the silver ions removed from the lattice. W. C.

[Photographic] Ripening Process. IV. Lüppo-Cramer (*Z. wiss. Phot.*, 1925, **23**, 227—232; cf. this vol., ii, 574).—The sensitiveness of a Lippmann emulsion is enormously increased by digestion at 60°, and the ripened emulsion can be markedly desensitised by treatment with chromic acid, although the minimum sensitiveness thus attainable is higher than that of the unripened emulsion. With coarser-grained emulsions, the sensitiveness can be reduced to that of the original emulsion. The difference is due to the light absorption of the ripened Lippmann emulsion being much higher than that of the unripened emulsion, whereas with coarser grained emulsions, the absorption is not so different in the

two cases. Conclusions of Weigert and Schöller (A., 1922, ii, 10), that in a silver chloride print-out emulsion not the silver chloride but adsorbed silver is the sensitive material, are criticised. Their experimental results are in accordance with the usual view of chemical sensitisation by silver salts etc. The preparation and properties of "photometer-papers" are considered. The behaviour of emulsions to printing-out is in no way parallel with their ordinary photographic sensitiveness. W. C.

History and Theory of the Latent Image. III. LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 216—226).—Evidence for the mechanical and chemical views of the action of light on the photographic plate is discussed, prominence being given to older observations with iodised silver, and to physical development and "development by light." (Cf. this vol., ii, 575.) W. C.

Effect of Light on the Interaction of Water and Sodium and Potassium Amalgams. S. S. BHATNAGAR, M. PRASAD, and D. M. MUKERJI (*J. Indian Chem. Soc.*, 1925, **1**, 263—272).—The effect of light on the rate of evolution of hydrogen when sodium or potassium amalgam reacts with water is measured. The amalgams react in the dark, but the rate of evolution of the hydrogen is increased by the action of light from a carbon arc (λ=366—525$\mu\mu$). The increase is greater the greater is the percentage of metal in the amalgam up to a certain point, after which the difference decreases with an increase in the concentration of the sodium or potassium. J. W. B.

Effect of Light on the Thermoelectric Power of Selenium. R. M. HOLMES (*Physical Rev.*, 1925, [ii], **25**, 826—834).—Illumination causes a decrease of about 5% in the thermoelectric power of selenium, corresponding with a five-fold increase in conductivity. The effect may be explained by assuming that a decrease in the potential energies of electrons in the interatomic space causes an increase in the mean free path of conducting electrons. A large thermal *E.M.F.* is developed in a circuit formed entirely of selenium homogeneous in every respect except that a region of temperature gradient of one sign is illuminated whilst that of the other sign is in darkness; the illuminated selenium is positive at the cold junction. A. A. E.

Photo-activation of Chlorine. W. TAYLOR (*Phil. Mag.*, 1925, [vi], **49**, 1165—1168).—On the assumption that the photosynthesis of hydrogen chloride measures the activation of chlorine, the reaction velocity has been determined for different spectral ranges. If $h\nu=\delta E=E_m-E_n$, the incident light, if it is active, must furnish δE. If the final state E_m is not quantified, ν will be a threshold frequency. The activating region of the spectrum actually corresponds with that of the general absorption of chlorine itself, *i.e.* the threshold frequency is about 4900 Å., and it would seem as if the vibratory motions are not quantified. The Ribaud fine structure bands do not correspond with the activating region. R. A. M.

Mechanism of Photosynthesis of Hydrogen Chloride in the Visible Spectrum. J. CATHALA (*Compt. rend.*, 1925, **181**, 33—36).—The reaction schemes as proposed by Coehn and others (A., 1923, ii, 206; this vol., ii, 142) are not in agreement with experiment. A more probable mechanism is suggested. Collision is only followed by reaction when the encounters occur within the active zones surrounding the molecules of water vapour. The catalytic activity of water vapour is directly proportional to the intensity of illumination. The following reaction scheme is suggested: (i) $Cl_2+h\nu=2Cl$; (ii) $Cl+Cl_2=Cl_3$; (iii) $Cl+O_2=ClO_2$; (iv) $Cl_3+O_2=ClO_2+Cl_2$; (v) $Cl_3+H_2=2HCl+Cl$. The expression representing the rate of formation of hydrogen chloride from considerations of the kinetics of the above reaction scheme is: $d[HCl]/dt = K' \cdot I^{3/2}[Cl_2]^{3/2} \cdot [H_2]/[O_2][K_1[Cl_2] + K_2I[H_2] + K_3[O_2]]$, where K', K_1, K_2, K_3 are constants and I the intensity of the illumination. The above formula is in excellent agreement with the experimental data of (Mrs.) Chapman (T., 1923, **123**, 3062). The mechanism suggested is further supported by the work of Baly and Barker (T., 1921, **119**, 653). J. S. C.

Action of Light on Dyes Applied to Cotton Fabrics. Summary of the Literature. P. W. CUNLIFFE (*J. Text. Inst.*, 1924, **15**, T, 173—194).—A review under the headings: comparative tests of fading; absolute measurements; sources of light; influence of the atmosphere; influence of the colour of the light; relation between active rays and absorption spectra of the dyes; influence of temperature; influence of added substances and the protection of dyed fabrics from fading; theories of fading action; and the relation between chemical constitution and fading. J. C. W.

Xenon Hydrate. DE FORCRAND (*Compt. rend.*, 1925, **181**, 15—17).—A crystalline hydrate containing 6 or 7 molecules of water is readily formed on introducing xenon and water into the tube of a Cailletet apparatus. The dissociation pressures of the hydrate have been measured over the temperature range 1·4—23·5°, 24° being the critical temperature of decomposition. The heat of formation from liquid water is 18·266 cal. The stabilities of the hydrates of the inert gases increase with increasing molecular weight of the gas, the dissociation pressures expressed in atms. at 0° for the respective hydrates being: xenon 1·15, krypton 14·5, argon 98·5. Neon hydrate is not obtained even under pressures as high as 260 atm. at 0°. Hydrate formation is the only chemical process in which the inert gases participate. J. S. C.

Artificial Magnesium Silicate. A. DAMIENS (*Compt. rend.*, 1925, **180**, 1843—1845).—The magnesium silicate obtained by the reaction of magnesium sulphate and alkali silicates is always contaminated with alkali; this occurs to the extent of 1% even when excess of magnesium salt is employed. The product is partly colloidal and is especially so when the silicate solution is in excess. When the silicate used is $Na_2Si_2O_5$, the larger particles of precipitate

correspond with the formula $(Na_2Mg)Si_2O_5$, and the smaller colloidal particles after prolonged fractionation vary from 1·48 $(Na_2Mg)O,2SiO_2$ to $(Na_2Mg)Si_2O_5$ or $(Na_2Mg)SiO_3$. The last formula (mixed metasilicate) corresponds with the maximum percentage of sodium obtained in the experiments. At the moment of precipitation the larger particles of magnesium silicate absorb sodium silicate to form the salt $(Na_2Mg)Si_2O_5$, whereas the smaller, negatively charged particles adsorb sodium ions. The limiting composition $(Na_2Mg)SiO_3$ is reached by the finest particles. If instead of $Na_2Si_2O_5$ the salt $Na_2Si_3O_7$ is substituted, the larger particles correspond with $(Na_2Mg)Si_3O_7$ and if Na_2SiO_3 is used the large grains consist of $(Na_2Mg)SiO_3$. The potassium silicates behave similarly. R. A. M.

Thermal Behaviour of Hydrated Barium Aluminate. G. Malquori (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 445—448).—Barium aluminate pentahydrate, $BaAl_2O_4,5H_2O$, prepared by boiling precipitated alumina with saturated barium hydroxide solution in absence of carbon dioxide, loses 3 mols. of water at 190°, becomes anhydrous at 310°, and exhibits two arrests in the heating curve, at 725° and 1040°, respectively, corresponding with two stages in the decomposition of the compound. T. H. P.

Mercury–Ammonia Compounds. P. Ray and P. C. Bandopadhyay (*J. Indian Chem. Soc.*, 1925, **1**, 235—246).—By the action of ammonia and ammonium carbonate on mercuric chloro-iodide and of potassium thiocyanate, chromate, and arsenate on infusible white precipitate, several new mercury–ammonia compounds and derivatives of Millon's base are prepared. The addition of a solution of mercuric chloro-iodide (obtained by saturating a solution of mercuric chloride with mercuric iodide) dropwise to a concentrated ammonia solution yields the *compound*

$$6NHg_2Cl,NHg_2I,2H_2O,$$

orange-yellow, whilst by the addition of dilute ammonia to an excess of the mercuric chloro-iodide solution the *compound* $4NH_2HgCl,NHg_2Cl,2HgCl_2$, white, is formed. Addition of an excess of ammonium carbonate solution to mercuric chloro-iodide solution yields the *compound* $NHg_2Cl,2HgCl_2,NH_3$; whilst the reverse procedure yields the *compound* $NH_2HgCl,HgCl_2,2NH_3$. Addition of the corresponding mercuric bromo-iodide to ammonia yields mixtures of variable compositions, the reverse process yielding dimercurammonium bromide, which is also obtained by the action of ammonium carbonate. The action of potassium salts on infusible white precipitate (cf. Balestra, A., 1893, ii, 278) proceeds through the formation of a stable intermediate compound to form derivatives of Millon's base, potassium thiocyanate yielding the *compound* NHg_2SCN; potassium chromate yields

$$(NH_2Hg_2O)_2CrO_4$$

(cf. Hensgen, A., 1887, 218); potassium bromide and iodide yield the dimercurammonium bromide and iodide, respectively. Potassium arsenite reduces an infusible white precipitate, but the *compound* $(NH_2Hg_2O)_3AsO_4,3H_2O$, which may be regarded as the

arsenate of Millon's base, is obtained when freshly-prepared mercuric arsenate is digested with ammonia. Nitrogen trioxide passed into a cold aqueous suspension of infusible white precipitate forms a double salt of mercuric chloride and ammonium nitrite which could not be isolated in the pure state. Zinc and cadmium ammonium chlorides react with infusible white precipitate to produce fusible white precipitate. J. W. B.

Chemical Compounds of Salts in the Electric Arc. T. PECZALSKI and G. MOKRZYCKI (*Compt. rend.*, 1925, **180**, 1829—1831).—Two carbon poles are maintained at a fixed distance apart and connected to a constant voltage supply. One pole tapers to a point and in the crater of the other mixtures of definite composition are placed. The fall of potential across the arc is measured. Using known mixtures of lime and alumina, the observed voltage is plotted against the percentage of either constituent. On the same graph, the m. p. curve of mixtures is plotted. On both curves two minima are observed corresponding with the compounds Al_2O_3,CaO and $3Al_2O_3$,5CaO. Further results indicate the existence of a compound 3KCl,NaCl which would only be formed at the temperature of the arc. The higher is the m. p. or b. p. of the salt in the crater, the less is the energy needed to maintain the arc. Thus, as in thermal analysis, whenever maxima or minima occur in the potential–composition curves, these correspond with mixtures of which the m. p. or b. p. are sharply different from those of neighbouring mixtures, *i.e.*, the discontinuities may correspond with definite compounds. R. A. M.

Hydrolysis of Mica. P. A. ZEMIATTSCHENSKI (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1925, **2**, 484—485).—When heated with water, muscovite undergoes energetic hydrolysis and gradually approaches kaolinite in composition. The extent to which this change takes place depends on the duration of the action and on the fineness of the mica; the change may be accelerated and rendered complete by raising the temperature. Muscovite is decomposed more readily than kaolinite when treated with 10% hydrochloric acid solution. Slight hydrolytic decomposition of muscovite doubtless plays a large part in the process of the decay of mica. T. H. P.

Stannic Iodide Complexes. V. AUGER and T. KARANTASSIS (*Compt. rend.*, 1925, **180**, 1845—1847).—Stannic iodide is gradually hydrolysed in dilute hydriodic acid solution and more readily in aqueous solution. Addition of sodium, potassium or ammonium odide to these solutions does not modify their properties, but addition of rubidium or cæsium iodides or of the hydriodides of strong bases leads to the formation of stable complex salts, of which the following (X_2SnI_6) are described: *rubidium stannic iodide*, *cæsium stannic iodide*, *tetramethylarsonium stannic iodide*. Mixed crystals of the composition $K_2[SnBr_{5\cdot75}I_{0\cdot25}]$ and $NH_4[SnBr_{5\cdot35}I_{0\cdot65}]$, respectively, are obtained on adding potassium or ammonium iodide to concentrated solutions of stannic bromide. L. F. H.

So-called Lead Suboxide. A. E. VAN ARKEL (*Rec. trav. chim.*, 1925, **44**, 652—654).—An examination of the *X*-ray spectrum of lead suboxide, obtained by carefully heating lead oxalate, shows this to be a mixture of tetragonal lead oxide and the metal. The dimensions of the unit cell of the tetragonal lead oxide existing in this mixture are: length of base, 3·87 Å., and height, 5·02 Å. L. L. B.

Imino Group. E. OLIVERI-MANDALÀ (*Gazzetta*, 1925, **55**, 271—279).—Consideration of Schmidt's results (A., 1924, i, 721) in the light of the work of the author since 1913 shows that, in Schmidt's reactions, not addition of the imino radical resulting from the decomposition of the azoimide by the action of the sulphuric acid, but rather a preliminary addition of the azoimide to the carbonyl group of the aldehyde or ketone, with initial formation of the corresponding azides, must be assumed. These azides are then readily able to undergo further changes to yield the compounds obtained by Schmidt. That such addition of azoimide can occur may be proved by the fact that anhydrous solutions of azoimide in a ketone or an aldehyde often form crystalline deposits, presumably of the additive compounds. T. H. P.

Complex Salts of Antimony Trichloride. S. MIYAKE (*Mem. Coll. Eng. Kyushu*, 1925, **3**, 187—193).—Equilibria in the system, potassium chloride : antimony trichloride : 10·55% aqueous hydrochloric acid solution, have been determined at 25°. The solubilities of potassium chloride in water and 10·55% hydrochloric acid solution are 26·27% and 12·75%, respectively, and of antimony trichloride 90·90% and 90·07%. Two complex salts, $2KCl,SbCl_3$ and $7KCl,3SbCl_3$, have been shown to exist, but no mixed crystals such as found by Jordis (A., 1903, ii, 603). M. S. B.

Selenic Acid and the Selenates. V. LENHER and E. J. WECHTER (*J. Amer. Chem. Soc.*, 1925, **47**, 1522—1523).—The selenites of potassium, sodium, lithium, rubidium, cæsium, barium, and strontium are converted into selenates on roasting in the air. Selenates are also formed when the corresponding carbonates are roasted with selenium dioxide or selenium. Solutions of selenic acid may be obtained by treatment of aqueous suspensions of barium selenate or solutions of potassium selenate with sulphuric or perchloric acids, respectively. Selenic acid of a high degree of purity is obtained by the latter method. J. S. C.

Cobalti-ammine Chromates and Chromato-cobalti-ammines. P. RAY and P. V. SARKAR (*J. Indian Chem. Soc.*, 1925, **1**, 289—296; cf. Briggs, T., 1919, **115**, 67).—The action of chromic acid on carbonato-tetrammine- and carbonato-pentammine-cobaltic salts is investigated. The following new co-ordination compounds are prepared and evidence for their constitution is given: *chromato-tetramminecobaltic dichromate monohydrate*,

$$[(NH_3)_4CoCrO_4]_2Cr_2O_7,H_2O$$

(anhydrous compound obtained by drying over sulphuric acid), by the action of the carbonato-tetramminecobaltic nitrate on chromic acid: *dichromato-tetramminecobaltic dichromate*,

$$[(NH_3)_4CoCr_2O_7]_2Cr_2O_7,H_2O,$$

is obtained when a larger proportion of chromic acid is employed; *dichromato-pentamminecobaltic chromate*,

$$2[(NH_3)_5CoCr_2O_7]_2CrO_4,3H_2O,$$

and *aquopentamminecobaltic dichromate*,

$$[(NH_3)_5CoH_2O]_2(Cr_2O_7)_3,2H_2O,$$

are obtained under corresponding conditions from the carbonato-pentammine salt. By the action of ammonium dichromate and ammonia on freshly-precipitated cobalt hydroxide *chromato-pentamminecobaltic chromate*, $[(NH_3)_5CoCrO_4]_2CrO_4,2H_2O$, is obtained which on recrystallisation from dilute acetic acid yields the *aquopentamminechromate dichromate*, $[(NH_3)_5CoH_2O]_2CrO_4(Cr_2O_7)_2,H_2O$.

J. W. B.

Reaction Products of Ruthenium Tetroxide and Hydrochloric Acid. S. AOYAMA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 1—24).—Ruthenium tetroxide reacts with dry hydrogen chloride to form very hygroscopic, reddish-brown needles of *tetrachlorodioxyruthenic acid*, $H_2RuO_2Cl_4,3H_2O$. This compound is very soluble in water and alcohol; the dilute aqueous solution rapidly hydrolyses giving a black colloidal precipitate. With ammonium chloride a black, crystalline precipitate of a mixture of ammonium hexachlororuthenate and pentachlororuthenite is formed and the mother-liquor contains ruthenium tetroxide. When heated with an excess of ammonia the solution deposits violet crystals of a new *ruthenium ammine*, $Ru(NH_3)_3(H_2O)_2Cl_2$. Concentrated hydrochloric acid and chlorine convert tetrachlorodioxyruthenic acid into hexachlororuthenic acid which yields a brown, crystalline ammonium salt, $(NH_4)_2RuCl_6,0{\cdot}5H_2O$, readily soluble in water, but insoluble in concentrated hydrochloric acid. *Ammonium hexachlororuthenate* solutions slowly give a violet-black precipitate with hydrogen sulphide, precipitation of the ruthenium being complete in 24 hrs.; no blue intermediate compound is formed in this reaction. *Potassium hexachlororuthenate*, K_2RuCl_6, obtained in a similar way to the ammonium salt, crystallises in dark brown octahedra, readily soluble in water, giving a yellow solution which yields a black precipitate of ruthenium tetrahydroxide when boiled with sodium hydroxide. When potassium hexachlororuthenate is heated at 540° in a current of hydrogen chloride, a new *potassium pentachlororuthenite* (K_2RuCl_5) is obtained which differs in many properties from those described by Howe (A., 1904, ii, 490) and earlier workers. Its aqueous solution is much paler in colour and more stable than those of the other two forms, and gives a deep blue colour with sodium hydroxide which changes, on keeping, to a greenish-yellow, and finally a black precipitate is deposited. With hydrogen sulphide, the solution slowly becomes bright green, then azure-blue, and finally colourless. When tetrachlorodioxyruthenic acid is heated at 400° in a stream of oxygen,

ruthenium dioxide is obtained as a lustrous, black mass resembling graphite. A. R. P.

Preparation of Conductivity Water. I. BENCOWITZ and H. T. HOTCHKISS, jun. (*J. Physical Chem.*, 1925, **29**, 705—712).—A still has been designed which supplies, practically continuously, water of a conductivity of $0{\cdot}06$—$0{\cdot}07\times10^{-6}$ ohm^{-1}. Twenty litres of tap water are digested near the b. p. with alkaline permanganate and distilled into a second boiler where carbon dioxide is removed by passing a current of purified air through the hot water. This water is in turn distilled and the vapour enters a preliminary air condenser and steam trap, where about 20% is collected; 80% of the steam passing this is condensed in a warm water condenser and constitutes the conductivity water. The still is constructed of copper and block tin and is completely water-sealed against influx of laboratory air. A. G.

Preparation of Selenic Acid and of certain Selenates. V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, **47**, 1521—1522).—The halogen acids formed in the preparation of selenic acid by oxidation of selenious acid by chlorine or bromine are best removed by addition of silver carbonate in quantity slightly in excess of that necessary to precipitate the halogen. The small amount of soluble silver selenate is decomposed by hydrogen sulphide. The acid solution can be concentrated on the water-bath to about 80% and to higher concentrations under diminished pressure. From the mixed acid solution obtained by chlorination of selenious acid, selenates may be prepared by neutralisation with metallic carbonates. The sparingly soluble selenates of lead, barium, strontium, and calcium are obtained as precipitates. In the case of soluble selenates, metallic chlorides are removed by treatment with alcohol or acetone, the residue being redissolved in water and reprecipitated by either of these solvents. J. S. C.

Molybdenum Pentoxide. W. WARDLAW and F. H. NICHOLLS (*J. Chem. Soc.*, 1925, **127**, 1487).—Molybdenum pentoxide can be prepared by heating the oxysulphate (A., 1924, ii, 766) or the oxyoxalate (J., 1925, **127**, 1311) of tervalent molybdenum in a current of nitrogen: $Mo_2O(SO_4)_2=Mo_2O_5+2SO_2$; $Mo_2O(C_2O_4)_2=Mo_2O_5+4CO$. W. T.

Hydrogen Electrode. F. VLÈS and C. VELLINGER (*Bull. Soc. chim.*, 1925, [iv], **37**, 771—772).—The apparatus, which is designed for p_H measurements, consists of two vessels connected by a three-way cock with a lateral discharge tube. The liquid under test (about 3 c.c.) is placed in the upper vessel, which is slightly conical in form and carries a thermometer, in addition to the platinum spiral forming the hydrogen electrode. The level of the liquid is adjusted by opening the cock to the discharge tube so that the platinum spiral is immersed about 2—3 mm. below the surface of the liquid, whilst on the four or five spirals remaining above the liquid a current of hydrogen impinges from a side tube, the gas escaping by a second side tube in the upper part of the vessel. The

lower vessel serves as the calomel electrode and is connected by a side tube with a reservoir containing saturated potassium chloride solution, a second side tube admitting the wire contact with the mercury. R. B.

Apparatus to Measure the Coefficient of Deviation from Boyle's Law. Determination for Acetylene. J. T. HOWARTH and F. P. BURT (*Trans. Faraday Soc.*, 1925, **20**, 544—549).—Improvements in the design of the apparatus used by Whytlaw-Gray and Burt (T., 1909, **95**, 1659) for measuring the compressibility of gases are described. The compressibility at 0° of acetylene after very careful purification has been measured for pressures from 105·42 mm. to 757·34 mm. of mercury. The relation between pv and p over the experimental pressure range is linear and the coefficient of deviation from Boyle's law $(d(pv)/dp \,.\, 1/p_0v_0)$ between 0 and 1 atm. is −0·00884. Experiments indicate that the variation of the sorption of acetylene on the glass walls is negligible. F. G. S.

Spiral Springs of Quartz. H. G. SMITH (*Nature*, 1925, **116**, 14—15).—A description of the method of making spiral springs of silica for use in the measurement of sorption. A. A. E.

Substitute for a Liquid Air Trap for Mercury Vapour in Vacuum Systems. A. L. HUGHES and F. E. POINDEXTER (*Nature*, 1925, **115**, 979).—About 1 g. of sodium or potassium is placed in a trap between the diffusion pump and the apparatus to be exhausted and, after evacuation, is distilled on to the walls. The method is as efficient as that employing liquid air, the lowest pressure obtained, 5×10^{-9} mm., being probably due to insufficient heat treatment of the ionisation gauge and connecting tubes. A. A. E.

Simple Circulation Pump for Gases. A. W. C. MENZIES, E. M. COLLINS, and P. L. TYSON (*Science*, 1925, **61**, 288).—Mercury droplets are carried to an upper reservoir by means of an air blast; in the fall-tube (2·5 mm. bore), the droplets paddle the gas round a closed system the walls of which are of glass and mercury only. The apparatus requires about 7 c.c. of mercury, and will operate against back pressures corresponding with a head of 30 cm. of water at a rate of 2 litres per hr.; if the back pressure or resistance is negligible, 8 litres per hr. may be circulated. A. A. E.

Hydrogen Liquefying Cycle and Cryostat for the Maintenance of Low Temperatures. W. M. LATIMER, R. M. BUFFINGTON, and H. D. HOENSHEL (*J. Amer. Chem. Soc.*, 1925, **47**, 1571—1576).—A combined hydrogen liquefier and cryostat, suitable for use in the determination of physical constants at very low temperatures, is described. Electrolytic hydrogen may be freed from oxygen by passing first over concentrated sulphuric acid to remove alkali spray and then through a tube containing a nickel catalyst. A convenient catalyst is obtained by soaking small pieces of porous brick in nickel nitrate, heating to convert into oxide and later reducing to nickel in the catalyst tube. By this means the oxygen content may be reduced to 0·01%. Small amounts of oxygen may be determined by bubbling a known volume of gas through an

alkaline solution of pyrocatechol and ferrous sulphate, the resulting red tint being compared with those obtained from known oxygen–hydrogen mixtures. Permanent standards for comparison may be prepared from known concentrations of ferric salt. J. S. C.

Ionisation and Catalysis Experiments suitable for Lecture Demonstrations. I. M. KOLTHOFF (*Chem. Weekblad*, 1925, **22**, 356—357).—The substance most suitable to illustrate association of ions of a salt in solution, and consequent precipitation, on addition of another solution containing either the cation or the anion, is silver salicylate. A 0·01*N*-solution of mercuric chloride in 0·1*N*-mercuric nitrate gives no precipitate with silver nitrate unless a large excess of the latter is added. Many well-known experiments suitable for illustration of catalytic reactions are mentioned. S. I. L.

Mineralogical Chemistry.

Chemical Classification of the Mica Group. I. Acid Micas. A. F. HALLIMOND (*Min. Mag.*, 1925, **20**, 305—318).—Analyses selected from the literature are calculated to molecular proportions with $(Si,Ti)O_2=600$. In the soda and potash micas K_2O+Na_2O is then near 100. The molecular proportions of R_2O_3 plotted against RO give points along a line from

$$K_2O,3Al_2O_3,6SiO_2,2H_2O$$

(muscovite) to $K_2O,2Al_2O_3,RO,6SiO_2,2H_2O$ (phengite), showing a replacement of R_2O_3 by RO, as previously suggested for glauconite (A., 1922, ii, 861). In the lithia micas $SiO_2=600$, $K_2O=100$, $Li_2O=100$, and R_2O_3 plotted against RO gives two series: $K_2O,Li_2O,2Al_2O_3,6SiO_2,2H_2O$ (lepidolite) to

$$K_2O,Li_2O,Al_2O_3,RO,6SiO_2,2H_2O$$

(cryophyllite), and lepidolite to $K_2O,Li_2O,2Al_2O_3,3RO,6SiO_2,2H_2O$ (protolithionite). Abbreviated graphical formulæ are given for these. L. J. S.

Tourmalinisation in the Dartmoor Granite. A. BRAMMALL and H. F. HARWOOD (*Min. Mag.*, 1925, **20**, 319—330).—The various modes of occurrence of tourmaline in the Dartmoor granite mass are described (A., 1923, ii, 777). Little of it seems to be a primary constituent of the rock, and it has been largely developed at the expense of the felspar and biotite by pneumatolytic processes connected with the later more acid types of intrusion. Dark nodules consisting of an intimate intergrowth of tourmaline and quartz represent basic clots in the magma. L. J. S.

Potash-oligoclase from Mt. Erebus, Antarctic, and Anorthoclase from Mt. Kenya, East Africa. E. D. MOUNTAIN (*Min. Mag.*, 1925, **20**, 331—345).—Loose crystals of felspar, previously referred to anorthoclase, from the crater of Mt. Erebus, are of two types with respect to their crystal habit. They have *d* 2·620, refractive indices α 1·536, β 1·539, γ 1·541, and gave analyses

I and II, corresponding with $Or_{18}Ab_{64}An_{18}$ and $Or_{19}Ab_{64}An_{17}$, respectively. The felspar crystals from Mt. Kenya also occur in tuffs in the crater; these have d 2·602, refractive indices α 1·526, β 1·530, γ 1·532, and gave analysis III, corresponding with $Or_{27}Ab_{63}An_{10}$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.
I.	62·79	22·12	0·36	0·41	3·76	—
II.	62·49	21·86	0·30	1·31	3·74	0·16
III.	64·33	20·94	0·20	0·58	2·01	—

	Na_2O.	K_2O.	$H_2O + 110°$.	$H_2O - 110°$.	Total.
I.	7·35	2·98	0·19	0·07	100·03
II.	7·20	3·26	0·04	—	100·36
III.	7·22	4·71	0·27	0·10	100·36

These and certain other felspar analyses taken from the literature when plotted on a triangular diagram with Or,Ab,An at the three corners fall along a line between $Ab_{65}Or_{35}$ and $Ab_{65}An_{35}$. The physical constants (cleavage-angle, extinction-angles, refractive index, optic axial angle, and density) are plotted against the composition for these felspars. Those towards the $Ab_{65}An_{35}$ end are called potash-oligoclase, whilst those towards the $Ab_{65}Or_{35}$ end are called anorthoclase. The nomenclature of the felspars as representing a three-component system is discussed, and the bearing of this on petrographical nomenclature is pointed out. L. J. S.

Chalk and Flint. G. Linck and W. Becker (*Chemie der Erde*, 1925, 2, 1—14).—An outline is given of the various views on the formation of flint in chalk. Experiments were made with solutions of colloidal silica (containing 0·5—0·8% SiO_2) in the presence of precipitated calcium carbonate (vaterite and calcite). The amount of silica adsorbed is greater with smaller sizes of grain of the calcium carbonate. Precipitates obtained from solutions of calcium hydrogen carbonate in the presence of soluble silica contain up to 17% SiO_2, the amount depending on the concentration of the solutions. Treatment of these precipitates, after heating at 50—200°, with dilute solutions of sodium chloride, sodium hydroxide, ammonia, etc., causes a portion of the adsorbed silica to pass into solution again. It can be again coagulated by the action of magnesium carbonate or of calcium carbonate solution in the presence of sodium chloride. The conclusion is therefore reached that in the formation of chalk the silica was originally distributed throughout the material, as a pellicle around the minute grains of calcium carbonate. The re-dissolution of the silica in the presence of alkali and ammonia from organic remains would leave the calcium carbonate with a loose open texture. Migration and coagulation in cavities and crevices would give rise to nodules, bands, and veins of flint. Analyses of chalk from Rügen show 0·81—1·54% SiO_2, the amount varying with the distance from the bands of flint.

L. J. S.

Chemical Alteration of Granite beneath Peat. E. Blanck and A. Riesser (*Chemie der Erde*, 1925, 2, 15—48).—A detailed review and discussion is given of the literature on the formation of

clay or kaolin by weathering processes, more particularly in association with peat and lignite deposits. Analyses are compared of fresh granite, from the Harz Mts., and of the weathered rock taken from below a layer of peat and from the surface. There is no evidence of the formation of kaolin under these conditions. Sulphuric anhydride was found in the weathered products, in peat, sphagnum-moss, and moor-waters; and it is concluded that this has some action in the weathering processes. L. J. S.

Weathering of Sandstone by Circulating Solutions. F. KLANDER (*Chemie der Erde*, 1925, **2**, 49—82).—The peculiar forms of weathering shown by the sandstones of Saxon Switzerland and the Palatinate are attributed to the action of circulating solutions containing humus compounds and sulphates derived from the surface vegetation. Analyses are given of the portions extracted by water from the rocks and from the soils derived from them. L. J. S.

Chemical Constitution of the Gehlenite–Melilite Group. B. GOSSNER (*Chemie der Erde*, 1925, **2**, 103—113).—The isomorphous mixing of such complex molecules as suggested by Buddington (A., 1922, ii, 155) is regarded as improbable; and the author traces a connection between the minerals of the gehlenite-melilite group and the monoclinic ("pseudo-tetragonal") pyroxenes. They are regarded as double compounds CaO+pyroxene, of the form $CaO,[SiO_3Ca,SiO_3Mg]$, where SiO_3Mg is replaceable by Al_2O_3, and Si_2O_6MgCa by Si_2O_6AlNa. Gehlenite is written $CaO,[SiO_3Ca,Al_2O_3]$ and melilite as $2CaO,[Si_2O_6MgCa,Si_2O_6AlNa]$. Åkermanite approaches $CaO,[SiO_3Ca,SiO_3Mg]$. L. J. S.

Relations between Hydrocarbons and Carbonates in Silex and Phtanites. J. DE LAPPARENT (*Compt. rend.*, 1925, **180**, 1858—1859).—In certain siliceous carbonates, the carbonate appears to have been destroyed, leaving a liquid inclusion probably of hydrocarbons. Small rhombohedra of carbonates are often found. The liquid inclusion has a polyhedric contour made up of faces of crystals. R. A. M.

White Chlorite from Madagascar. J. ORCEL (*Compt. rend.*, 1925, **180**, 1672—1674).—A description of a white chlorite found in the form of very large crystals in Madagascar. The composition corresponds approximately with the empirical formula

$$7SiO_2,3Al_2O_3,12MgO,10H_2O.$$

The crystals are very good electrical insulators, d 2·735, n_{D_α}=1·5904; n_{Dm}=1·5754 (calc.); n_{D_β}=1·5749. W. H.-R.

Analytical Chemistry.

New Type of Nephelometer. R. KINGSLAKE (*Trans. Opt. Soc.*, 1924—25, **26**, 53—62).—Concentrated light from a small source is reflected upwards into two vertical glass tubes, one long

one containing a standard and the other, a short one, the solution to be examined. The incident light passes vertically upwards, the scattered light being observed from the front; a Nutting prism is employed to bring the two fields into optical contact. The long tube containing the standard is moved vertically up or down until the fields balance. As standards, known equivalent amounts of silver nitrate and sodium chloride in pure water, boiled and filtered sterilised soap solutions, and silica gels are suggested.

S. I. L.

New Method of Quantitative Analysis by Means of *X*-Rays. E. DELAUNEY (*Compt. rend.*, 1925, **180**, 1658—1661).—If a monochromatic beam of *X*-rays is passed through an aqueous solution contained in a cell of standard size, the absorption may be represented by a relation of the type $I=I_0e^{-(a_1m_1+a_2m_2+\cdots)}$, where I and I_0 refer to the solution and to pure water, respectively, m_1,m_2 . . . are the weights of the different elements dissolved in unit volume of the solution, and a_1,a_2 . . . are characteristic constants for the elements concerned for the particular wave-length used. Hence if a_1,a_2 . . . are previously determined for various wave-lengths, measurements of *X*-ray absorption will enable the concentrations of the different elements in a solution to be determined. In general, if n elements are present, n different wave-lengths must be used so as to make the number of equations equal to the number of unknown quantities, but in practice the relatively small absorption of some elements enables these to be neglected and may simplify the problem, whilst in cases of single salts the molecular absorption may be substituted for that of the different elements. When tested with solution of barium and strontium chlorides, and of alkali halides, the relative error found varied from 10% to <1%.

W. H.-R.

Modified Electrometric Method for the Determination of Hydrogen-ion Concentration. S. GLASSTONE (*Analyst*, 1925, **50**, 327—330).—A small platinised platinum cathode placed in the solution of which the hydrogen-ion concentration is required was found to have the same potential as that of an ordinary hydrogen electrode in the same solution, if a small polarising current is applied until the evolution of bubbles just commences. The hydrogen-ion concentration may then be determined from the equation

$$e=RT/F \log_e[H^{\cdot}],$$

that is, $e=0{\cdot}058 \log_{10}[H^{\cdot}]$ at 18°. By this method the apparatus necessary for the supply of pure hydrogen is eliminated and equilibrium may be rapidly attained, and with alkaline solutions the superiority of the method is very marked. It is necessary that the p_H value of the solution should be less than 3 or more than 11 unless the solutions are well buffered.

D. G. H.

Application of the Quinhydrone Electrode to the Measurement of p_H Values in Solutions Containing Copper Ions and Other Bivalent Ions. J. B. O'SULLIVAN (*Trans. Faraday Soc.*, July 1925, advance proof, 3 pp.).—The quinhydrone electrode may

be used for determining the p_H of many solutions of metallic salts where the hydrogen electrode on account of its greater reducing power is inapplicable, *e.g.*, in solutions of nickel, copper, lead, and cadmium salts. By the use of this electrode the p_H of a 0·1*N*-copper sulphate solution made from salt of *A.R.* quality was found to be 4·14 and the degree of hydrolysis 0·072%. A. R. P.

Determination of Organically Combined Halogen. M. BUSCH (*Z. angew. Chem.*, 1925, **38**, 519—521).—In alcoholic potash solution hydrazine can be decomposed by a suitable catalyst into nitrogen and hydrogen. If this reaction is carried out in the presence of an organic halogen compound, the halogen is completely eliminated and can be determined. The catalyst is prepared by treating calcium carbonate with a solution of palladium chloride. The method cannot be used for compounds containing sulphur, phosphorus, arsenic, or mercury, owing to their poisonous effect on the catalyst. A series of results is given in which the accuracy of the method is established. F. R.

Micro Determination of Chlorides, Bromides, and Iodides together. R. STREBINGER and I. POLLAK (*Mikrochem.*, 1925, **3**, 38—59).—Whilst macrochemical separation of iodine from chlorine and bromine by means of thallous iodide is quantitative, the solubility of the latter is sufficient to affect microchemical determinations, even in presence of ammonium salts, alcohol, pyridine, or acetone. The best results are obtained with acetone and water (1 : 2 by vol.), using 5% thallous sulphate solution, but are 1—2% too low. The electrolytic determination of halogens, using a silver anode, is also found unsuitable for micro determinations. The insolubility of palladium iodide, however, affords a suitable basis for accurate microanalysis. Palladium chloride is added in the cold, the whole left 6—8 hrs., and filtered slowly; the precipitate is washed with warm water, then with alcohol, and dried in a current of air at 90—95°. Accurate results are obtained for quantities down to 0·3 mg. of iodine. The method is suitable for micro determinations of chlorine and iodine and of bromine and iodine together; in the latter case, precipitation is carried out in presence of concentrated hydrochloric acid, in both cases the total halogen being determined by the ordinary silver method. Chlorine and bromine together are determined microchemically by precipitation as silver salts; the dried and weighed precipitate is dissolved in 3—4% potassium cyanide solution, the solution diluted to 1%, and electrolysed. Corrosion of the platinum electrodes is reduced by addition of 1 drop of alkali hydroxide. A special washing arrangement is necessary to prevent access of air when removing the electrode for weighing, as silver is readily redissolved by the cyanide in presence of oxygen. The exact procedure necessary to secure accurate results is described in detail. S. I. L.

Rapid Separation of Sulphur Precipitates in Analytical Reactions. M. AWSCHALOM (*Anal. Asoc. Quím. Argentina*, 1924, **12**, 461—462).—Finely-divided sulphur precipitated in analytical operations, *e.g.*, by the action of hydrogen sulphide on ferric

salts, may be removed by shaking with a small quantity of ether. The sulphur is brought to a flocculent state in which it can readily be removed by filtration. G. W. R.

Inhibition of Bumping in the Determination of Nitrogen in Soil. F. E. HANCE.—(See i, 1032.)

Gunning–Arnold and Winkler Boric Acid Modifications of the Kjeldahl Method for the Determination of Nitrogen. K. S. MARKLEY and R. M. HANN (*J. Assoc. Off. Agric. Chem.*, 1925, **8**, 455—467).—Detailed examination of the boric acid absorption modification of the official Gunning–Arnold method, showed it to be as accurate as the latter, provided water-cooled condensers were used and the temperature of the receiving flasks did not rise above 50°. Bromophenol-blue proved satisfactory as an indicator by artificial light. A. G. P.

Determination of Phosphoric Acid as Magnesium Ammonium Phosphate. G. JØRGENSEN (*Z. anal. Chem.*, 1925, **66**, 209—224).—Polemical. Repetition of McCandless and Burton's procedure (this vol., ii, 157) gave precipitates contaminated with $Mg(NH_4)_4(PO_4)_2$ from ammoniacal solutions and with magnesium molybdate and normal phosphate from neutral solutions. Balareff's criticism (A., 1921, ii, 518) of the author's method (A., 1906, ii, 579) is based on the results of experiments conducted with solutions of greatly different concentration from those used in ordinary analyses. [Cf. *B.*, 1925, 574.] A. R. P.

Determination of Phosphorus and Magnesium. C. P. STEWART and W. ARCHIBALD (*Biochem. J.*, 1925, **19**, 484—491).—By a micro-Neumann method for the determination of phosphorus, it is possible to determine within 3% 0·05 mg. of phosphorus in 20 c.c. of fluid. A smaller error is obtained with higher concentrations. In determining magnesium in blood or serum the calcium is removed by Kramer and Tisdall's method (A., 1921, ii, 595) and the magnesium is precipitated as ammonium magnesium phosphate, in which compound the phosphorus is determined as above. S. S. Z.

Determination of Carbon Monoxide by Hæmoglobin Absorption. M. NICLOUX (*Compt. rend.*, 1925, **180**, 1750—1753; cf. A., 1923, ii, 578).—By slight modifications of the method of passing air containing carbon monoxide through blood containing a preservative and a reducing agent, better contact between the gas and the liquid is obtained, and carbon monoxide to the extent of 0·00001% may be detected, using 500 c.c. of air. The application of the law of mass action to the reaction between carbon monoxide and hæmoglobin under anaërobic conditions is questioned. L. F. H.

Determination of Carbon Dioxide and Carbon Monoxide. P. LEBEAU and P. MARMASSE (*Compt. rend.*, 1925, **180**, 1847—1850).—The amount of carbon dioxide present in a gaseous mixture is determined by condensation of the carbon dioxide by means of

liquid air, measurement of its volume, and absorption by barium hydroxide as a check. Carbon monoxide is determined by first removing condensable gasses by cooling, then oxidation of the carbon monoxide present by passage over heated iodine pentoxide, and determination of the carbon dioxide formed as above. Presence in the gaseous mixture of a large percentage of hydrocarbons does not interfere with the determination. L. F. H.

Potentiometric Study of the Reaction between Halogens and the Cyanogen Ion. E. MÜLLER and A. SCHUCH (*Z. Elektrochem.*, 1925, **31**, 332—334).—The reaction between the halogens and potassium cyanide in solution (0·1*N*) may be followed potentiometrically, a sudden large change in the potential occurring when the equivalent quantities for the equation $X_2+CN'=CNX+X'$ are present. The values of this potential (measured in millivolts against a normal calomel electrode) for chlorine, bromine, and iodine, respectively, are +560, 580, 210 when the halogen solution is titrated with the potassium cyanide solution, and 790, 580, and 220 when the reverse procedure is employed, the difference in the chlorine values probably being due to the appreciable reversibility of the reaction. The change in potential is greatest in the case of chlorine, least in the case of iodine, bromine occupying an intermediate position. The method has been applied to the electrolytic preparation of chlorocyanogen to indicate when either component is in excess. J. W. B.

Determination of Potassium. R. MEURICE (*Ann. Chim. Analyt.*, 1925 [ii], **7**, 161—163).—Potassium may be precipitated as hydrogen tartrate in the presence of alcohol (99% methyl alcohol containing only traces of acetone was used) and after well washing the precipitate, the potassium is determined by titration with sodium hydroxide solution in the presence of phenolphthalein. If the proportion of potassium chloride be between 1 and 0·8 g., dissolution of the precipitate in the alcohol is negligible and results are accurate to 0·5%. The presence of nitrates and magnesium does not affect the results, and sulphates merely lengthen the time of precipitation. [Cf. *B.*, 1925, 615.] D. G. H.

Separation of Small Quantities of Calcium from Large Amounts of Magnesium. BACH (*Chem.-Ztg.*, 1925, **49**, 514).—Contrary to the statements of Rodt and Kindscher (this vol., ii, 158) small quantities of calcium may be accurately separated from much magnesium by means of ammonium oxalate provided the correct conditions are observed. The solution should either be very dilute and contain at least 3% of ammonium chloride, or, alternately, an excess of ammonium oxalate equal to 100 times the weight of magnesium present is added in the form of a hot concentrated solution. A. R. P.

Determination of Small Quantities of Zinc in Materials of Organic Nature: Microchemical Method based on the Fluorescence of Zinc Salts with Urobilin. R. E. LUTZ (*J. Ind. Hygiene*, 1925, **7**, 273—290).—A method for determining zinc in amounts from 0·01 to 0·5 mg., to within 10%, is to compare the

green fluorescence obtained on adding standard urobilin solution with the fluorescence obtained in a control test. The zinc solution is obtained in the necessary state of freedom from other salts by a process involving the entrainment of the sulphide precipitate by means of copper, with subsequent elimination of the copper. [Cf. *B.*, 1925, 615.] D. G. H.

Use of Potassium Ferrocyanide in Gravimetric Analysis. [Determination of Cadmium.] G. LUFF (*Chem.-Ztg.*, 1925, **49**, 513—514).—Cadmium is quantitatively precipitated as cadmium ammonium ferrocyanide by the addition of potassium ferrocyanide to the warm cadmium solution containing 10 g. of ammonium chloride and 20 c.c. of ammonia (*d* 0·92) per 100 c.c. After keeping the solution for 4 hrs. at 80°, the crystalline precipitate is collected in a Gooch crucible, dried at 100°, and weighed as $Cd(NH_4)_2Fe(CN)_6$. A. R. P.

Detection and Determination of Cobalt by Spectroscopy and Colorimetry. G. DENIGÈS (*Compt. rend.*, 1925, **180**, 1748—1750).—The blue colour shown when hydrochloric acid is added in excess to solutions of cobalt salts furnishes an excellent absorption spectrum (4 bands) easily perceptible at great dilution with a direct vision spectroscope. In any aqueous solution of metallic salts (other than those of iron and copper) cobalt may be determined colorimetrically by addition of concentrated hydrochloric acid and comparison with standards. If the solutions contain iron or copper, reduction is effected by stannous chloride in order to render the method applicable. The method is specially suitable for determining traces of cobalt in commercial nickel salts. R. A. M.

Separation and Determination of Tin in Alloys. B. S. EVANS (*Analyst*, 1925, **50**, 330—334).—The tin may be determined by effecting a preliminary separation of tin, antimony, and arsenic from the alloy. Since the bromides of these three metals are volatile, they may be obtained free from other metals by cautiously acting on the powered alloy with bromine, and distilling the resulting liquid. No appreciable quantities of the bromides of copper, iron, lead, nickel, cadmium, manganese, or zinc are carried over, and these metals may be determined in the residue. [Cf. *B.*, 1925, 636.] D. G. H.

Separation of Celtium [Hafnium] and its Arc Spectrum. J. BARDET and C. TOUSSAINT (*Compt. rend.*, 1925, **180**, 1936—1938).—The mixture of sulphates is dissolved in concentrated sulphuric acid and enough 80% phosphoric acid is added to precipitate about 20% of the oxides. 1·5 Volumes of water are added slowly, with stirring, so that a slow precipitation of phosphates occurs in a strongly acid medium. After keeping over-night, the acid is decanted off, 3 volumes of water are added to the precipitate, which is then filtered. The filtrate is added to the decanted acid, which is then heated until sulphur trioxide is evolved. The procedure is repeated with this liquid. The phosphate precipitates are converted into sulphates by fusion with alkali carbonates followed by treatment

with sulphuric acid. The fresh phosphates are decomposed by concentrated sodium carbonate solution. The sulphates are then submitted to the original process. Spectroscopic methods are used to control the experiments. The arc spectrum of hafnium has been measured between 2300 and 3500 Å. All the lines found by Hansen and Werner (A., 1924, ii, 79) are confirmed and a certain number of important lines have been added. Forty-eight lines are tabulated with an accuracy of 0·05 Å. R. A. M.

Platinum and Palladium Dimethylglyoximes. R. A. Cooper (*J. Chem. Met. Min. Soc. S. Afr.*, 1925, **25**, 296—297).—Platinum dimethylglyoxime forms a fine blue, crystalline precipitate having a characteristic metallic bronze lustre when sodium formate is added to a slightly acid solution of platinic chloride containing an alcoholic solution of dimethylglyoxime. Precipitation is quantitative, but the compound cannot be ignited to metal without loss, although it can be dried at 100° to $C_8H_{14}O_4N_4Pt$ for weighing. When sodium hydroxide is added to water in which platinum dimethylglyoxime is suspended, it dissolves completely, but an excess causes precipitation of a purple unstable compound; palladium dimethylglyoxime dissolves in sodium hydroxide and is not further affected by excess. A. R. P.

Generally Applicable Method of Conducting an Elementary Organic Analysis by the Wet Way. G. Vortmann (*Z. anal. Chem.*, 1925, **66**, 272—275).—The substance is heated with an excess of potassium iodate and sulphuric acid and the carbon dioxide evolved is collected in the usual absorption tube. The potassium iodate remaining unattacked is determined by diluting the acid liquid and titrating in the usual way. From this, the amount of oxygen consumed in the combustion may be calculated and this figure together with the weight of carbon dioxide produced supplies the data for calculating the composition. A. R. P.

Paramœcial Method for Determining the Phenol Coefficient of Disinfectants. A. Schneider.—(See i, 1006.)

Nitrosomethylurethane as a Reagent for Pyrocatechol Tannins. W. Vogel (*Collegium*, 1925, 189).—Pyrocatechol tannins give a heavy precipitate with nitrosomethylurethane, whereas pyrogallol tannins, with the exception of chestnut and algarobilla, give no precipitate. Chestnut and algarobilla extracts give a slight turbidity. When pyrogallol tannins are treated twice with nitrosomethylurethane and then with iron alum and sodium acetate, they give the typical blue coloration, whereas pyrocatechol tannins treated similarly gives no coloration. The nitrosomethylurethane test is better than the formaldehyde–hydrochloric acid test. D. W.

Rapid Determination of Small Amounts of Dextrose in the Urine in Diabetes. J. R. Williams and G. U. Casey.—(See i, 998.)

Determination of Invert-sugar in presence of Sucrose. N. SCHOORL (*Chem. Weekblad*, 1925, **22**, 285—286).—The amount of potassium iodide required in the author's method (this vol., ii, 445) may be reduced to one-tenth of the amount given by addition of potassium thiocyanate after acidifying the reduced liquor. By the procedure given, 1 mg. of invert-sugar requires 0·33 c.c. of 0·1*N*-thiosulphate solution; no increase in reducing action due to the presence of sucrose could be detected. S. I. L.

Rapid Determination of the Acid Value of Oils. S. SOMAZZI (*Boll. Ind. Pelli*, 1923, **1**, 44; from *Chem. Zentr.*, 1924, ii, 1530).—Exactly 1 g. of oil is shaken in a graduated pipette with an equal volume of ether and alcohol to complete solution, when the acid is titrated with 0·1*N*-sodium hydroxide, using phenolphthalein as indicator. R. B.

Bromometric Determination of Thiocyanates and Cyanides. F. OBERHAUSER (*Z. anorg. Chem.*, 1925, **144**, 257—262).—Thiocyanates may be determined bromometrically if excess of bromine is added and, after keeping for 10 min., the titration completed with arsenious acid and bromine; the reaction is represented by the equation: $KCNS+8Br+4H_2O=KBr+BrCN+H_2SO_4+6HBr$. This process may be utilised for the determination of copper by precipitating as thiocyanate and titrating the precipitate; any nitric acid must first be removed. Cyanides may be determined according to the equation: $KCN+Br_2=CNBr+KBr$, and ferrocyanides by oxidation with bromine to ferricyanides. Ferricyanides are quantitatively reduced by arsenious acid if a zinc salt is added to precipitate the ferrocyanide as soon as formed; the excess of arsenious acid is then determined by titration with bromine, the insoluble ferrocyanide being unaffected. Complex cyanides may also be determined by converting into mercuric cyanide and proceeding as above. A. G.

Determination of Indole and Skatole in Bacterial Cultures. C. R. FELLERS and R. W. CLOUGH.—(See i, 1015.)

Electrocapillary Analysis of Colloidal Colouring Matters. W. KOPACZEWSKI (*Compt. rend.*, 1925, **180**, 1530—1533).—By measuring the rise of colloidal dyes (natural and synthetic) up strips of filter-paper, it is found that the rise of electrolytes is independent of their charge. Electro-negative colloids rise as high as water, the upper portion of the filter-paper being more deeply coloured; electro-positive colloids rise scarcely at all, whilst the point of contact with the liquid is the most deeply coloured. Amphoteric colloids show bands of light and deep colour, and substances of low surface tension rise considerably on the filter-paper irrespective of their charge. By their behaviour when placed on filter-paper, therefore, a qualitative determination of the charge of a colloidal dye may be made. L. F. H.

General, Physical, and Inorganic Chemistry.

Continuous Hydrogen Spectrum. H. Schüler and K. L. Wolf (*Z. Physik*, 1925, **33**, 42—47).—The intensity of the continuous spectrum observed in the positive column, which begins at 4800 Å., is shown to be unrelated to that of the Balmer series or of the many-lined spectrum. Its intensity is increased by an electric field. As the long wave-length limit corresponds with the heat of dissociation of the hydrogen molecule, the spectrum is attributed to the combination of the atoms in an electric field. Possibly the radiation emitted may also depend on the state of excitation of the hydrogen atoms. E. B. L.

Further Spectra Associated with Carbon. R. T. Birge (*Nature*, 1925, **116**, 207).—The final states of the six new "double-double-headed" bands described by Johnson (this vol., ii, 723) are identical with the initial states of the comet-tail bands, thus proving the correctness of the author's assignment of vibrational quantum numbers (this vol., ii, 836). The comet-tail bands must have a double electronic level in the initial state, of spacing $\Delta\nu=126$. Each band has a double "origin" given by the heads of the two Q branches, according to Baldet's analysis. Similarly, the new bands each have a double origin with the same spacing. A. A. E.

Doublet Separation in C II and Si IV. R. J. Lang and S. Smith (*Nature*, 1925, **116**, 244).—A brief account of work to be published elsewhere. A. A. E.

Arc Spectrum of Scandium. S. Piña de Rubies (*Compt. rend.*, 1925, **181**, 108—110).—The wave-lengths and intensities are tabulated of 185 lines of the arc spectrum of scandium between 2232 and 3394 Å. F. G. T.

Spark Spectra in the Schumann Region. L. Bloch and E. Bloch (*J. Phys. Radium*, 1925, [vi], **6**, 154—165).—Full lists are given of the spark-spectrum wave-lengths for manganese between 1869 and 1464 Å., chromium between 1926 and 1505, copper between 1930 and 1359, silver between 1889 and 1389, gold between 1919 and 1342, and platinum between 1991 and 1330 Å. Lines are noted which may be due to contamination with iron or carbon. W. A. C.

Low-voltage Arcs in Rubidium and Cæsium Vapours. F. H. Newman (*Phil. Mag.*, 1925, [vi], **50**, 463—470; cf. this vol., ii, 450).—The voltages required to strike an arc and to maintain it in rubidium and cæsium vapours have been measured at temperatures between 160° and 300°. The arc was struck between an anode of sheet metal and a tungsten-filament cathode heated by passing a

suitable current. The electrodes were enclosed in an evacuated bulb containing sufficient of the metal to form saturated vapour at the highest temperature used. The bulb was heated in an electric furnace. With rising temperature, the striking voltage diminishes; thus for rubidium it is 7·3 volts at 185° and falls to 3·2 volts at 289°. At constant temperature it decreases with increase of the filament current. The same rules apply to the voltage required to maintain the arc, which in all cases is slightly less than the striking voltage. The mechanism of the arc is briefly discussed. A. B. M.

Electromagnetic Susceptibility of the Iodine Atom. Change of Intensity in the Line Spectrum. W. STEUBING (*Z. Physik*, 1925, **33**, 113—127).—The spectrum was produced in discharge tubes with carbon electrodes excited either by 10,000 volts direct current, or by alternating current with a periodicity of 50, both with and without capacity. The electromagnet gave a field up to 15,000 gauss. In addition to photographs, the spectrum was recorded by means of a Moll thermopile and galvanometer. The arc and spark lines behave quite differently in the magnetic field; the former vary in intensity but remain sharp, whilst the latter become less sharp and are broadened on the red side. New lines also appear, but no Zeeman effect could be noticed. The loss in sharpness is ascribed to the molecular Stark effect; it increases with increase in pressure of the iodine vapour and also in the presence of foreign gases. The intensity of the spectrum is reduced by the presence of a foreign gas, the effect being greater the higher the molecular weight and the greater its chemical affinity. In a mixture of helium and neon, faint diffuse lines can be resolved into components, and strong new lines appear, presumably due to collisions of the second kind. E. B. L.

X-Ray Radiation from Hot Sparks. A. BJÖRKESEN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 413—415).—In a high-potential condensed discharge in a high vacuum stripped atoms emit strong spectrum lines, and the hot sparks radiate *X*-rays. The *X*-radiation exhibits all the known characteristic lines in the *L* series for silver and the *K* series for aluminium, silicon, sulphur, and copper. No new lines were observed nor was any shift or broadening noticeable in the known lines. The *X*-rays are thus not produced by the stripped atoms in the vapour; they originate at the solid electrodes, and apparently the multiple ionisation which gives rise to the enhanced *X*-ray lines of the *K*-series must be due to simultaneous ejection by a single impact. R. A. M.

Quantum Explanation of the Zeeman Effect. A. M. MOSHARRAFA (*Nature*, 1925, **116**, 96—97; cf. Hicks, this vol., ii, 729). A. A. E.

Quantum Explanation of the Zeeman Effect. A. W. CONWAY (*Nature*, 1925, **116**, 97). A. A. E.

Theory of the Zeeman Effect. G. GIANFRANCESCHI (*Nature*, 1925, **116**, 207—208). A. A. E.

Stark Effect Patterns in Helium. J. S. FOSTER (*Nature*, 1925, **116**, 135).—New observations prove that the simple displacements (1/1) reported by Stark and Nyquist for the members of the sharp and principal series of helium are correct (cf. Takamine and Kokubu, A., 1919, ii, 379). A new weak perpendicular component of the parhelium combination line 4384 Å. has been observed. Two examples of the pattern 2/3 are mentioned. A. A. E.

Multiplet Structure. A. BRAMLEY (*Phil. Mag.*, 1925, [vi], **50**, 375—381).—From the equations of motion of an electron describing a path about a central charge the author deduces an expression for the frequency separation of the components of multiplets in the optical spectra of elements with more than one electron in the atom. The closeness of agreement between computed and experimental frequency differences is illustrated by data from the spectra of potassium and calcium. A. B. M.

Optical Screening-constant Regularities. A. C. MENZIES (*Phil. Mag.*, 1925, [vi], **50**, 414—422).—The screening-constant s in the relativity doublet formula $\delta\nu=K(Z-s)$ has been calculated from the doublet separations $\delta\nu$ in the optical spectra of a number of the elements. The following are the principal observed regularities: (1) The values of s for the alkaline-earth spark spectra are approximately nine-tenths those of the corresponding alkali arc spectra. (2) For the same sub-groups of the periodic table s varies directly as the atomic number Z. (3) The s–Z curves for different sub-groups have almost the same slope; for additions to Z of 8, 18, and 32, the additions to s are 5, 13, and 23, respectively. These regularities are to be expected from simple theoretical considerations. The evidence is considered as favouring a magnetic rather than a relativistic origin of multiplets. A. B. M.

Red Limit and Work of Escape of Photo-electric Electrons. R. SUHRMANN (*Z. Physik*, 1925, **33**, 63—84).—The curves of photo-electric sensitivity for platinum, gold, and silver near the red limit were measured with the most delicate instruments possible. All three metals show the influence of surface films, but only platinum and gold show any considerable diminution in emission after continued heating at a high temperature in order to remove occluded gas—probably hydrogen in the case of gold and platinum, oxygen in the case of silver. From the curves characteristic constants can be deduced by applying the theory of thermionic emission, and the value for the work of escape and the red limit can be calculated for absolute zero. A temperature scale can be constructed and the photo-electric cell may be used as a total radiation pyrometer.
E. B. L.

The Photo-electric Effect in Potassium Vapour as a Function of the Frequency of the Light. E. O. LAWRENCE (*Phil. Mag.*, 1925, [vi], **50**, 345—359).—The photo-electric effect in potassium vapour has been measured for incident light between 2200 and 3200 Å. A stream of potassium vapour from a reservoir of the metal heated at about 300° traversed the previously evacu-

ated ionisation chamber, condensing on a surface cooled by liquid air on the opposite side. The source of light was a Pfund iron arc, combined with a monochromator. The beam of light passed through the stream of vapour and the positive ions formed were measured. The intensity of the light was determined by a potassium photo-electric cell. Light of wave-length greater than 2610 Å. produces no effect. For shorter wave-lengths, the effect increases with diminishing wave-length, the relation between wave-length of incident light and photo-electric effect being nearly linear over the range investigated. The discrepancy between the observed photo-electric threshold and that required by the Bohr theory is regarded as due probably to a molecular state of the vapour. A. B. M.

Ionic Mobilities in Ethyl Ether as a Function of Pressure. L. B. LOEB (*Proc. Nat. Acad. Sci.*, 1925, **11**, 428—435).—In permanent gases, newly-formed positive ions have higher mobilities than the positive ions a few hundredths of a second old, the higher value being equal to the mobility of the negative ion. In ethyl ether, the mobility is small because of the high dielectric constant and the mobility of the positive ion does not equal that of the negative ion. The positive mobility falls from a higher value to a constant lower value in 0·03 sec.; in air this takes about 0·004 sec. The most satisfactory explanation is given by Erikson, that the change in mobility of the positive ion with time is due to a change in the diameter of the ion with increasing complexity; possibly that the newly-formed ions are unimolecular, whilst the aged positive ions are bimolecular. R. A. M.

Selective Photo-electric Effect on Strontium. R. DÖPEL (*Z. Physik*, 1925, **33**, 237—245).—The strontium was deposited as a mirror on glass by distillation and full precautions were taken to exclude any hydrogen or moisture. The maximum photo-current was produced at 350$\mu\mu$, distinctly shorter than that for barium, and showed the characteristic change with the angle of incidence of the plane of the polarised light. E. B. L.

Electric Charges Carried by Individual Microscopic Particles. T. SEXL (*Physical Rev.*, 1925, [ii], **26**, 92—96; cf. following abstracts).—A criticism of Derieux' computation by Millikan's method of the elementary electrical charge on mercury droplets. A. A. E.

[Electric Charges Carried by Individual Microscopic Particles.] J. B. DERIEUX (*Physical Rev.*, 1925, [ii], **26**, 97—98).—A reply to Sexl (preceding abstract). A. A. E.

Nature of the Evidence for the Divisibility of the Electron. R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **26**, 99—104; cf. preceding abstracts).—Polemical. A discussion of the criticisms of Sexl and others. A. A. E.

Ionisation Produced in Air during the Complete Absorption of Slow Electrons. J. F. LEHMANN and T. H. OSGOOD (*Nature*, 1925, **116**, 242).—Approximate determinations show that the

ionisation per electron in air increases steadily with the initial energy of the ionising electron over the range 100 to 1000 volts. The average energy expended per ion-pair decreases from 35 volts (initial energy 200 volts) to 22 volts (initial energy 1000 volts). The behaviour of helium is similar. A. A. E.

Isotopes of Mercury. F. W. ASTON (*Nature*, 1925, **116**, 208).—Preliminary results for mercury indicate that the mass numbers and corresponding approximate intensities of the most important constituents of mercury are: 198 (4), 199 (5), 200 (7), 201 (3), 202 (10), 204 (2), in agreement with the accepted atomic weight. Gold, if obtainable by the transmutation of mercury, should have an atomic weight at least as high as 198. A. A. E.

Isotope Effect in Band Spectra. III. Spectrum of Copper Iodide as Excited by Active Nitrogen. R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **26**, 1—32).—By the action of active nitrogen on the vapours of the copper halides, the band spectra are characterised by sharpness and clearness of the heads; the mechanism involved is probably (1) the dissociation of Cu_2X_2 or CuX molecules giving neutral, unexcited atoms which are subsequently excited by impact with N_2' molecules, and (2) dissociation yielding the ions Cu^+ and X^-. Band spectra of cuprous fluoride, chloride, bromide, and iodide were obtained using cupric fluoride, cuprous and cupric chloride, cupric bromide, and cuprous iodide, and some observations are recorded on the excitation by means of active nitrogen of the spectra of lead iodide, mercuric iodide, and mercuric bromide; in the latter case, process (1) (above) is even more definitely indicated. The author discusses the nature of excited electronic states in copper halide molecules, and the band spectra of polar compounds; the formation of CuX_2 molecules is correlated with the excitation of CuX. The absence of electronic band spectra for the hydrogen, silver, and alkali halides is possibly due to the non-occurrence of compounds of the type $NaCl_2$; its presence in the case of the alkaline-earth halides leads to the assumption that the real emitter is then of the type MX, the spectrum of which is excited by the addition of MX_2 to a flame in a manner analogous to the excitation of the sodium *D* lines (*i.e.*, spectrum of M) by the use of sodium chloride (*i.e.*, MX).

Complete data for the cuprous iodide band spectrum and an analysis of the results are tabulated, the wave-lengths of about 260 heads between 5650 and 3890 Å. being measured; no other bands are present between 1900 and 7000 Å. Every $Cu^{63}I$ band was found, wherever of sufficient resolution and intensity, to be accompanied by a weaker $Cu^{65}I$ band. The $Cu^{63}I$ bands fall into five systems, one in the green, and the others in the blue and violet. So far as data could be obtained, the calculated and observed values of the isotopic displacement are in complete agreement, within the experimental error, for the entire range of values of the vibrational quantum numbers n' and n'' in all the systems. For cuprous iodide (and probably for the chloride and bromide), the equations indicate that the five (six, or four) systems all correspond with a common

final electronic state, probably the normal state of the molecule. An energy level diagram is given for the cuprous iodide molecule. Numerically large values of $n''-n'$ are associated with large values of n', causing the maximum intensity in band sequences (having the same value for $n''-n'$) to shift from the first to higher members as the sequence considered is further away from the system-origin.

A. A. E.

Stopping Power of Hydrogen Atoms for α-Particles. R. H. FOWLER (*Proc. Camb. Phil. Soc.*, 1925, **22**, 793—803).—Bohr calculated the stopping power of light atoms for α-particles on the basis of classical principles. About one-half of the loss of energy by the α-particles comes from transfers to electrons in distant atoms of amounts less than the energy required to transfer those atoms to their next higher stationary state. The author has calculated the mechanical transfer of energy from an α-particle to an electron moving in its normal circular orbit in a hydrogen-like atom. The calculation depends on perturbation theory carried to a second approximation. In Bohr's calculations the equation $-dT/dx = 4\pi LN^2e^4/mV^2 . \log \gamma mV^3/2\pi Ne^2\omega$ was deduced; $-dT/dx$ is the rate of loss of energy by an α-particle of charge Ne and velocity V moving through a gas containing L atoms with a single electron (mass m, charge $-e$) per c.c. The frequency of these elastically bound electrons is ω, and γ is a constant, 1·123. In the present calculation, ω is the orbital frequency of revolution and γ is the constant 2·42. The equation is unchanged in form. Gurney's results (this vol., ii, 256) are used to test the calculation. If γ is taken as 1 instead of 2·42, the results are in almost exact agreement with experiment. The reasons for this change are discussed.

R. A. M.

Theory of the Influence of Magnetic Fields on the Stopping Power of Gases for α-Particles. R. DE L. KRONIG (*Proc. Camb. Phil. Soc.*, 1925, **22**, 773—776).—A calculation following on the work of Fowler (preceding abstract) of the influence of space quantisation on the stopping of α-particles by matter.

R. A. M.

Long-range Particles Emitted by the Active Deposits of Radium. N. YAMADA (*Compt. rend.*, 1925, **181**, 176—178; cf. Bates and Rogers, A., 1924, ii, 84; Pettersson, *ibid.*, 380; Rutherford and Chadwick, *ibid.*, 814).—Radium-*C* emits only long-range particles of range 9·3 cm., the reported particles of longer range being probably hydrogen nuclei, since they can be eliminated by preliminary careful heating in a vacuum to remove traces of water vapour etc. There are approximately 20 particles of 9·3 cm. range per 10^6 α-particles of ordinary range.

J. S. C.

Variations of Range, Initial Velocity, and Ionising Power of the α-Particles from Polonium. (MLLE.) I. CURIE (*Ann. Physique*, 1925, [x], **3**, 299—401).—A connected account of work already published, with minor changes in detail (cf. A., 1922, ii, 606; *Compt. rend.*, 1923, **176**, 1462; *J. Phys. Radium*, 1923, [vi], **4**,

170; A., 1923, ii, 207; this vol., ii, 175, 348, 621). The initial velocity of the α-particles from polonium is $1{\cdot}593\times10^9$ cm./sec. and the range at 15° and 760 mm. is 3·87 cm. in air. Maximum ionisation occurs 4·5 mm. from the end of the range in air at 15° and 760 mm.; the velocity at that point is $0{\cdot}57\times10^9$ cm./sec.

A. S. R.

Proposed Model for the α-Particle, and some Nuclear Series. R. HARGREAVES (*Phil. Mag.*, 1925, [vi], **50**, 470—491).—The nucleus is taken to be a structure of positive and negative electrons, rotating about a common axis, with their relative positions unaltered, under attractions and repulsions following the simple electrostatic laws. The model proposed for the helium nucleus is discussed in detail, and it is shown how the same type of model may be extended to represent the nuclei of elements of higher atomic weight. A. B. M.

Effective Wave-length of γ-Rays. D. SKOBELTZYN (*Nature*, 1925, **116**, 206—207).—Polemical (cf. Gray, this vol., ii, 84).

A. A. E.

Transmutation of Mercury into Gold. H. NAGAOKA (*Nature*, 1925, **116**, 95—96).—The formation of ruby glass is successfully used to detect the production of gold from mercury, employing a discharge between tungsten and mercury electrodes in paraffin oil, in which a potential difference of $1{\cdot}5\times10^5$ volts/cm. could be maintained. A. A. E.

Chemical Properties of Atoms according to the Bohr Theory. H. A. KRAMERS (*Naturwiss.*, 1924, **47**, 1050—1054).—An account of the development of the Bohr atom and the formulation of the periodic table in terms of quantised atoms and groups of electrons. E. B. L.

Quantum Theory and the Bohr Atom. A. SOMMERFELD (*Naturwiss.*, 1924, **47**, 1047—1049).—A general account of the ideas underlying the application of the quantum theory in the Bohr atom and a discussion of outstanding problems. E. B. L.

Theory of Emission in the Rutherford-Bohr Atom. J. PALACIOS (*Anal. Fís. Quím.*, 1925, **23**, 259—276).—Assuming that emission in the Bohr atom gives rise to trains of undamped waves and that the escape of electrons is regulated by the laws of chance, a theory is developed by which the measurements of Wien with canal rays can be explained. From this theory and from the experimental data, it follows that the Hβ and Hγ rays have the same emission time. It follows from this that Planck's constant h may be considered as the product of two universal constants, namely, a time quantum and an energy quantum, the magnitudes of which, calculated from the experimental data, are given. The theory in question makes it possible to deduce the degree of stability of the different orbits, starting from the damping observed in the luminescence of the canal rays. G. W. R.

The Epstein–Sommerfeld Quantum Rule. L. KORDYSCH (*Z. Physik*, 1925, **33**, 214—218).—The quantum theory of the Zeeman effect is based on the Epstein–Sommerfeld empirical rule; it depends on a use of the principle of selection which is not free from objection. The quantum rule for the polarisation is derived by considering the meridional and equatorial motion and selecting from the possible forms those which do not contradict the quantum hypothesis. E. B. L.

Atomic and Molecular Collisions and their Chemical Significance. J. FRANCK (*Naturwiss.*, 1924, **47**, 1063—1068).—Recent progress in the application of quantum theory to collisions between electrons, atoms, and molecules in the normal and in the excited condition is described. An electron or normal atom in colliding with a normal atom may raise the latter to a higher quantum state (collisions of the first type). Conversely, internal energy of excitation may be converted into translational energy by the collision of an excited atom with a slow-moving normal atom or molecule (second type). In the formation of a molecule from two atoms, it will rarely happen that the total energy contributed by the atoms will be precisely what is required for any of the definite quantum states of the molecule which are a condition of its continued existence. The excess energy must therefore be removed, either as radiation or by collision with a third atom or molecule which has not participated in the reaction—a conception which seems to be justified by recent work on reaction velocities (third type). E. B. L.

Band Spectra and Molecular Properties. A. KRATZER (*Naturwiss.*, 1924, **47**, 1054—1058).—A short account of how band spectra yield information concerning the moment of inertia, the nature and strength of linking, the energy of dissociation and other details affecting molecular structure. Consideration of the variation of moment of inertia with temperature as indicated by band spectra has made it possible to express the specific heat of gases from very low to very high temperatures by means of a theoretical curve. Magnetic properties are also discussed. E. B. L.

Intensities in Band Spectra. G. H. DIEKE (*Z. Physik*, 1925, **33**, 161—168).—The rule of Burger and Dorgelo for the intensity of the lines of a multiplet is applied to band spectra and is found to lead to results in agreement with experiment. The *P* branch is stronger in emission than the *R* branch. The course of the intensity is different when the band consists of unresolved doublets from cases in which its consists of really single lines. An explanation is given of the alternation in intensity observed in many bands. E. B. L.

Band Spectra Associated with Carbon. R. T. BIRGE (*Nature*, 1925, **116**, 170—171).—The author has arranged in progressions and assigned vibrational quantum numbers to the thirteen band groups associated with carbon and its compounds. It is probable that both the first negative group and the comet-tail bands are due to ionised carbon monoxide. A. A. E.

Absorption Process in Photo-electrically-conducting Sodium Chloride Crystals. Z. GYULAI (*Z. Physik*, 1925, **33**, 251—260).—The absorption of sodium chloride crystals exposed to intense bluish-green light was compared with the absorption of the unexcited crystal; the absorption curve showed a diminution in the maximum position, but a considerable extension towards the red end. Only 60% of the "centres" could be excited. Light of long wave-length restored the excited crystal to the unexcited condition as a result of the absorption following quantum laws, one quantum of long wave-length light producing a positive current equal to the negative current resulting from the liberation of the electrons. E. B. L.

Absorption of Ultra-violet Light by Inorganic Halides. F. H. GETMAN (*J. Physical Chem.*, 1925, **29**, 853—864; cf. Crymble, T., 1912, **101**, 266; Brannigan and Macbeth, T., 1916, **109**, 1277; Macbeth and Maxwell, T., 1923, **123**, 370).—The absorption coefficients of a number of chlorides have been measured; the calculated molecular extinction coefficients increase with the atomic weight of the combined metal. The chlorides of calcium, strontium, magnesium, zinc, and aluminium absorb ultra-violet radiation selectively, the wave-length corresponding with the head of the absorption band of each salt being approximately 2730 Å. (cf. Brannigan and Macbeth, *loc. cit.*). The presence of this characteristic absorption band throughout a series of chlorides is shown not to be due to the common ion. Calcium chloride solutions do not follow Beer's law, and from this fact it is doubtful whether the law applies strictly to any strongly polar compounds. F. G. S.

Carbon Disulphide Band at 320mμ. G. BRUHAT and M. PAUTHENIER (*Compt. rend.*, 1925, **181**, 104—105).—The extinction coefficients and refractive indices of carbon disulphide in the neighbourhood of, and within, the band at 320mμ may be represented by formulæ of the Ketteler–Helmholtz type. This band belongs to the type which may be resolved into lines, although when measurements are made with liquid carbon disulphide, it appears continuous. When a vapour possesses large bands and the variations of absorption are regular, the absorption curve may be superposed on a curve representing a δ term of the Ketteler formula. This superposition is impossible with carbon disulphide owing to the asymmetry of the curve, and to the fact that the extinction coefficient alters rapidly on the edge, and is markedly constant in the centre, of the band. It is shown that the above band is formed by the juxtaposition of widened lines. A formula derived solely from absorption measurements permits the calculation of the anomalous dispersion, giving values which agree well with those of direct measurement. The interval between the maximum and minimum anomaly has a calculated value of 260 Å., the observed value being 280 Å. F. G. T.

Absorption Spectra of Several Ketones. J. PLOTNIKOV (*Rec. trav. chim.*, 1925, **44**, 798—799).—Polemical against Langedijk

(this vol., i, 408) and Wegscheider (A., 1923, ii, 49). The author maintains from examples of the photo-chemical decolorisation of dyes that the action depends on the quantity of light absorbed and not on the intensity, and that when heat rays are not superimposed on the true light rays his photo-chemical absorption rule is valid.

J. W. B.

Spectro-chemistry in the Ultra-red. VII. Absorption of certain Homologous Ketones. G. B. Bonino (*Gazzetta*, 1925, **55**, 335—340; cf. A., 1923, ii, 711).—The law connecting the values of the maximum molecular absorption coefficients of two compounds in a homologous series with the numbers of hydrogen atoms in their molecules is obeyed also by the series: acetone, methyl ethyl ketone, methyl propyl ketone, and methyl butyl ketone, these compounds showing the ultra-red absorption band assumed to be characteristic of oscillators composed of hydrogen atoms united to carbon atoms. T. H. P.

Spectro-chemistry in the Ultra-red. VIII. Absorption of certain Halogenated Hydrocarbons. G. B. Bonino (*Gazzetta*, 1925, **55**, 341—348; cf. preceding abstract).—With ethyl bromide, *s*-dibromo-, tetrachloro-, and pentachloro-ethane, and di- and trichloroethylene, a maximum value of the molecular absorption coefficient is shown in the ultra-red at 3·51μ, whilst with tetrachloroethylene and hexachloroethane no such maximum is observed.

T. H. P.

Absorption Spectra of Benzophenone Derivatives. T. Tasaki (*Acta Phytochim.*, 1925, **2**, 49—73).—Benzophenone in M/10,000 alcoholic solution shows an absorption band at frequency 4000 Å., uninfluenced by methylation of the benzene nucleus. Ortho- and para-hydroxy substitution have a much greater effect than meta-hydroxy substitution. The *o*-hydroxy derivative shows two bands, whilst *p*-hydroxy substitution has a bathochromic influence which is much stronger in the dihydroxy derivatives. The 2 : 3 : 4-substituted compounds show in general a broad band at frequency 3200. Substitution in both nuclei shows in general a greater effect than substitution in one nucleus. The structural formulæ of the naturally occurring cotoin, phloridzin, and phloretin are confirmed spectrographically. P. W. C.

Changes in the Ultra-violet Absorption of Gelatin. T. T. Baker and L. F. Davidson (*Nature*, 1925, **116**, 172).—When the p_H of gelatin is above the isoelectric point (p_H 4·7) there is a characteristic increase in absorption from about 3500 Å. towards the red, whereas with a fall in p_H there is an increase in absorption in the region of shorter wave-lengths. A. A. E.

Fluorescence of Cadmium Vapour. W. Kapuscinski (*Nature*, 1925, **116**, 170).—When a beam of light containing radiation of wave-length below 3000 Å. is passed through heated cadmium vapour, a blue fluorescence, strictly limited to the path of the exciting beam, appears first at 450°, is very pronounced at 600—

750°, and can be observed with diminished intensity up to 950°. Diffusion of hydrogen through the silica container destroys the effect. The spectrum, which is analogous to the fluorescence spectrum of mercury vapour, shows a continuous band from 5000 to 3950 Å.; the maximal intensity is at approximately 4630 Å.

A. A. E.

Regularities in the Resonance Spectrum of Iodine Vapour and the Determination of the Moment of Inertia. A. KRATZER and E. SUDHOLT (*Z. Physik*, 1925, **33**, 144—152).—The fluorescence spectrum excited by the green mercury line is analysed and its term-formula obtained. The value found for the moment of inertia of the normal molecule is $8{\cdot}63 \times 10^{-38}$ g. cm.^{2}, and the distance apart of the atoms $2{\cdot}87 \times 10^{-8}$ cm. E. B. L.

Influence of an Alternating Magnetic Field on the Polarisation of Resonance Radiation. E. FERMI and F. RASETTI (*Z. Physik*, 1925, **33**, 246—250).—The resonance spectrum of mercury vapour was examined under the influence of a weak magnetic field of constant amplitude but variable frequency produced by a thermionic valve circuit. The depolarising effect diminished as the frequency diminished, for frequencies of the order a million per second. E. B. L.

Chemical Luminescence with Active Hydrogen. K. F. BONHOEFFER (*Z. physikal. Chem.*, 1925, **116**, 391—400; cf. this vol., ii, 365).—Wood's active hydrogen produces visible luminescence with mercury, anthracene, the vapour of sodium and other alkali metals, and other substances. Spectrographic investigation showed that (i) Wood's hydrogen itself luminesces in the ultra-violet (3064 Å.); (ii) the hydride band is produced by the action of the gas on liquid mercury, a liquid hydride apparently being formed. The mercury line 2537 Å. also appears as a result of the latter reaction. L. F. G.

***X*-Ray Stimulation of Phosphorescence of Fused Silica.** F. L. HOPWOOD and W. V. MAYNEORD (*Nature*, 1925, **116**, 98).—After exposure to ultra-violet light, castor oil blackens a photographic plate only if the vapour is brought into contact with it. Silica, but not castor oil, when exposed to *X*-rays blackens a photographic plate, some specimens of silica exhibiting phosphorescence and fluorescence. A. A. E.

Light Filter in Interferometry. J. B. FERGUSON (*J. Washington Acad. Sci.*, 1925, **15**, 279).—Visual acuity in work with the Rayleigh–Zeiss type of interferometer is increased by using the potassium dichromate–neodymium nitrate liquid filter. R. A. M.

Ionisation of Hydrogen by Electron Impact as Interpreted by Positive Ray Analysis. T. R. HOGNESS and E. G. LUNN (*Physical Rev.*, 1925, [ii], **26**, 44—55).—Since at low pressures only H_2^+ ions are formed, the formation of H_3^+ ions increasing in proportion to the increase in pressure (as also did that of H^+

ions up to 4%), the conclusions of Dempster and Smyth, that the primary process in the ionisation of hydrogen is the ionisation of the molecule without dissociation, are confirmed. The ionisation potential at 16 volts is that for the formation of H_2^+, a secondary process resulting also in the formation of H_3^+. The percentage of H^+ ions produced by electron impact in helium containing hydrogen was greater than that of H_2^+ ions, whilst no H_3^+ ions were observed. Evidence was found for the existence of ions HeH^+ and possibly HeH_2^+. A. A. E.

Dielectric Constant and Molecular Association of some Liquids. L. LANGE (*Z. Physik*, 1925, **33**, 169—182).—The dielectric constants of mixtures of organic liquids were determined by Nernst's method at various concentrations and temperatures. Debye's theory of the molecular dipole was applied to the results, and tables of molecular polarisation are given. The curves exhibiting the effect of concentration indicate that association occurred in every case except that of ethyl ether. The effect of increase of temperature is to decrease association, but the dipole moment may increase or decrease according to the type of compound. The values for this moment are given for eight substances of which the molecules are only slightly associated. E. B. L.

Molecular Volume of Salts at the M. P. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **145**, 88—94).—The molecular volumes of salts at the ordinary temperature are about 0·8 times those at the m. p. The molecular volumes of the alkali halides at the m. p. are only approximately additive. The molecular volumes of alkali halides, carbonates, sulphates, and nitrates increase with increasing atomic weight of the metal or halide and in the order nitrates > carbonates > sulphates. A. G.

Theory of Colour Production. J. STIEGLITZ (*J. Franklin Inst.*, 1925, **200**, 35—49).—A lecture, with experimental illustrations, describing the author's theory (cf. A., 1923, ii, 713). F. G. T.

Calculation of Rotatory Power from Molecular Structure. R. DE MALLEMANN (*Compt. rend.*, 1925, **181**, 106—108; cf. *ibid.*, 1923, **177**, 427).—Previous suggestions are made more precise by analysing the action of the intermolecular field. Account is taken of the variation of amplitude in the small volume under consideration, and of the particular value of the field at the points considered in evaluating equations of motion of each electron. This more detailed analysis does not modify the general form of the expressions previously obtained for molecular polarisation, refraction, and rotatory power. At the same time, the equations of motion may now be written in a symmetrical form, without this symmetry necessarily existing in the imaginary terms of the total polarisation. By these modifications the optical activity becomes calculable from the configuration of the molecular system. The simplest configuration compatible with optical activity is that of the irregular tetrahedron, and the rotatory power depends on the differences in length of the sides of this tetrahedron, and on the

products of the refractivities of the constituent atoms, taken three at a time. The order of the rotations thus calculated is that of the average experimental values for molecules of normal dimensions. F. G. T.

The Co-ordination Theory in its Application to the Study of Mordant Dyes. G. T. MORGAN and J. D. M. SMITH (*J. Soc. Dyers and Col.*, 1925, **41**, 233—241).—A *résumé* of work already published (cf. T., 1921, **119**, 704; 1922, **121**, 160, 2866; A., 1924, i, 1359. See also *B.*, 1925, 664). W. A. S.

Tridentate Groups in Complexes of Tetrahedral and Octahedral Symmetry. J. D. M. SMITH (*J. Chem. Soc.*, 1925, **127**, 1682—1687).—Tridentate groups are those which can be attached at three points to a nuclear atom. They comprise three fused chelate groups represented by ABC to indicate the three chelate groups AB, AC, BC. Tridentate groups are classified according to the number of different chelate groups comprised and are of three types, AAA, AAB, and ABC. With tetrahedral complexes, only one main type is possible, consisting of one tridentate group and one unitary group. The main type gives three classes, (1) AAAb, (2) AABc, (3) ABCd, where the small letter represents the unitary group. Class (1) consists of a single optically inactive form, whilst (2) and (3) each consist of two optically active (enantiomorphous) isomerides. In octahedral complexes (co-ordination number 6), the remaining groups may be either unitary or chelate groups, and if one tridentate group is present there are three main types comprising twenty-four classes, which are tabulated and their isomerism and optical activity indicated. W. H.-R.

Valency Relations: An Element of Atomic Number Zero with an Atomic Weight of Unity. F. H. LORING (*Chem. News*, 1925, **131**, 50—52).—It is shown that an element having zero atomic number, zero valency, and an atomic weight of unity can be fitted into the periodic table (cf. Rutherford, A., 1920, ii, 541). The valencies of the elements are discussed in detail. G. M. B.

Valency in Boron Compounds. E. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 382—385).—To explain the peculiar series of hydrides of boron, it is suggested that the two inner electrons of the boron atom can play a part in combinations as well as the three outer ones. Assuming that heteropolar hydrides can only be formed when there is no other way of arriving at a rare-gas configuration of the boron atom, it is shown that whilst homopolar BH_3 cannot exist, homopolar B_2H_6 may have one inner electron of each boron atom in common, so that the latter has the neon configuration. In the same way the hydrides B_4H_{10}, B_6H_{10}, and $B_{10}H_{14}$ may be built up as chain compounds, and B_5H_9 and B_5H_{11} as cyclic compounds. To account for the existence of BMe_3, one of the carbon atoms is supposed to have an inner electron in common with the boron atom. Among elements having two electron-shells, any two elements can form homopolar compounds by means of the

outer electrons only if the sum of the outer electrons is equal to or greater than 8 (or 5 if hydrogen is involved), but not otherwise; hence the exceptional position of boron. W. A. C.

Metallo-organic Bases. F. Hein and H. Meininger (*Z. anorg. Chem.*, 1925, **145**, 95—116).—The hydroxides $Sn(OH)_4$, $Hg(OH)_2$, $Pb(OH)_4$, $Tl(OH)_3$, and $Cr(OH)_4$ are weak acids or very feeble bases, but, when all the hydroxyl groups except one are replaced by ethyl (or phenyl) radicals, relatively strong bases are obtained; thus the molecular conductivities at a dilution of 64 litres are: $SnEt_3{\cdot}OH$, 0·45; $HgEt{\cdot}OH$, 1·20; $PbEt_3{\cdot}OH$, 8·10; $TlEt_2{\cdot}OH$, 140·00; $CrPh_3{\cdot}OH$, 212·0. Triphenylchromium hydroxide is nearly as strong a base as sodium hydroxide. The alkalinity of the metallo-organic bases decreases with increasing weight of the organic radical. The nature of the metal has a predominating influence in determining the alkalinity, whilst in the corresponding compounds of sulphur, iodine, nitrogen, and phosphorus the central atom has little influence. This is probably because in the latter compounds the hydroxyl group is in the outer sphere of the co-ordinatively saturated central atom, whilst in the metallo-organic bases the hydroxyl group is more closely connected to the central atom. A. G.

Lattice Energy of Ammines. W. Biltz and H. G. Grimm (*Z. anorg. Chem.*, 1925, **145**, 63—87).—The lattice energy of ammines is equal to the sum of that of the ammonia-free salt and the heat of formation of the ammine. Ammines with different cations become increasingly similar as the number of ammonia molecules with which the cation is surrounded increases. The relative stability of the ammines of the different halides depends on the nature of the cation; when the heat of formation of the halides increases in the order chloride to iodide, then the stability of the ammines increases in this order also, and this is the case for the metals of the principal series of the periodic system. The heats of formation of the halides of the metals of the secondary series (*e.g.*, silver) increase in the order iodide to chloride, and the stability of the ammines is in this order also. The process of ammine formation may be divided into two stages, the expansion of the molecule of the original salt and the addition of ammonia to the cation. The heat of formation is then equal to the heat of co-ordination less the work done in the separation of the ions of the salt. These two quantities may be roughly calculated; the heat of co-ordination of hexamminepotassium iodide is 14 kg.-cal. per molecule of ammonia, and for salts of the alkaline-earth metals it has double this value. The calculated heat of formation of hexamminecalcium fluoride is negative and this agrees with the fact that it cannot be prepared from gaseous ammonia and crystalline calcium fluoride. A. G.

Active Hydrogen. H. Collins (*Chem. News*, 1925, **131**, 33—38).—Theoretical. A discussion of the condition of hydrogen in the water molecule in various states; and of various physical constants (thermochemical etc.) of hydrogen. B. F.

Relationships between Hydrogen and Alkyl Compounds of Non-Metals. A. VON GROSSE (*Ber.*, 1925, **58**, [*B*], 1342—1345).—Hantsch and Becker (this vol., ii, 359) have shown that the graph obtained by plotting the absolute b. p. of the alkyl halides against the number of carbon atoms contained in their molecule is a straight line from which the b. p. of the halogen acids can be derived if the value $n=-1$ is used. This rule is also followed by the completely alkylated derivatives of the elements of the fourth, fifth, and sixth groups of the periodic systems, exceptions being met with in the hydrides of tellurium and polonium and in water and ammonia, which are associated. Similarly, if the molecular volumes of fully alkylated derivatives of elements of the sixth and seventh periods are plotted against n, a straight line is obtained from which, for $n=0$, values are derived for the molecular volumes of the hydrides which agree well with those observed experimentally.

H. W.

Refraction and Electron Constraint in Ions and Molecules. C. P. SMYTH (*Phil. Mag.*, 1925, [vi], **50**, 361—375).—The forces necessary to displace the outer electrons in ions and molecules are calculated from the ionic and molecular refractions. It is shown that the electron constraint increases with increase of nuclear charge when the number of underlying shells remains the same, but with increase of the latter the constraint decreases. The constraint upon an electron in an ion is increased by the proximity of other ions or molecules, particularly if combination occurs. The values of the constraints for the bonding electrons in the group C·C, C·H, H·H, are given as $9{\cdot}58\times10^5$, $6{\cdot}79\times10^5$, and $5{\cdot}6\times10^5$, respectively. Unsaturation decreases the constraint; the value for the electrons in the C:C bond is $5{\cdot}58\times10^5$. The constraints in various other electron groups are discussed. A. B. M.

Quantum Hypothesis and Gas Theory. A. SCHIDLOF (*Arch. Sci. phys. nat.*, 1924, [v], **6**, 281—293, 381—392).—Expressions are developed for the free energy and the entropy of a molecule of monatomic gas in a volume V, at a temperature T, first from the point of view of the generalised phase-space of Boltzmann and Gibbs, and, secondly, with an additional restriction, characteristic of the quantum hypothesis, that each element in the λ dimensional phase-space shall have a "volume" $h\lambda$, where h is Planck's constant. The quantum restriction only introduces a term $\log 1/h^3$ into the expressions. This theory is open to the objection that both classical and quantum ideas are used which are not strictly compatible. Moreover, the application of quantised motions to a gas molecule would result in velocity "jump," especially if the temperature is low, comparable with the mean velocity given by statistical methods. A deduction of Planck's radiation formula is given. The statistical theory of Bose is applied to eliminate the above difficulties, and it is shown that the formulæ of the kinetic theory of gases are in accord with the quantum theory.

C. W. B.

Determination of Molecular Dimensions and of Avogadro's Number from Colloidal Solutions. P. L. DU NOUY (*J. Phys. Radium*, 1925, [vi], **6**, 145—153; cf. *J. Gen. Physiol.*, 1919, **1**, 521).—By the measurement of the force required to lift a platinum ring from the surface of a colloidal solution, surface tensions may be determined continuously from the freshly-agitated down to the static condition of the liquid. The static surface tensions of colloidal solutions, plotted against concentration, show steep and definite minima at definite concentrations. These occur, for sodium oleate at 22°, at 1 in 750,000 (64 dynes/cm.^{2}), 1 in 1,220,000 (66 dynes/cm.^{2}) and 1 in 1,390,000 (73 dynes/cm.^{2}). After allowance is made for the sodium oleate adsorbed by the vessel, the thicknesses of surface-adsorbed oleate are found to be 12·30, 7·56, and 6·64 $\times$ 10^{-8} cm., respectively. The three figures are considered to represent the dimensions of the sodium oleate molecule, which is oriented along its longest axis at the first and along the others at the second and third minima. Hence the volume of the sodium oleate molecule is calculated to be $617{\cdot}44 \times 10^{-24}$ c.c.; the value of Avogadro's number, N, $6{\cdot}004 \times 10^{23}$, follows directly. W. A. C.

Precision *X*-Ray Measurements by the Powder Method. F. C. BLAKE (*Physical Rev.*, 1925, [ii], **26**, 60—70).—Corrections were applied for (*a*) the unequal shrinking of the photographic films and the influence of humidity on their length, and (*b*) the influence of the substance examined on the absorption of the *X*-rays. The lattice constant for iron is 2·8603$\pm$0·0002 Å.

A. A. E.

***X*-Ray Diffraction Patterns from Plant Fibres.** O. L. SPONSLER (*Nature*, 1925, **116**, 243).—The interplanar spacings 5·80, 3·30, and 2·60 reported by Herzog and Jancke (*Z. Physik*, 1920, **3**, 196) have been resolved, the new values being, respectively, 6·10, 5·40; 3·40, 3·20; 2·62, 2·58. The so-called 2·90 line did not appear when the $K\beta$ wave-lengths were screened out.

A. A. E.

Impulse Radiation and Compton's Scattered Radiation. G. MIE (*Z. Physik*, 1925, **33**, 33—41).—The free electron is supposed to be capable of existing in stationary states of different internal energy; in the lowest or stable state it does not radiate, but in higher states it radiates according to the Bohr $h\nu$ law. Impulse radiation is then explained as the result of a collision of the first kind (kinetic energy transformed into energy of excitation); the Compton scattered radiation is the reciprocal effect, it is the radiation which, according to the classical theory, must accompany the beginning of the sudden jump of the photo-electron ejected by the *X*-ray. The Compton electron and the photo-electron have the same origin, they differ merely in that the former completes its radiation and becomes a recoil electron whilst the latter suffers a collision of the second kind and receives kinetic energy instead.

E. B. L.

Crystal Structure of Chromium and Titanium. R. A. PATTERSON (*Physical Rev.*, 1925, [ii], **26**, 56—59).—Chromium is body-centred cubic, a_0 2·872 Å.; titanium is hexagonal close-packed, a_0 2·951 Å., axial ratio c 1·590; the computed densities are 7·23 and 4·49, respectively. Heat treatment does not affect the crystal form of titanium, but merely changes the size of the crystals. A. A. E.

Crystal Structure and Isomorphism of the Fluorides of Lithium and Magnesium. A. FERRARI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 664—671).—A structure analogous to that of rutile is assigned to magnesium fluoride from X-ray measurements of the powdered crystals. The elementary cell has the dimensions a=4·64 Å., c=3·06 Å., c/a=0·6596. The calculated density, 3·14, is in agreement with the observed. The X-ray intensities were calculated from the above measurements for magnesium fluoride, and from those of Bruni and Levi (this vol., ii, 281) for lithium fluoride. Results equally satisfactory were obtained from the formulæ of Debye and Scherrer, and of Ewald, which assume respectively that the intensities are proportional to the square of the structure factor, and to the structure factor. The volume of the elementary cell of lithium fluoride, containing 4 mols., is 65·55 Å.^{3}, and that of magnesium fluoride, containing 2 mols., is 65·85 Å.^{3} It is suggested from these results that the isomorphism between these salts, of elements of different valency, is explained by the equality of the elementary cell volumes. F. G. T.

Crystal Structure of Alkali Monosulphides. I. A. CLAASSEN (*Rec. trav. chim.*, 1925, **44**, 790—794).—The crystal structure of lithium and sodium sulphides is determined by means of Debye–Scherrer photograms and is found to be of the fluorspar (face-centred lattice) type. The lattice parameter for lithium sulphide is 5·70 Å. and the number of lithium sulphide particles per unit cell is four. For sodium sulphide the lattice parameter is 6·53 Å., and hence assuming the fluorspar structure the density of the anhydrous sulphide is calculated to be 1·85, in good agreement with the value 1·89 determined experimentally by the pyknometric method in xylene. The sums of the atomic radii for lithium and sodium sulphides are 2·47 and 2·83 Å., respectively, in good agreement with the values 2·52 and 2·79 Å. obtained by Bragg (A., 1920, ii, 537). J. W. B.

Two-stage Transformation of Magnetite into Hæmatite. L. A. WELO and O. BAUDISCH (*Phil. Mag.*, 1925, [vi], **50**, 399—408).—The change in magnetic permeability when magnetite is oxidised to ferric oxide at 220° has been measured; an increase in the maximum permeability from 2·93 to 3·39 was observed. When the magnetic ferric oxide was further heated at 550° in nitrogen, the permeability fell to 1·045, the value for the almost non-magnetic normal hæmatite. Magnetite can be heated at 800° in an inert atmosphere without permanent loss of permeability. By considering the crystal structure of magnetite, it is shown that the

extra oxygen required by the change $2Fe_3O_4 \longrightarrow 3Fe_2O_3$ can be inserted without undue strain, leaving the structure essentially unchanged. It is suggested that this structure represents the magnetic ferric oxide. A. B. M.

Magnetic Form of Ferrous Oxide. J. B. Ferguson (*J. Washington Acad. Sci.*, 1925, **15**, 279).—Since iron, ferric oxide, and ferro-ferric oxide undergo magnetic changes at 790°, 678°, and 530°, respectively, ferrous oxide might be expected to behave similarly. Ferrous oxide containing ferro-ferric oxide was reduced to free iron and in the subsequent recombination of the free iron the decrease in magnetic permeability did not correspond with the decrease in the free iron content of the sample. The results indicate that there is a magnetic form of ferrous oxide. R. A. M.

Non-magnetic Films of Nickel. L. R. Ingersoll and S. S. De Vinney (*Physical Rev.*, 1925, [ii], **26**, 86—91).—Nickel films, sputtered in hydrogen with a direct-current generator at 1000 volts, are initially non-magnetic, but when heated at 300—400° become magnetic. *X*-Ray spectrograms show that the magnetic film has the ordinary face-centred cubic lattice, but that the non-magnetic film is amorphous; it therefore appears that the ferro-magnetism of nickel is a property, not of the individual atom, but of the crystalline aggregate. The original film gave a very small Hall effect; its electrical resistance decreased on heat-treatment. A. A. E.

The Four Transverse Effects and their Relations in certain Metals. E. H. Hall (*Proc. Nat. Acad. Sci.*, 1925, **11**, 416—422).—A theoretical discussion of the Hall and allied effects. The author's theory of electric and thermal conductivity explains qualitatively the four transverse effects and gives approximately the connexion between the values for thermomagnetic and electromagnetic coefficients. R. A. M.

Crystal Tempering: Softening of Hard-drawn Tungsten Single-crystal Wire. F. Koref (*Z. Metallk.*, 1925, **17**, 213—220).—Fine tungsten wires consisting of a single crystal may be softened by tempering for a short time above 2100° without recrystallisation taking place, provided that the amount of deformation which the metal has undergone does not exceed a certain critical limit depending on the nature of the drawing and the thickness of the wire. Thick wires readily recrystallise after only slight reduction in area, whereas thin wires may be reduced 80% in area before recrystallisation sets in on tempering. All metallic single crystals appear to be strained internally during growth, and unless this strain is removed by suitable tempering the metal works badly and readily recrystallises on subsequent annealing. The density of the wires increases during tempering and the electrical resistance also changes. [Cf. *B.*, 1925, 637.] A. R. P.

Electric Moments of the Molecules of Monocarboxylic Acids and their Esters. C. P. Smyth (*J. Amer. Chem. Soc.*, 1925, **47**, 1894—1900; cf. A., 1924, ii, 810).—The electric moments

of a number of monocarboxylic acids and their esters have been calculated. The structures are assumed to be formed by the linking of atoms by electron pairs symmetrically located at the apices of regular tetrahedra. The causes of the differences in moments and the influence of chlorine substitution are considered. Support is given to the idea that valency forces are highly localised and directive in character. J. S. C.

Electrical Conductivity of Solid Crystal Hydrates. S. JAKUBSOHN and M. RABINOVITSCH (*Z. physikal. Chem.*, 1925, **116**, 359—370; cf. A., 1923, ii, 822).—The specific conductivities of the hexahydrates of the nitrates of zinc, manganese, cobalt, nickel, and copper were measured both in the solid and liquid states, and by extrapolation of the data relating to the latter state the degree of loosening of the crystal lattice, at 25° below the m. p. of each salt, was calculated. The conductivities of the solid salts increase from zinc to copper. Colour and conductivity are correlated. L. F. G.

Distilled Water in Biological Work. E. CANALS and R. GENEVET (*Bull. Soc. Chim. biol.*, 1925, **7**, 673—677).—Redistillation in glass vessels of water previously distilled from copper vessels, first from chromic acid and then from barium hydroxide, causes successive decreases in its conductivity. Water redistilled from barium hydroxide, and thus having a p_H nearer neutrality, attacks glass more readily than that distilled from acid. The purest water from an all-glass distillation apparatus had a conductivity of $1{\cdot}9\times10^{-6}$ and p_H 6·4 at 15°. H. J. C.

Spectro-chemistry of Compounds Containing Nitrogen. K. VON AUWERS and R. KRAUL (*Z. physikal. Chem.*, 1925, **116**, 438—465).—Optical data (refraction and dispersion) and densities are given for aniline, diphenylamine, carbazole, acridine, pyridine, quinoline, and a number of their derivatives. The relations between the chemical constitution and optical properties of these substances are discussed, and correlated with earlier observations. L. F. G.

New Determinations with the Micro Bomb Calorimeter. II. M. PADOA and B. FORESTI (*Ber.*, 1925, **58**, [*B*], 1339—1342; cf. A., 1923, ii, 737).—Determinations of the heat of combustion of benzoic acid and sucrose show that the authors' method is not inferior to any of those generally employed. The amount of material required in ordinary determinations is 0·01, in precise determinations 0·05—0·03 of that which is customary. H. W.

Lattice Energies, Heats of Hydration, and Heats of Solution. E. LANGE (*Z. physikal. Chem.*, 1925, **116**, 337—349).—Theoretical. Recently obtained data on the heats of solution of six alkali halides (this vol., ii, 791) are used to substantiate Born's formula for the lattice energies. It is probable that the repulsion term, n, in the formula has not the same value for all sodium and potassium halides. The heats of hydration of the ions in a saturated aqueous sodium iodide solution are calculated approximately and are smaller than those calculated by Fajans for infinite dilution. L. F. G.

Determination of the Heat of Dissociation of Mercury Molecules from the Band Spectrum of Mercury Vapour. E. KOERNICKE (*Z. Physik*, 1925, **33**, 219—230).—The mercury band at 2540 Å., just on the long wave-length side of the bright mercury line, is ascribed to the molecule Hg_2. From the strength of this absorption band at various temperatures and pressures the heat of dissociation is found to be 1·4 kg.-cal., the strength of the absorption being taken as an indication of the relative number of molecules present. E. B. L.

Possible Limits for the Heat of Dissociation of Oxygen. O. R. WULF (*J. Amer. Chem. Soc.*, 1925, **47**, 1944—1945).—The heat of dissociation of molecular oxygen into atomic oxygen is greater than 56,400 and less than 137,400 cal. per mole. J. S. C.

Improved Differential Method for the Exact Determination of Specific Heats of Aqueous Solutions; Including Results for Various Salts and Organic Acids. T. W. RICHARDS and F. T. GUCKER, Jr. (*J. Amer. Chem. Soc.*, 1925, **47**, 1876—1893).—The apparatus and technique for the precise determination of specific heats are described. The specific heats of thirteen solutions have been determined with an accuracy of 1 in 10,000. The results have been recalculated in terms of absolute heat capacity and also reduced to instantaneous heat capacities at 14°, 16°, 18°, 20°, and 22°. The minimum heat capacity of each solution occurs at a temperature lower than that of water. J. S. C.

M. P. of Inorganic Compounds and of Elements. E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **145**, 251—276; cf. this vol., ii, 374).—Considering uni-, bi-, ter-, and quadrivalent compounds of the type AB_1 (of which sodium fluoride, calcium oxide, scandium nitride, and titanium carbide may be taken as representatives), it is found that the number of valencies between the two elements exercises a fundamental influence on the m. p. Thus, lithium fluoride has m. p. 1115° Abs., magnesium oxide, m. p. 2920° Abs., titanium nitride, m. p. 3200° Abs., and niobium carbide, m. p. 4100° Abs. In compounds A_1B_1 of the same valency, the highest m. p. is found when there is approximate equality of the atomic or ionic volumes of the constituents. If the volume of the cation is small compared with that of the anion, a low m. p. may be expected (*e.g.*, lithium fluoride, chloride, and bromide compared with the corresponding sodium compounds). The magnitude of the volume of the anion of a compound appears to exercise an extreme influence on the position of the m. p., which decreases with increase in size of the anion. The condition for a compound to be gaseous at low temperatures is that the anion must be overwhelmingly great in comparison with the cation. The ratio necessary may be approximately calculated from Henglein's relation between molecular volume and m. p. (cf. A., 1922, ii, 44). The conclusions reached from a study of the m. p. of compounds are applied to the elements, special attention being paid to the influence of valency. The m. p. of elements may be considered as a function

of the force by which the atoms are held together by means of the valency electrons. By plotting m. p. against valency, it is concluded that at that region of the periodic system where metal passes into metalloid, the atoms possess the greatest possibility of mutual binding of the electrons, and the highest m. p. are also to be found.

L. L. B.

Structure of Glass. N. Seljakov, L. Strutinski, and A. Krasnikov (*Z. Physik*, 1925, **33**, 53—62).—The index of refraction and coefficient of expansion of glass show a maximum near 575°. This is the transition temperature of α- to β-quartz. Since *X*-ray analysis of glass shows no signs of small crystals of quartz, it is suggested that the peculiarity at this temperature is due to a change in the molecule of the silicate and that glass can truly be regarded as a supercooled, amorphous fluid. The structure of α-cristobalite is deduced from *X*-ray data and that of β-cristobalite is suggested.

E. B. L.

Stability Relations of the Modifications of the Polymorphous System Al_2SiO_5. F. Neumann (*Z. anorg. Chem.*, 1925, **145**, 193—238).—From specific heat determinations and the application of Nernst's heat theorem, the $A-U$ and $U-U_0$ relations for andalusite, disthene, and sillimanite have been investigated. Measurements have also been made with mullite, consisting of 62·89% Al_2O_3 and 37·11% SiO_2. The heats of transformation of the four modifications were determined by measurement of the heats of solution in 40% hydrofluoric acid. The values 90·13, 89·67, 83·42, 83·67 cal./mol. were found for the heats of solution of andalusite, disthene, sillimanite, and mullite, respectively, the experimental temperature being between 14° and 15°. The mean specific heats between the ordinary temperature and 300° to 1300° or 1400° were determined by the calorimetric mixture method, and from the values found the true specific heats were obtained graphically, with a mean error of ±0·5%. From these, the molecular heats were calculated and plotted against temperature. Molecular heat values are also tabulated for temperatures down to that of liquid hydrogen. The values at low temperatures are proportional to the cube of the absolute temperature, the proportionality factor for andalusite being 383×10^{-7}, for sillimanite, 310×10^{-7}. This holds up to about 25° Abs. The $A-U$ diagram for the system andalusite–sillimanite shows that, at atmospheric pressure from −273° to 1487°, sillimanite is the stable modification, whilst at higher temperatures andalusite is stable. The diagram for the disthene–sillimanite system shows that disthene is totally unstable. The andalusite–disthene diagram is not given, on account of the small difference between the heats of solution of these modifications. On heating at 1200°, andalusite undergoes a considerable change of structure, being converted into mullite and amorphous silica. Disthene is also converted into mullite and silica by heating at 1400°, but sillimanite undergoes no change on heating at 1300°.

L. L. B.

Calculation of the Vapour Pressure of a Solution of a Non-volatile Solute. S. B. MALI (*Phil. Mag.*, 1925, [vi], **50**, 141—145).—Theoretical. The case of a solvent which is monatomic in both the liquid and vapour states is considered. Stern's method (*Physikal. Z.*, 1913, **14**, 629) is modified by making allowance for the fact that the mutual attraction of the solute molecules and the surrounding solvent molecules results in the distribution of the solvent molecules just around a solute molecule being somewhat different from the distribution at points further away from the solute molecules. Further, owing to the presence of the solute molecules, the general distribution of the solvent molecules at points beyond the immediate influence of the solute molecules will be somewhat different from that in the pure solvent, even although solution is unaccompanied by any volume change. Subject to modifications for these effects, Stern's method leads to the equation $\log p = -\lambda_0'/kT - 0{\cdot}5 \log T + \log (2\pi m)^{3/2}\nu^3/\sqrt{k}$, where λ_0' denotes the latent heat of evaporation of a gram-mol. of solvent from the solution, and m and ν the mass and vibration frequency respectively of a solvent molecule. This expression differs only in the first term from that of Stern for the vapour pressure of the pure solvent, and, combined with the latter, leads directly to Raoult's law. F. G. T.

Vapour Pressures of Common Metallic Chlorides and a Static Method for High Temperatures. C. G. MAIER (*U.S. Bur. Mines, Tech. Paper* 360, 1925).—A static method of determining vapour pressures up to 1250° is described which involves no assumptions relative to the behaviour of the vapour according to the gas laws. Vapour pressure data for the commoner metallic chlorides, accurate enough for technical purposes, are recorded, together with the b. p. and the calculated heats of vaporisation. The vapour pressure of barium chloride is very small; that of calcium chloride is too small to measure. Ferric chloride, manganous chloride, and possibly cobalt chloride show traces of thermal dissociation at about 1000°. At high temperatures, the double salt, $NaAgCl_2$, appears to be formed from the separate chlorides; it has a vapour pressure greater than the sum of the vapour pressures of the separate chlorides at a definite temperature. The results for lead chloride agree with those of Eastman and Duschak (*U.S. Bur. Mines, Tech. Paper* 225, 1919); the vapour pressures of arsenic trichloride do not agree well with those found by Baxter, Bezzenberger, and Wilson (A., 1920, ii, 531). Cupric chloride has no measurable vapour pressure below its decomposition temperature. Anhydrous zinc chloride is prepared by passing chlorine over anhydrous zinc oxide at 600—700°. S. K. T.

Saturation Pressure of Liquids at Corresponding Densities. W. HERZ (*Z. anorg. Chem.*, 1925, **145**, 378—380; cf. this vol., ii, 494).—The ratio $p_{T_2}:p_K$, where p_{T_2} is the saturation pressure at the absolute temperature, T_2, at which the density is twice the critical density, approximates to a mean value of 0·464 for a large number of organic liquids and liquefied gases. Notable exceptions are helium (too low), tin tetrachloride (too low), methyl and ethyl

alcohols (too high). Ratios of pressures at temperatures corresponding with densities 2·75 times the critical density are also given, but the agreement is not good. L. L. B.

Isotherms of Several Gases between +400° and −183°. L. HOLBORN and J. OTTO (*Z. Physik*, 1925, **33**, 1—11).—Tables of new values of pv are given for hydrogen and neon, and also tables for helium, nitrogen, air, argon, and oxygen. E. B. L.

Preparation and Analyses of Constant Mixtures of Air and Carbon Dioxide. J. JOHNSTON and A. C. WALKER (*J. Amer. Chem. Soc.*, 1925, **47**, 1807—1817).—Marked changes in the direction or velocity of the wind are usually accompanied by variations in the carbon dioxide content of the air. An artificial mixture of air and carbon dioxide in fixed proportion is obtained on allowing air, under a constant pressure-head, to stream past one surface of a thin rubber diaphragm, and carbon dioxide, also under a constant head, to stream past the other surface. Carbon dioxide diffuses through the rubber much faster than the air, and the thin rubber sheet serves to regulate the mixing. The composition of the resulting mixture, under comparable conditions, depends on the effective area of the diaphragm. Certain refinements are introduced into the Pettenkofer method for the determination of carbon dioxide in air. J. S. C.

Vapours of the System Acetic Acid–Water. G. POVARNIN and V. MARKOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 381—382).—Preliminary results are given for the relation between the b. p. of aqueous acetic acid and the percentages of the acid in the liquid and in the vapour. For the 77% acid, corresponding with $C_2H_4O_2+H_2O$, the vapour contains approximately 62·5% of acid, corresponding with $C_2H_4O_2+2H_2O$. T. H. P.

Physical Equilibrium in the System Acetic Acid–Acetic Anhydride. G. POVARNIN and V. MARKOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 375—380).—The relation between the composition of the liquid and vapour phases is given by the equation $x(100-y)/y(100-x)=0{\cdot}419\mp0{\cdot}030$, where x and y denote the percentage concentrations of the anhydride in the vapour and liquid respectively. The b. p. varies linearly with the composition and is given by the expression, $T=118°+(22{\cdot}7°\pm1{\cdot}7°)y$. If suitable scales are used, the curve connecting b. p. and composition of the vapour coincides with that showing the relation of composition of vapour to composition of liquid. T. H. P.

Reversible Anomaly of Copper–Nickel Alloys in the Paramagnetic Region. P. CHEVENARD (*Compt. rend.*, 1925, **181**, 28—31).—The thermo-electric power, coefficient of thermal expansion, and electrical resistivity of copper–nickel alloys change suddenly at 450° in alloys containing about 50% Cu, the maximum effect occurring in the 52% Cu alloy (approximately CuNi). A. R. P.

Solubility of Mixtures of Hydrogen and Nitrogen in Liquid Ammonia. A. T. LARSON and C. A. BLACK (*Ind. Eng. Chem.*, 1925, **17**, 715—716).—The solubilities of hydrogen and nitrogen (3 : 1) in liquid ammonia have been determined between −25° and +22° at pressures of 50, 100, and 150 atm. The temperature coefficient is positive and the solubility is very nearly proportional to the pressure. [Cf. *B.*, 1925, 669.] D. G. H.

Solubilities of Sulphur Dioxide and Ammonia in Water. T. K. SHERWOOD (*Ind. Eng. Chem.*, 1925, **17**, 745—747).—The partial pressures of sulphur dioxide and ammonia over their aqueous solutions have been tabulated and graphed. [Cf. *B.*, 1925, 669.] D. G. H.

Solubility of the Crystallohydrates of Nickel Sulphate. N. V. TANCOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 335—341).—The solubilities of heptahydrated, blue hexahydrated, and green hexahydrated nickel sulphates per 100 parts of water are, respectively: 20°, 37·70, 40·09, 44·37; 25°, 40·40, 41·56, 45·36; 30°, 43·28, 43·56, 46·56; 35°, 47·03, 45·58, 47·76; 40°, 50·42, 47·60, 49·16. The corresponding temperature coefficients of solubility at 30° are 0·67, 0·49, and 0·24, respectively. The heptahydrate passes into the blue hexahydrate at 31·55°, and into the green hexahydrate at 36·7°. T. H. P.

Influence of Pressure on the Solubility of Substances. V. The System Naphthalene–Tetrachloroethane. E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 108—118).—The solubility of naphthalene in tetrachloroethane has been measured at 30° under pressures up to 1000 atm., the apparatus being similar to that previously described (A., 1923, ii, 386). The results are expressed very closely by the equation $\log c = 1{\cdot}54504 - 0{\cdot}26840 \times 10^{-3}p + 0{\cdot}0432 \times 10^{-6}p^2$, where c is the concentration in g. per 100 g. of solution, and p is the pressure in atmospheres. The existence of a minimum solubility, shown possible on theoretical grounds, is not established within the range of pressure investigated. A. B. M.

Solubility Relations of Isomeric Organic Compounds. I. J. JOHNSTON (*J. Physical Chem.*, 1925, **29**, 882—888).—The study of the equilibrium diagrams of *ortho*, *meta*, and *para* isomerides has been undertaken with a view to determine the relative proportion of these isomerides in reaction mixtures. The theory of ideal solutions is discussed. F. G. S.

Solubility Relations of Isomeric Organic Compounds. II. Determination of Freezing Temperatures of Binary Mixtures. D. H. ANDREWS, G. T. KOHMAN, and J. JOHNSTON (*J. Physical Chem.*, 1925, **29**, 914—925).—An apparatus for the accurate determination of time–temperature curves for pure substances and for binary or ternary mixtures is described. The principal advantages are: the effective temperature head is controlled and measured, only small quantities of material are necessary, and the temperature

is measured by means of a thermo-element of small heat capacity and small lag. The theory of cooling curves and the mode of interpretation of such curves for binary mixtures are discussed.

J. S. C.

Solubility of Ampholytes. H. VON EULER and K. RUDBERG (*Z. anorg. Chem.*, 1925, **145**, 58—62).—According to Bjerrum's theory (A., 1923, i, 444), the solubility of ampholytes should be increased by the addition of neutral salts. This is not the case for the pairs *l*-tyrosine–sodium chloride, *l*-tyrosine–lithium nitrate, and leucine–sodium chloride, but the solubility of glycylglycine is slightly increased by the addition of sodium chloride. The solubilities of amino-acids should also be greater in the presence of each other, but this is not the case for *dl*-leucine and *l*-tyrosine. In agreement with the theory, methyl-orange is more soluble in a dilute glycine solution than in water. Measurements of the influence of p_H on the solubility of glycine are in agreement with those of Kolthoff (this vol., i, 296).

A. G.

Solubility and Size of Grain. D. BALAREV (*Z. anorg. Chem.*, 1925, **145**, 122—126).—The increase in electrical conductivity of a saturated solution of barium sulphate, which occurs when the crystals are rubbed, is probably due to (1) the presence of barium chloride in the sulphate, (2) the greater solubility of broken than of complete crystals, and (3) the breaking up of atomic complexes. It is doubtful whether the greater solubility of small particles is an important factor. The subsequent fall in conductivity (cf. A., 1901, ii, 493; 1905, ii, 247) may be due partly to the crystallisation of barium sulphate on account of the dissolution of the chloride, but the velocity of crystallisation is much greater than the rate of fall of conductivity and the latter is probably mainly due to the slow restoration of equilibrium between the complete and broken crystals.

A. G.

Supersaturated Solutions. I. Mechanism of Separation of Salts from Supersaturated Solutions and the Formation of Rhythmic Precipitates in Gels. W. M. FISCHER (*Z. anorg. Chem.*, 1925, **145**, 311—364).—If supersaturated solutions of salts with valency product 1 are inoculated and shaken, crystallisation occurs immediately for the smallest degree of supersaturation. When the valency product is greater than 1, there is an induction period for slightly supersaturated solutions, during which no crystallisation occurs. At a certain supersaturation, this period vanishes, and crystallisation occurs immediately after inoculation. Salts which show an induction period possess, under the same conditions, a greater dissolution velocity than crystallisation velocity. The connexion between the length of the period (t) and the degree of supersaturation (x) is given by the relation $x/\sqrt{t}$=constant [although the author's numerical results and curves show that x decreases linearly with increase in $\sqrt{t}$.—ABSTR.]. The same relation, $x/\sqrt{t}$= const., applies to rhythmic precipitation, which occurs only with those salts which show an induction period. In the presence of agar-agar, gelatin, and dyes, all sparingly soluble salts can be

obtained as rhythmic precipitates. In accordance with a new theory of rhythmic precipitation, based on the variation of the time of precipitation from supersaturated solutions, periodic precipitates of barium sulphate and strontium sulphate have been obtained. It is found that a relation exists between the length of the induction period for a given degree of supersaturation and the cube of the crystallisation velocity of the salt. The larger the period, the smaller is the cubic crystallisation velocity. L. L. B.

Equilibrium between two Liquid Phases in the System Aniline–Acetic Acid–Water. E. ANGELESCU and D. MOTZOC (*Bul. Soc. Chim. România*, 1925, **7**, 11—24).—A study of the effect of acetic acid on the mutual solubilities of aniline and water has shown that with certain constant proportions of acetic acid closed solubility curves are obtained having an upper and a lower critical temperature. The formation of these curves indicates that a readily hydrolysed aniline acetate is formed in the solution. A. R. P.

Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum. I. R. MCHAFFIE and S. LENHER (*J. Chem. Soc.*, 1925, **127**, 1559—1572).—The adsorption of water on surfaces of glass and platinum has been studied by a new method in which a limited quantity of water was placed in an evacuated vessel of known dimensions, and the pressure measured at different temperatures. Above a certain temperature the pressure–temperature curve is linear, and the total number of water molecules present can be calculated. At lower temperatures, owing to adsorption, the pressure is less than the expected value, and the amount of water adsorbed can be calculated from the decrease in pressure. The adsorption and its accompanying free energy change are much greater on glass than on platinum. The thickness of the adsorbed film varies from 0 to 39 layers of molecules, according to the temperature and pressure. With platinum surfaces, this kind of adsorption begins at a definite pressure, below which no measurable adsorption occurs. W. H.-R.

Absorption of Hydrogen by Cerium, Lanthanum "Mischmetall," and Cerium–Magnesium Alloys. A. SIEVERTS and E. ROELL (*Z. anorg. Chem.*, 1925, **146**, 149—165; cf. A., 1924, ii, 185).—Using (1) impure cerium containing 95% of cerium and 4% of other rare-earth metals, (2) a lanthanum "mischmetall" containing 10% of cerium, and, (3), cerium–magnesium alloys containing up to 12% of magnesium, the absorption of hydrogen has been studied at temperatures from 20° to 1200°. For hydrogen at atmospheric pressure, the temperature–absorption curves of cerium and lanthanum "mischmetall" follow one another closely and show a marked fall in absorption between 1100° and 1200°. At 1100°, saturation can only be reached by heating specimens previously saturated at a lower temperature or by immediately treating the molten metal with hydrogen. If at 1100° specimens are first treated with hydrogen at low pressure, they will not take up the full amount of hydrogen necessary for saturation if the

pressure is raised. Saturated specimens lose all their hydrogen on prolonged keeping in a vacuum; their pressure–absorption isotherms show the general form previously described (Sieverts, *loc. cit.*), but are not satisfactorily reproducible. Unsaturated products do not lose all their hydrogen in a vacuum, and show normal absorption isotherms. The addition of 12% of magnesium only slightly lowers the absorptive power of cerium. These alloys are pyrophoric, but an alloy containing approximately 80% of cerium, 11% of magnesium, and 6% of aluminium is stable in air. Hydrogen from commercial compressed cylinders is absorbed less than electrolytic hydrogen, probably owing to the presence of organic sulphur compounds. W. H.-R.

Absorption of Arsenic and Oxalic Acids by Certain Calcined Oxides. P. P. KOZAKEVITSCH (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 477—492).—The dependence of the composition of the precipitates formed by the interaction of various oxides with arsenic and oxalic acids on the concentration of the acid in the liquid phase has been investigated (cf. Cox, A., 1904, ii, 563; 1906, ii, 757). T. H. P.

Adsorption of Silver Salts by Silver Iodide. J. S. BEEKLEY and H. S. TAYLOR (*J. Physical Chem.*, 1925, **29**, 942—954).—Investigations on the adsorption of various uni-univalent silver salts by silver iodide at 25° show that the order of decreasing adsorbability is: benzoate (1·4), acetate (8·2), nitrite (3·2), bromate (1·0), naphthalenesulphonate (4·8), benzenesulphonate (170), nitrate (1860), chlorate (100), ethylsulphate (1540), perchlorate (3240). The figures in parentheses denote the relative solubilities at 25°, the solubility of silver bromate, 0·0081 millimol. per g. of water, being taken as unity. Although there is no quantitative connexion between adsorbability and solubility, the less soluble salts are more strongly adsorbed than the more soluble salts. J. S. C.

Adsorption and Schulze's Law. H. B. WEISER (*J. Physical Chem.*, 1925, **29**, 955—965).—Schulze's law is merely a qualitative rule. The view of Dhar and others (A., 1924, ii, 737), that ions with the lowest precipitating power are adsorbed the most and *vice versa*, is disproved. The adsorption of barium ion during precipitation of arsenious sulphide sols has been determined from solutions of barium chloride and from mixtures of barium chloride with hydrogen chloride and the alkali metals. The adsorption of barium is reduced by the univalent ions in the order: hydrogen > potassium > sodium > lithium, which gives therefore the order in which these univalent ions are adsorbed. The same series is derived from the precipitation values, the salt containing the most readily adsorbed cation precipitating in lowest concentration. This method of determining relative adsorbabilities is of general application. The amounts of precipitating ion carried down on precipitation of a sol are determined by (i) adsorption by the electrically charged particles during neutralisation, (ii) adsorption by the neutral particles during agglomeration. The amounts of

(i) will, under comparable conditions, be equivalent, but those of (ii) will vary with the nature and concentration of the electrolyte. The adsorption values approach equivalence the less the adsorption capacity of the precipitated particles; thus the values are more nearly equivalent with arsenious sulphide sols than with hydroxide sols which have a large adsorption capacity. J. S. C.

Capillarity and Wetting. K. SCHULTZE (*Kolloid-Z.*, 1925, **37**, 10—17; cf. this vol., ii, 287).—The height of capillary rise, the influence on the formation of solutions, and the wetting of capillaries of non-circular cross-section are discussed. E. M. C.

Adsorption Activity and Surface Energy of Solids. B. ILJIN (*Z. physikal. Chem.*, 1925, **116**, 431—437; cf. A., 1924, ii, 663; *Physikal. Z.*, 1924, **25**, 369).—Theoretical. Three different methods give the following values for the effective adsorbing surface of 1 g. of charcoal: 10^5, $3{\cdot}3\times10^5$, $1{\cdot}8\times10^5$ sq. cm. The heat of adsorption for the same mass of a particular gas on equal areas of quite different surfaces (charcoal, mica) is constant. The surface energy of an adsorbent is correlated with the heat of adsorption, the dielectric constant, and the thickness of the film of the adsorbed gas. L. F. G.

Theory of Adsorption and Partition. A. FRUMKIN (*Z. physikal. Chem.*, 1925, **116**, 501—503).—Theoretical. The work done in transferring a molecule of a member of an homologous series from one phase to another is a term of an arithmetical progression; the partition coefficient is therefore a term of a geometrical progression. Consideration of the work done in transferring CH_2 groups from the surface of solutions of fatty acids to the space above leads to the conclusions of Langmuir and of Adam (A., 1922, ii, 687) regarding the orientation of these substances. L. F. G.

Simple Method of Testing Gibbs' Theorem. A. FRUMKIN (*Z. physikal. Chem.*, 1925, **116**, 498—500).—A dilute solution, of known strength, of lauric acid in light petroleum was added drop by drop to a measured water surface until no further change of surface tension indicated the formation of a saturated adsorption layer. The water surface is saturated by $5{\cdot}2\times10^{-10}$ mol. of lauric acid per sq. cm., Gibbs' equation giving $5{\cdot}7\times10^{-10}$ mol./cm.^{2} L. F. G.

Capillary Curves of Higher Fatty Acids and the Equation of State of the Surface Film. A. FRUMKIN (*Z. physikal. Chem.*, 1925, **116**, 466—484).—The surface tensions of octoic, decoic, and lauric acids were measured by Wilhelmy's method; the results are expressed graphically. The difference between the form of the curves for these acids and of those for the lower fatty acids is ascribed to the occurrence of attractive forces and of condensation phenomena in the adsorbed film (cf. Adam, A., 1921, ii, 488; 1922, ii, 687; 1923, ii, 539; this vol., ii, 195; *Proc. Roy. Soc.*, 1922, **A**,

101, 452), *i.e.*, the adsorbed films approximate in their behaviour to the unimolecular films which the insoluble fatty acids form on a water surface. By the introduction of a term which corrects for the mutual attraction of the adsorbed molecules, Szyzskovski's equation is modified to a form which gives fair agreement with the observed data. A comprehensive theory must allow, however, for the formation of molecular aggregates. L. F. G.

Effect of Sodium Hydroxide on the Surface Tension of a Solution of Sodium Nonoate. W. D. HARKINS and G. L. CLARK (*J. Amer. Chem. Soc.*, 1925, **47**, 1854—1856).—The surface tension of 0·1*N*-sodium nonoate at 20°, 20·2 dynes/cm., is increased to 48·8 dynes/cm. in presence of 0·008*N*-sodium hydroxide, further addition of base causing a linear decrease. The results indicate that the extremely low surface tension of sodium nonoate solutions is due to a surface film of the salt together with nonoic acid formed by its hydrolysis. The amount of colloid present in these solutions is by no means negligible (cf. McBain and Martin, T., 1914, **105**, 967), and the state of the colloid is dependent on the hydroxyl-ion concentration of the solution. J. S. C.

Surface Tension of Gelatin Solutions of Different Hydrogen-ion Concentration. L. DE CARO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 729—733).—Surface tension measurements of 2% gelatin solutions with varying hydrogen-ion concentrations have been made at 30° by the stalagmometric method. These solutions behave like those of other proteins. With increasing hydrogen-ion concentration, the surface tension rises to a maximum between p_H 8 and 9, falls then to a minimum at about p_H 4·5, and finally, in acid solutions, passes through a second maximum at p_H 3, which is lower than that occurring in alkaline solutions.

The author accepts the explanation advanced by Bottazzi and d'Agostino (A., 1913, ii, 115), according to which the protein lowers the surface tension of the solvent most when it is present in non-dissociated form. F. G. T.

Surface Concentration of Casein, Crystalline Egg-albumin, and Crystalline Hæmoglobin. J. M. JOHLIN (*J. Physical Chem.*, 1925, **29**, 897—913).—The changes of surface tension with time of aqueous solutions of casein, egg-albumin, oxyhæmoglobin, reduced hæmoglobin, and hæmoglobin–carbon monoxide and the influence of the addition of acid and alkali on the surface tensions of the first two substances have been investigated at 25° by the capillary rise method. The surface tension decreases with time according to the author's equation (this vol., ii, 388), the behaviour of alkaline solutions of egg-albumin being exceptional in that periodicity is observed. J. S. C.

Adsorption of the Phosphoproteins of Yeast by Various Adsorbents and the Elution of the Adsorbates. A. FODOR and R. SCHÖNFELD (*Kolloid-Z.*, 1925, **37**, 37—40).—The phosphoprotein of macerated yeast is readily adsorbed by aluminium and

ferric hydroxides and to a less extent by kaolin. The adsorption results in a loosening of the combination between phosphoric acid and the protein. The phosphoprotein precipitated by acid from macerated yeast gives up small quantities of phosphoric acid on treatment with ammonia. The elution with ammonia of the kaolin adsorbate liberates a considerable amount of phosphoric acid. A second eluate with ammonia of the aluminium hydroxide adsorbate gives a greater quantity of phosphoric acid than does the first, whilst in the case of the ferric hydroxide absorbate traces only are obtained. E. M. C.

Adsorption and Heterogeneous Catalysis. I. E. V. ALEKSEEVSKI (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 403—433).—Animal charcoal which has been heated and subsequently cooled in a desiccator acts as an extremely active adsorbent towards gases and vapours and retains its properties unchanged for a long period. The adsorption of a vapour is greatly accelerated if air saturated with the vapour is passed over the adsorbent. The results obtained with a large number of liquid organic compounds of various types show that the absorption does not depend on the physical constants, but is influenced greatly by the chemical nature of the compounds. Adsorption of acetylene, ethylene, *iso*butylene, alcohol, and benzene by catalysts such as floridin, alumina, powdered glass, kaolin, etc., is much less pronounced than by animal charcoal. The influence of charcoal on the reaction between ethylene and chlorine, and on various syntheses in which acetylene participates, has been investigated. T. H. P.

Hydration and Solution. H. A. TAYLOR (*J. Physical Chem.*, 1925, **29**, 995—1003).—The present position of the hydrate theory is reviewed and various criticisms are offered. From a study of the partition ratio of hydrochloric acid between benzene and aqueous solutions of various neutral salts and of glycerol, it is concluded that these aqueous solutions behave like pure water, there being no difference between combined and free water. This conclusion is confirmed by a study of the effect of sodium and potassium chlorides at *N* concentration on the partial pressure of hydrogen chloride over its concentrated aqueous solutions.
J. S. C.

Molecular Weight and Solution. W. D. BANCROFT (*J. Physical Chem.*, 1925, **29**, 966—972).—A consideration of the similarities and dissimilarities between true and colloidal solutions.
J. S. C.

Ebullioscopic Measurements in Mixed Solvents. B. H. CARROLL, G. K. ROLLEFSON, and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1925, **47**, 1791—1799).—An apparatus for ebullioscopic measurements capable of an accuracy of 1% is described. The values obtained for the change in b. p. of a binary liquid mixture on addition of a non-volatile solute are in fairly satisfactory agreement with those calculated from the equation of Lewis (A., 1906, ii, 524). J. S. C.

Effect of a Non-volatile Solute on the Partial Pressures of Liquid Mixtures at the B. P. B. H. CARROLL, G. K. ROLLEFSON, and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1925, **47**, 1785—1791).—Quantitative measurements of the changes in partial pressure produced by addition of a non-volatile solute to various binary liquid mixtures at the b. p. show that the diminution of the partial pressure of that component in which the added substance is more soluble is greater than that exhibited by the second component.
J. S. C.

Nature of Soap in Alcohol. W. A. PATRICK, W. L. HYDEN, and E. F. MILAN (*J. Physical Chem.*, 1925, **29**, 1004—1008).—Determinations of the b. p. of anhydrous and moist alcoholic solutions of sodium oleate over the concentration range 0·005—0·15*M* show that the soap is considerably ionised in dilute solution at the b. p. J. S. C.

Composition of a Constant-boiling Solution of Hydrogen Bromide in Water. D. T. EWING and H. A. SHADDUCK (*J. Amer. Chem. Soc.*, 1925, **47**, 1901—1904).—The constant-boiling mixture of hydrogen bromide and water at 760 mm. contains 47·795% of the former, showing that the distillate is not $HBr,5H_2O$ (47·381% HBr), as reported by Calm (*Ber.*, 1879, **12**, 613). The figure is higher than that recently determined by Carrière and Cerveau (A., 1923, ii, 555, 47·5% HBr). The constant-boiling temperature is about 125°. The distillate is $5·9061N_w$. J. S. C.

Internal Friction of Aqueous Sulphate Solutions. H. GRUNERT (*Z. anorg. Chem.*, 1925, **145**, 394—396).—Measurements of the viscosities of ammonium sulphate, sulphuric acid, and ammonium hydrogen sulphate solutions show that the formation of the acid salt is accompanied by an increase of the internal friction.
L. L. B.

Viscosity of Acetic Acid Solutions. N. DE KOLOSSOVSKI (*J. Chim. Phys.*, 1925, **22**, 321—324).—The viscosities of approximately 10% acetic acid solutions have been measured between 11° and 30°. The results confirm those of Davis and Jones (A., 1915, ii, 423), but disagree with Wijkander's figures. Re-calculation of the apparent molecular heat of acetic acid in solution gives a mean value of 41, the observed value being 37. Acetic acid, therefore, is not hydrated in solution. S. K. T.

Diffusion of Water through Collodion Membranes between Solutions of Mixed Electrolytes. E. F. ADOLPH (*J. Biol. Chem.*, 1925, **64**, 329—368).—The diffusion of water through a collodion membrane, either untreated or saturated with gelatin, is not affected by the presence of a non-electrolyte in one of the solutions separated by the membrane; in the case of plain collodion membranes the effect of electrolytes is small except that multivalent anions increase the rate markedly. With membranes treated with gelatin, the rate of diffusion is much greater in all cases; the magnitude of the effect increases with the valency of the ions, but the

predominating influence is exerted by those ions of which the electrical charge is opposite to that of the protein in the membrane. In the case of mixed electrolytes, some ions tend to depress the action of others, and the ultimate rate of diffusion is determined by the relation between the concentration of "depressing" cations and that of effective anions. The depressing influence of such a salt as sodium chloride on the effect of (*e.g.*) potassium ferrocyanide is still greater when the two electrolytes are on different sides of the membrane than when they are on the same side, with pure water on the other. It is considered that, within the range of variation of concentrations of biological fluids, the effect of the ions in themselves is not sufficient to account for water transport across cell-membranes. C. R. H.

Ionic Antagonism. R. MINAKAMI (*Biochem. Z.*, 1925, **158**, 306—318).—If the chlorides of various uni- and di-valent radicals are added to soap solutions, there is a marked change in the surface tension. The physiologically antagonistic sodium chloride and calcium chloride exhibit no antagonistic action when added together to a soap solution, whereas lithium and magnesium or lithium and barium show marked antagonism. The relatively coarse-grained structure which is brought about in soap solutions by the addition of a univalent cation, particularly lithium, is changed by very small quantities of calcium or, better, magnesium into a fine-grained structure. This latter state of division can only be achieved by the addition of a definite quantity of magnesium or similar ions, not by diminishing the lithium content without addition of magnesium. H. D. K.

Colloidal Bismuth. A. GUTBIER and T. KAUTTER (*Z. anorg. Chem.*, 1925, **146**, 166—178; cf. Meyer, A., 1903, ii, 285).—One part of a 10% solution of bismuth nitrate in 88—90% glycerol is treated with 36 parts of 0·45% aqueous gum-arabic, the mixture reduced with 5 parts of 1% aqueous sodium hyposulphite solution, and the whole quickly diluted with 60 parts of water; the resulting colloidal solution is filtered and on careful evaporation a black, metallic residue is obtained which dissolves completely in water to form a colloidal solution. The particles migrate to the anode in Coehn's apparatus. The black residue contains 18% of bismuth and about 1% of sulphur, which is present as colloidal sulphur and not as sulphide. Gelatin and extract of "Tubera Salep" are less satisfactory protective agents for the preparation of colloidal bismuth, which is unstable if prepared by reduction without such an agent. W. H.-R.

Preparation of Colloidal Ferric Hydroxide Solutions by Oxidation of Ferrous Hydrogen Carbonate. N. N. GAVRILOV (*Kolloid-Z.*, 1925, **37**, 46—50).—The oxidation of ferrous hydrogen carbonate by means of air yields only a precipitate of ferric hydroxide, which is not peptised in presence of small amounts of hydrochloric acid or ferric chloride. With larger quantities of ferric chloride, colloidal ferric hydroxide is formed, but only from the

added ferric chloride. Hydrogen peroxide gives a white precipitate with ferrous hydrogen carbonate, but in the presence of ferric chloride or hydrochloric acid a colloidal solution of ferric hydroxide is rapidly formed. The minimum amount of ferric chloride necessary for peptisation in the oxidation of ferrous hydrogen carbonate is about 7% of the total iron. E. M. C.

Technical Preparation of Colloidal Ferric Hydroxide Solutions. G. STADNIKOV and N. GAVRILOV (*Kolloid-Z.*, 1925, **37**, 40—46).—Colloidal ferric hydroxide solution for use as a coagulator in the drying of peat can be prepared by the oxidation of solutions of ferrous hydrogen carbonate by means of chlorine water or hypochlorous acid. The necessary concentration (0·04% of ferrous iron) can be obtained on a commercial scale by the treatment of iron turnings with water and a current of flue gas. A progressive diminution in concentration occurs on repeated treatment with mixtures of air and carbon dioxide when the carbon dioxide content is greater than one-half. [Cf. *B.*, 1925, 711.] E. M. C.

Silicic Acid Sol. H. R. KRUYT and J. POSTMA (*Rec. trav. chim.*, 1925, **44**, 765—789).—Changes in the viscosity and p_H values of a silica sol with time and length of dialysis have been determined and correlated, and the effects produced by the addition of various electrolytes investigated. The sols were prepared by pouring a solution of sodium silicate into 20% hydrochloric acid and dialysing and were found by cataphoresis measurements to be negatively charged. Poiseuille's law holds good and the sols are more stable at the ordinary than at higher temperatures. By adding a solution of 50 g. of sodium silicate in 200 c.c. of water to 70 c.c. of acid, sols are obtained for which p_H=4·5 and the viscosity of which increases with time; on the other hand, by using a solution of 50 g. of sodium silicate in 150 c.c. of water, the p_H value is >6 and the viscosity of these sols decreases with time, the latter phenomenon being due to the occlusion of sodium silicate from the more concentrated solution. The addition of hydrochloric acid to the latter sols in quantities sufficient to reduce the p_H value to 4·5 or less converts these into sols of increasing viscosity, whilst the addition of sodium hydroxide or silicate solutions to sols of the first type causes an initial increase in viscosity on account of the greater electroviscous effect due to the greater negative charge, and then converts them into sols of decreasing viscosity. Addition of hydrochloric acid or salt solutions to a sol of increasing viscosity first removes the negative charge and hence lowers the initial relative viscosity due to the removal of the electroviscous effect, whilst on further addition the sol becomes positively charged and the viscosity rapidly increases with final gelation or flocculation. The initial viscosity is considerably lowered by the addition of 50% of water to the sols, but on account of the dilution, changes in the viscosity of such sols are extremely small. Addition of alcohol to the sols also causes an initial decrease in the viscosity, but in this case the viscosity continues to decrease due to the

slight dehydrating action of the alcohol. The action of hydrochloric acid, barium chloride, and aluminium chloride in producing flocculation of the sols is not the same. The sols take up hydroxyl and chlorine ions, the disappearance of the former on the addition of sodium hydroxide or silicate to the sol being established by p_H determinations. The larger the number of hydroxyl ions added to the sol, the more sodium chloride but the less barium chloride is necessary to cause gelation; no explanation of this phenomenon is at present forthcoming. J. W. B.

Elasticity of Ammonium Oleate Solutions and the Variable Viscosity of Two-phase Systems. E. HATSCHEK (*Kolloid-Z.*, 1925, **37**, 25—26).—The elasticity of ammonium oleate is readily demonstrated. After being rotated, the solution comes to rest by moving in a direction opposite to that of the rotation. The effect is shown by solutions as dilute as $N/140$ with a relative viscosity of 1·08. A variation of viscosity with the shear-gradient is found with coarse suspensions as well as with emulsoid sols and may be accounted for by postulating a labile sheath of rigid liquid around the particles, the thickness of the sheath depending on the shear-gradient. E. M. C.

Elasticity of Gelatin in Relation to p_H and Swelling. G. W. SCARTH (*J. Physical Chem.*, 1925, **29**, 1009–1021).—The elastic properties of gelatin gels in their dependence on the p_H value have been examined. The reciprocal of the extension—the resistance to stretch—has a minimum value at p_H 4·7 and maxima at p_H 3 and p_H 11, the alkali maximum being the higher. Young's modulus for isotropic gelatin varies but slightly between p_H 4·7 and 11. Lanthanum nitrate has the same general effect on gelatin at a p_H of 4·7 as is produced by the addition of acid or alkali to isoelectric gelatin. Volume and resistance to stretch increase up to a concentration of salt 10^{-2}—$10^{-3}M$, and then decrease. The modulus of elasticity remains constant until fairly high salt concentrations are reached, and then decreases. Variation in p_H of the surrounding medium affects the elasticity of gelatin in three ways: (1) directly through combination or by adsorption with the reagent, acids reducing the elasticity whilst alkalis in low concentration cause a slight increase and at high concentration a decrease, (ii) by modification of imbibition resulting from such combination, swelling increasing the total resistance to stretch and maintaining the modulus of elasticity constant in spite of dilution, (iii) by causing structural changes entailing a loss of elasticity. Changes (i) and (ii) are reversible, whilst (iii) is partly reversible. Theories of swelling and of protoplasmic contraction are discussed. J. S. C.

Colloid Filtration. L. ZAKARIAS (*Kolloid-Z.*, 1925, **37**, 50—58).—The author has studied the relation between the solid support and the semi-solid membrane in ultra-filters of collodion supported on unglazed porcelain. In filtration through unglazed porcelain alone, a considerable resistance is offered by air within the capillaries; the rate of filtration rises to a maximum and rapidly falls.

Evacuation of the plate and the use of air-free water doubles the rate of filtration. For plates of unglazed porcelain of different porosities there is a close proportionality between the rates of filtration before and after treatment with a constant collodion solution. The rate of filtration through plates treated repeatedly with collodion is inversely proportional to the number of treatments. Increase of pressure increases the permeability as well as the rate of filtration for both hydrophilic and hydrophobic colloids, although there is no simple relationship between permeability and rate of filtration. Increase of pore size by swelling of the membrane does not necessarily increase the rate of filtration on account of the compensating effect of the increase in length of the capillaries. A colloid filter with a semi-solid membrane is regarded as an adsorption sieve, capable of swelling, but swelling is not an essential feature of a colloid filter since a porcelain plate stopped by barium sulphate forms a dense filter. E. M. C.

Swelling. I. Swelling of Agar-agar Gels as a Function of Water Content before Swelling. B. L. Clarke (*J. Amer. Chem. Soc.*, 1925, **47**, 1954—1958).—The percentage swelling of agar-agar gels in water increases rapidly from about 800% when the gel contains so little water that none is extracted by drying over phosphorus pentoxide, to 3903% when the gel contains 0·313 g. of water per g. of agar. Further increase in water content occasions a sharp fall in swelling power, to a water content of 0·554 g. per g. of agar, the swelling power thereafter diminishing much more slowly with increase in water content of the original gel. Freshly-cast agar-agar gels are opaque, and on drying in thin plates, become transparent sharply at a water content of 0·554 g. per g. of agar, probably indicating a change of phase at the point at which the swelling power commences to increase rapidly with decreasing water content, although no corresponding discontinuity is exhibited by the vapour pressure isotherm (cf. Katz, A., 1917, ii, 245). The above results afford an explanation of the loss of swelling power of agar-agar gels on storage. F. G. W.

New Pattern Formed by Coloured Salts in Solid Gels. E. R. Riegel and L. Widgoff (*J. Physical Chem.*, 1925, **29**, 872—874).—Copper ferrocyanide formed by diffusion of copper sulphate in 1—5% aqueous solution into a gelatin cake containing 0·05—0·2% of potassium ferrocyanide, is not evenly distributed throughout the cake but is concentrated into dark red zones separated by clear spaces. Lead chromate formed in a similar way from 0·1% potassium chromate in gelatin and 5% lead nitrate solution gave both the zone pattern and rhythmic banding. The formation of clear zones reaching to the corners when the edges are sharp indicates that the entering soluble salt travels in straight lines perpendicular to the walls of the cake. F. G. S.

Protection of Colloidal Solutions by the Addition of Electrolytes in Quantities Insufficient to produce Flocculation. A. Boutaric and (Mlle.) G. Perreau (*Rev. gén. Colloid*, 1925, 3, 129—136, 167—176).—The stability of sols of gamboge, resin-

mastic, and arsenic trisulphide has been studied in the presence of varying amounts of electrolytes. The rate of flocculation of sols containing a given electrolyte has, in particular, been examined when larger quantities of the same electrolyte are added. Differences are shown to exist according to the period of time that has elapsed between the preparation of the sols and the time of the measurement. Sols which originally contained some electrolyte flocculate more slowly than those which were practically free from electrolyte. When the amount of electrolyte is increased the degree of protection at first increases, but further increase in the amount of electrolyte diminishes the protection. Especially interesting results are obtained with ammonium and lithium salts. The behaviour of the sols towards electrolytes other than those used in their preparation shows that the presence of lithium chloride protects arsenious sulphide sol from flocculation by potassium, magnesium, barium, and ammonium chlorides, whilst the flocculation is accelerated by cadmium and aluminium chlorides.

C. I. B. V.

Influence of Hydrogen-ion Concentration on the Protective Action of Gelatin on Zsigmondy's Standard Gold Sol. H. V. TARTAR and J. R. LORAH (*J. Physical Chem.*, 1925, **29**, 792—798).—The protective action of gelatin on Zsigmondy's standard gold sol has been measured in the presence of acetic, oxalic, hydrochloric, and phosphoric acids. The concentration of hydrogen ion has little effect on the protective action over the p_H range 8 to 5, but below a p_H of approximately 4·7 the protective action decreases very rapidly with increase of hydrogen-ion concentration. F. G. S.

Studies in Emulsions. W. SEIFRIZ (*J. Physical Chem.*, 1925, **29**, 834—841).—The effect of hydrogen and barium chlorides and sodium and barium hydroxides on olive oil emulsions stabilised by various emulsifying agents has been studied. Reversal of phases takes place with hydrochloric acid and frequently with barium chloride at a p_H of 7·2, but the main factor causing reversal cannot be ascribed to the hydrogen-ion concentration, for sodium and barium hydroxides may cause reversal in opposite directions and highly alkaline oil-in-water emulsions may be reversed by barium chloride. The effect of the phase volume ratio on the type, texture, and stability (cf. Robertson, A., 1910, ii, 697) is described using refined petroleum oils and aqueous casein. Reversal frequently occurs on keeping. The behaviour of vegetable oils (cf. Seifriz, A., 1924, i, 127) is compared with that of petroleum oils. All the water-in-oil emulsions of the vegetable oils are readily reversible by sodium hydroxide into stable oil-in-water systems, and may be reconverted into the former by barium chloride or barium hydroxide.

F. G. S.

Sensitisation of Congo-red by Globulin. G. ETTISCH and H. RUNGE (*Kolloid-Z.*, 1925, **37**, 26—31).—The sensitisation of Congo-red towards flocculation by salts which is produced by the addition of globulin, as observed by Brossa (A., 1923, i, 397) but not by

Becker (*Z. Immun. Therap.*, 1924, **41**, 378), depends on the reaction and salt content of the two systems. Congo-red should be used immediately after dialysis, since on exposure to air it takes up carbon dioxide, and becomes acid, turbid, and more deeply coloured. The reaction and conductivity of globulin suspensions remain constant only for 3 days. Pure Congo-red does not peptise globulin suspensions. The peptisation of globulin and Congo-red by acid, alkali, or salts is independent. Globulin may be peptised by acid at about p_H 4·0 without causing any colour change of Congo-red. There is no affinity between the micelles of globulin and of Congo-red, and the formation of a turbidity in a Congo-red–globulin mixture is a true protein flocculation. The sensitising action of lecithin towards Congo-red (cf. Beck, this vol., ii, 527) is similarly explained. E. M. C.

Theory of Liesegang Ring Formation. N. R. Dhar and A. C. Chatterji (*Kolloid-Z.*, 1925, **37**, 2—9; cf. A., 1922, ii, 627; 1924, ii, 158).—Further evidence is advanced in support of the theory that Liesegang rings are formed by the coagulation of a peptised sol and the adsorption of the same material from adjacent layers. Two types of ring structure are recognised, according as the precipitate layer is followed by a region free from precipitate or one which contains the peptised sol. Mercuric iodide, cadmium sulphide, antimony sulphide, and silver sulphide form the second type of structure, and it is shown that the corresponding sols are not adsorbed by the solid precipitate as is the case for substances giving the first type of ring structure. E. M. C.

Molecular Attraction and the Equation of State. K. K. Järvinen (*Z. physikal. Chem.*, 1925, **116**, 420—430; cf. *ibid.*, 1920, **96**, 367).—Theoretical. L. F. G.

Chemical Theory of Corresponding States. G. Bottard (*J. Chim. phys.*, 1925, **22**, 349—352).—Theoretical. In the reduced general equation of state, $F(\pi, \phi, \theta, \alpha, \beta, \ldots) = 0$, the theorem of corresponding states can only hold for fluids for which the parameters $\alpha, \beta, \ldots$ are constant. The latter characterise the chemical type of the fluids, and it is shown that the reduced vapour pressure, π, the reduced molecular volume of vapour, ϕ_1, and of fluid, ϕ_0, the reduced heat of vaporisation, $\lambda(= L/p_c v_c)$, and the reduced entropy, $\sigma(= \lambda/\theta)$, are functions of them. Thus, at a given reduced temperature, θ, π, ϕ_0, ϕ_1, and λ are constant for the different members of a chemical family. It is also shown that the change of entropy accompanying evaporation is constant for all fluids of the same chemical family at corresponding temperatures. S. K. T.

Molecular Interaction in the Liquid State. G. N. Antonov (*Phil. Mag.*, 1925, [vi], **50**, 265—289; cf. A., 1918, ii, 437).—The previous theory of molecular complexity in the liquid state is extended from liquid–liquid to liquid–gas systems, by assuming that the process of formation of liquids is due to the formation of associated molecules, and that the molecules forming the gaseous phase penetrate the liquid phase without suffering any substantial

change of concentration. The empirical law obtained by the author (A., 1924, ii, 829) for the variation with temperature of the difference between the densities of the liquid and vapour phases of a substance is deduced from the above assumptions, since the difference of the densities then represents the concentration of the associated molecules. The relation becomes $Ae^{\lambda\delta} = T+B$, where A, B, and λ are constants, T is the temperature reckoned from the critical temperature downwards, and δ the difference of density. Experimental data show that the δ–T curve for ethyl acetate is discontinuous, and consists of several portions, each satisfying the above equation, with different constants for each portion. From the similar behaviour of propyl alcohol and hexamethylene, it is suggested that this is a general law for all liquids, and that the molecular clustering which is assumed in the liquid state takes place according to the law of multiple proportions. Some liquids undergo between their m. p. and the critical temperature a greater number of such changes than other liquids. The relation between temperature and latent heat of evaporation, surface tension, and viscosity is investigated, and it is shown that these curves also are discontinuous, breaks occurring at the same temperatures in the different curves for the same liquid. Each portion of the curves for density and latent heat of evaporation satisfies the above equation, which is general for normal and associated liquids, and holds good for all ranges of temperature. Each portion of the curves for surface tension (α) and viscosity (η) is represented by the equation $\alpha+B=Ae^{\gamma T}$ or $\eta+C=De^{\kappa T}$. Discontinuity is an intrinsic characteristic of liquids, and it is probable that definite molecular changes occur in the several intervals of temperature. F. G. T.

Parameters Depending on Temperature in Statistics: the Debye Theory of Electrolytes. P. Gross and O. Halpern (*Physikal. Z.*, 1925, **26**, 403—407; cf. A., 1923, ii, 459, 724; 1924, ii, 386; this vol., ii, 171, 513).—Theoretical. A mathematical analysis of temperature effects, the results being applied to the Debye–Hückel theory of strong electrolytes. The variation of the dielectric constant with the temperature is considered in reference to the calculated and observed heats of dilution. Within the range imposed by its assumptions the Debye theory is regarded as valid. R. A. M.

Derivation of the Fundamental Equation from the Law of Mass Action for Condensed and Heterogeneous Systems. J. J. van Laar and R. Lorenz (*Z. anorg. Chem.*, 1925, **145**, 239—250).—A mathematical development of the equilibrium equation derived by Lorenz (cf. A., 1924, ii, 761) on the basis of the law of mass action, the vapour-pressure theory of van Laar, and the conception of thermodynamic potentials. The equation is applied first to the case of ideal gases, and an equation is obtained which gives the molar potentials of the components of an ideal gas mixture. Similar considerations are also applied to van der Waals' equation of state. L. L. B.

Third Law of Thermodynamics and Calculation of Entropies. T. J. WEBB (*J. Physical Chem.*, 1925, **29**, 816—833).—The entropy of cadmium chloride hydrate has been calculated on the assumption of the validity of the third law from the energetics of its formation from silver, lead, or mercurous chlorides, cadmium, and water. The values agree within the limit of experimental error, as do the values of the entropy of cadmium iodide obtained in a similar manner. Direct calorimetric measurements of the total energy change of a chemical reaction is often more accurate than its calculation from the free energy and the temperature coefficient of the free energy. A calorimetric determination of the heat of formation of solid silver iodide from solid silver and solid iodine has been made and the value 14,975±50 cal. obtained. This leads, on the assumption of the third law, to a value of 13·95 for the entropy of iodine as compared with 14·24 from a study of the formation of zinc iodide, and 13·95 obtained from the specific heat data of Lange (cf. this vol., ii, 96). The heat of formation of silver bromide has been determined and its entropy at 25° calculated by two methods.

F. G. S.

Free Energy of Dilution and the Activity of the Ions in Aqueous Solutions of Barium Chloride. J. N. PEARCE and R. W. GELBACH (*J. Physical Chem.*, 1925, **29**, 1023—1030).—The *E.M.F.* of concentration cells containing barium chloride, with and without ion-transference, have been measured with an accuracy of ±0·05 mv. The transference numbers of the barium and chloride ions and the free energy and heat content decrease attending the transfer of 1 mol. of barium chloride from concentration c to a concentration $0{\cdot}10M$ have been calculated. The activity coefficients derived from the *E.M.F.* data are in close agreement with those from f. p. data.

J. S. C.

Dissociation Constants of Selenious Acids. J. S. WILLCOX and E. B. R. PRIDEAUX (*J. Chem. Soc.*, 1925, **127**, 1543—1546).—Measured volumes of standard sodium hydroxide solution were added to 20 c.c. of a 0·05 *M*-solution of selenious acid in the presence of a suitable indicator. The colours were matched by the addition of the same alkali to 20 c.c. of the B,D.H. "universal" indicator containing the same number of drops of indicator. The hydrogen-ion concentrations were thus obtained, from which the first and second dissociation constants of selenious acid were calculated as $K_1=4{\cdot}0\times10^{-3}$, and $K_2=0{\cdot}87\times10^{-8}$. The first end-point gives accurate titrations with *p*-nitrophenol as indicator; cochineal, lacmoid, and resazurin should also be suitable. The second end-point is not so sharp, but fair results are obtained with thymolphthalein (to a full blue).

W. H.-R.

Ionisation of Weak Electrolytes in Water–Alcohol Solutions. II. Relations between Chemical Constitution and Alcohol Sensitivity of Acids and Bases. M MIZUTANI (*Z. physikal. Chem.*, 1925, **116**, 350—358; cf. this vol., ii, 793).—Data corresponding with those previously obtained for other substances are

given for dilute solutions of formic, butyric, and *iso*valeric acids, methylamine, dimethylamine, trimethylamine, ethylamine, aniline, methylaniline, dimethylaniline, *o*- and *m*-toluidine, and pyridine. New data for ammonia are given. The effect of alcohol on the ionisation of the aliphatic acids increases with the length of carbon chain. Benzoic acid behaves similarly to *iso*valeric acid. The introduction of a hydroxyl group (*i.e.*, to form lactic or salicylic acid) decreases the sensitivity of acids to alcohol. All the bases are less affected by alcohol than are the acids. Ammonia is the least affected, but substitution of hydrogen by methyl groups greatly increases the sensitivity. Similarly, the toluidines and the methylanilines are more sensitive than aniline, which is very nearly as insensitive as ammonia. L. F. G.

Ionisation of two Electrolytes in Alcohol–Water Mixtures; Influence of Environment on Ionisation. F. BRADLEY and W. C. McC. LEWIS (*J. Physical Chem.*, 1925, **29**, 782—791).—The ionisation of salicylic and of cyanoacetic acids, at dilutions of 8 to 1024 litres, has been examined in alcohol–water mixtures containing 0—100% of alcohol. A slight decrease of the ionisation constant was observed as the dilution was increased. The formula, $K=K_1(k_1/k_2)[H_2O]^n e^{(E_0'-E_0)/DRT}$, has been deduced, where K is the ionisation constant, D the dielectric constant of the medium, K_1 the equilibrium constant of the reaction $HA+nH_2O=HA,nH_2O$, k_1 and k_2 are the velocity coefficients for the ionisation and recombination of the ions, respectively, E_0 is the critical increment of ionisation in a medium of unit dielectric capacity, identified with the electrostatic work of separation of the ions, and E_0' the sum of the critical increments of the ions, identified with the work necessary to remove the solvent molecules with which the ions are hydrated. The values of the constants $K_1(k_1/k_2)$ and $(E_0'-E_0)$ were found by using two experimentally determined values of K for different solvent mixtures, and the value of n was found by trial to be 2. The ionisation constants calculated from the dielectric constants and the above data are in good agreement with the observed results. The critical increment of ionisation deduced for a medium of unit dielectric capacity is of the same order as that of the ionisation of other compounds in the gaseous state. F. G. S.

Direction of Spontaneous Crystallisations and Chemical Transformations. N. V. TANCOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 342—367).—A further discussion of this subject (cf. A., 1917, ii, 367). T. H. P.

Singular Points in Chemical Diagrams. N. S. KURNAKOV (*Z. anorg. Chem.*, 1925, **146**, 69—102).—A theoretical discussion of certain features exhibited by equilibrium diagrams. W. H.-R.

Singular Points in Chemical Diagrams. N. S. KURNAKOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 219—254).—A *résumé* of the subject. T. H. P.

Equilibrium Pressures of Hydrates of Gases. G. TAMMANN and G. J. R. KRIGE (*Z. anorg. Chem.*, 1925, **146**, 179—195).—The systems sulphur dioxide–water, chloroform–water, and carbon dioxide–water have been investigated by measurements of vapour pressure and of f. p. at high pressures and low temperatures. Sulphur dioxide forms a single hydrate, $SO_2,6H_2O$, which forms a eutectic with ice at $-2{\cdot}6°$. The dissociation pressures of this hydrate and the influence of pressure on the m. p. and eutectic temperatures have been determined. Chloroform forms a single hydrate containing less water than corresponds with the formula $CHCl_3,18H_2O$ given by Chancel and Parmentier (A., 1885, 363). Carbon dioxide forms a hydrate, $CO_2,6H_2O$, for which the dissociation pressures have been determined from $-20°$ to 43°. The gas hydrates $CO_2,6H_2O$, $N_2O,6H_2O$, $Kr,5H_2O$, and $A,(5—6)H_2O$ form a group for which the logarithmic dissociation pressure–temperature curves are nearly parallel. A second group is formed by the hydrates $Br_2,10H_2O$, $Cl_2,8H_2O$, and $SO_2,6H_2O$, for which the curves are parallel but of different slope compared with the first group.

W. H.-R.

System Sodium Sulphite–Sodium Hydroxide–Water. D. L. HAMMICK and J. A. CURRIE (*J. Chem. Soc.*, 1925, **127**, 1623—1628).—The equilibrium conditions have been investigated by Schreinemakers' residue method at 0·15°, 20°, 25°, and 32°. At 0·15°, the solubility of the sulphite in presence of excess of sodium hydroxide is very small, and the coexisting solid phases are sodium sulphite heptahydrate, anhydrous sodium sulphite, and sodium hydroxide tetrahydrate. The isotherms at 20° and 25° are very similar except that sodium hydroxide monohydrate replaces the tetrahydrate. At 32°, however, the sodium sulphite heptahydrate is no longer formed, in agreement with the value 31·5° found by Lewis and Rivett (J., 1924, **125**, 1156) for the transition temperature $Na_2SO_3,7H_2O \rightleftharpoons Na_2SO_3$, but contrary to the value 22° found by Hartley and Barrett (T., 1909, **95**, 1178). The discrepancies are possibly due to the existence of anhydrous sodium sulphite in more than one metastable phase.

W. H.-R.

System Chromium Trioxide–Boric Acid–Water. L. F. GILBERT (*J. Chem. Soc.*, 1925, **127**, 1541—1542).—The solubility of boric acid has been determined at 25° and 45° in solutions containing from 0 to 62·4% of chromic acid. In all cases the solid phase is boric acid the solubility of which is diminished by increasing content of chromic acid, chiefly owing to the common ion (hydrogen) effect.

W. H.-R.

Equilibria in Systems, with Solid Phases, Separated by a Semi-permeable Membrane. IV and V. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 157—165; 166—173).—Theoretical. The osmotic behaviour of ternary liquid systems in which (*a*) a solid binary compound or (*b*) a solid ternary compound occurs or (*c*) in which more than one solid phase may occur, is discussed in reference to phase diagrams.

A. B. M.

Work of Viscosity and Apparent Molecular Heat of Substances in Solution. N. DE KOLOSSOVSKI (*J. Chim. phys.*, 1925, **22**, 353—368).—The theoretical formula for the specific heats of solutions previously deduced (this vol., ii, 765, 791) is extended in application by the introduction of a term representing the work necessary to overcome the viscosity of the medium. Mathias' formula for the specific heats of solutions (A., 1889, 4) can be deduced directly from the theory outlined. According to the viscosity data for their aqueous solutions, ethyl and propyl alcohols are combined with $1H_2O$, lævulose with $2H_2O$, and acetic acid with $9H_2O$. The quantity ϵ [$=C-(2n+3)$, C being the apparent molecular heat of the dissolved solute and n the number of atoms in its molecule] is fairly constant for isomeric compounds and increases by about 16·4 for successive members of homologous series. The groups H, OH, and CO_2H have no influence on ϵ, which, for chemically analogous substances, appears to be proportional to the molecular weight. The revised formula causes only small changes in the degrees of hydration of the electrolytes previously recorded. Sodium iodide and nitric acid in solution now have 1 and $1{\cdot}5H_2O$, respectively; potassium and sodium bromides have, respectively, 4 and $6H_2O$ (cf. this vol., ii, 859). S. K. T.

Thermal Decomposition of Metallic Sulphates. I. (MLLE.) G. MARCHAL (*J. Chim. phys.*, 1925, **22**, 325—348).—The heats of formation and of solution in various solvents of hydrated and anhydrous beryllium oxide and sulphate are recorded. The molecular heat of solution of the anhydrous oxide in 30% hydrofluoric acid is 23·3 Cal., higher than found by Copaux and Philips (A., 1923, ii, 216); the molecular heat of hydration of the oxide is 2·9 Cal. The molecular heat of formation of anhydrous beryllium sulphate is 273·1 Cal.; the heat of formation of the anhydrous double sulphate, $K_2SO_4,BeSO_4$, is 8·4 Cal., and of the hydrated form ($2H_2O$), 14·7 Cal. S. K. T.

Heat of Mixture of Condensed Systems. J. J. VAN LAAR and R. LORENZ (*Z. anorg. Chem.*, 1925, **146**, 42—44).—Theoretical. By means of the thermodynamic potential, a complex expression is deduced for the calculation of the heat of mixture of condensed systems. W. H.-R.

Heats of Adsorption of Sulphur Dioxide and of Water Vapour by Silica Gel at 0°. W. A. PATRICK and C. E. GREIDER (*J. Physical Chem.*, 1925, **29**, 1031—1039; cf. Patrick and Grim, A., 1922, ii, 122).—The heat of adsorption of water vapour at 0° is given by the equation, $H=1{\cdot}091X^{0{\cdot}914}$, X being the number of mg. of water adsorbed per g. of gel and H the corresponding heat of adsorption in cal. per g. of gel. The respective values of H and X at saturation are 236·2 cal. and 361·2 mg. The net heat of adsorption, assuming the heat of liquefaction of the adsorbed water to be 215·6 cal. (596·8 cal. per g.), is 20·6 cal. The heat of adsorption of sulphur dioxide is represented by the equation $H=0{\cdot}316X^{0{\cdot}860}$. The respective values of H and X at saturation are 69·1 cal. and 525

mg. The net heat of adsorption is 21·2 cal. The difference between heats of adsorption and of liquefaction, *i.e.*, the net heat, may be interpreted in terms of the changes in surface and in surface energy involved. J. S. C.

Amendment to the Lyons Decisions (1922) Regarding the Thermochemical Standard Substance. P. E. VERKADE (*Rec. trav. chim.*, 1925, **44**, 800—804).—In view of the continued improvement in the accuracy of heat of combustion determinations (0·1 per thousand now being obtainable), it is essential that the temperature for which the internationally adopted standard value of benzoic acid (6324 cal.$_{15}$ per g. [air]) is valid, should be stated. The temperature coefficients of the molecular heats of combustion of benzoic and salicylic acids are calculated to be −29·0 and −27·5, respectively, hence the isothermal heats of combustions of these substances decrease by 0·038 per 1000 per 1° rise of temperature; therefore a difference of 5° in the experimental temperature involves an error greater than the experimental error. It is suggested that determinations of heats of combustion should all be carried out at a temperature in the near neighbourhood of 20°, it being assumed that the standard value holds for an isothermal reaction at 19·5°. If other temperatures must be employed, the above coefficients should be taken into account. J. W. B.

Conductivity of Electrolytes. II. Mobility of the Hydrogen Ion at 25°. C. W. DAVIES (*J. Physical Chem.*, 1925, **29**, 973—976).—Use may be made of the linear relationship between conductivity and the square root of concentration (this vol., ii, 541) in the extrapolation of conductivity data. The relationship holds exactly for the strong electrolytes and gives in the case of weak and transition electrolytes the limiting slope at infinite dilution. The value 351·3±0·1 is derived for the mobility of the hydrogen ion at 25° from considerations of the data of Kraus and Parker (A., 1923, ii, 6, 722) for hydrochloric and iodic acids. J. S. C.

Conductivity of Electrolytes. III. Correlation of Strong and Weak Electrolytes. C. W. DAVIES (*J. Physical Chem.*, 1925, **29**, 977—986; cf. preceding abstract).—The changes in conductivity of dilute solutions of electrolytes with increasing concentration is due partly to changes in ionic mobilities and partly to a decrease in the degree of ionisation. In the case of the strong electrolytes only the first of these causes is present. With weak and transition electrolytes the changes in ionic mobilities are given by the equation quoted (*loc. cit.*). Allowing for these mobility changes, the true degree of dissociation is calculable. True ionisation constants for weak and transition electrolytes are obtained by dividing the product of ion activities by the calculated concentration of the non-ionised molecules. J. S. C.

Conductivity of Potassium and Sodium Chloride in Aqueous Solution. R. LORENZ and A. VOIGT (*Z. anorg. Chem.*, 1925, **145**, 277—303).—The conductivity theory of Hertz (A., 1912, ii, 120) is supported by observations made with sodium and potassium

chloride solutions. Considerations based on the relation of the "universal" conductivity curve [*i.e.*, the curve obtained by plotting the values $\psi(u)$ of the Hertz function against the values of u] to the molar conductivity curve, lead to a value for the constant A which is practically identical with the theoretical value of 18·95 (at 18°). Investigation of the value of B shows that this is not constant.

L. L. B.

Measurement of Electrical Conductivity at High Temperatures and its Significance for Explaining the Nature of Solid Solutions. P. J. SALDAU (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 275—286).—Mostly published previously (cf. A., 1916, ii, 594; this vol., ii, 205). Equilibria in the system gold–cadmium have been investigated. At about 450° the compound Au_3Cd separates from alloys containing about 25 atoms % Cd. Further lowering of the temperature results in the formation of a new phase possessing two modifications: α_1 stable between 450° and 135° and α_2 below 135°. The existence of the compound Au_4Cd_3 is not confirmed. Maxima on the conductivity isotherms show the existence of the compounds AuCd and $AuCd_3$. T. H. P.

Electrical Conductance of Selenium Oxychloride Solutions. A. P. JULIEN (*J. Amer. Chem. Soc.*, 1925, **47**, 1799—1807).—The specific conductance of selenium oxychloride is $2{\cdot}0\pm0{\cdot}3\times10^{-5}$ mhos at 25°. The variation of the specific conductance with temperature is represented in a satisfactory manner by the equation $K_t=K_{25}+0{\cdot}0392t-0{\cdot}943-0{\cdot}0002(t-12)^2$, where K represents conductance. The molecular conductances of solutions of sodium, potassium, ammonium, mercuric, ferric, and barium chlorides at various concentrations in the solvent have been determined. A method for the determination of the water content of selenium dioxide is described: selenium dioxide is volatilised through heated potassium chromate; the oxide combines to form stable compounds, the water being collected and weighed. J. S. C.

Basis for the Physiological Activity of certain -onium Compounds. The Mobilities of the -onium Ions. I. Sulphonium Ions. I. BENCOWITZ and R. R. RENSHAW (*J. Amer. Chem. Soc.*, 1925, **47**, 1904—1916).—Conductivity measurements with trimethylsulphonium iodide and triethylsulphonium bromide, over the concentration range 0·04—1·0 millimole per litre, have been carried out in quartz apparatus. The values of λ_∞ for trimethylsulphonium iodide and triethylsulphonium bromide are 127·49 and 113·49, respectively. On the assumption that the value of λ_∞ at 25° of the iodide ion is 76·12 and that of the bromide ion 77·44, the λ_∞ values for trimethylsulphonium and triethylsulphonium are 51·36 and 36·05, respectively. J. S. C.

Transference Numbers of Solutions of Mixed Chlorides. D. A. MACINNES (*J. Amer. Chem. Soc.*, 1925, **47**, 1922—1927).—A re-examination of the transference data obtained by Braley and Hall (A., 1920, ii, 662) and by Schneider and Braley (A., 1923, ii, 456) for mixed solutions of sodium and potassium chlorides, which were

interpreted as indicating the existence of ionic complexes, leads to the conclusion that the results are in agreement with the view that only simple ions are present. J. S. C.

Transference Numbers of Sodium and Potassium Chlorides and of their Mixtures. J. DEWEY (*J. Amer. Chem. Soc.*, 1925, **47**, 1927—1932; cf. preceding abstract).—The experiments of Schneider and Braley (A., 1923, ii, 456) on the transference numbers of the sodium and potassium ions in mixed solutions of the two chlorides at a total concentration of 0·2*N*, have been repeated. No evidence was obtained that with a low proportion of sodium chloride the transference number of the sodium ion falls to nearly zero as reported by Schneider and Braley, and the present data are in good agreement with the assumption of simple ions as opposed to the suggested complexes. J. S. C.

Electrolyte Threads. I. Behaviour of Electrolyte Threads and their Deflection in a Magnetic Field. E. MANEGOLD (*Z. anorg. Chem.*, 1925, **145**, 181—192).—A thin thread of a coloured electrolyte (0·1*N*-hydrochloric acid and methyl-orange) was caused to flow through distilled water; the thread was 5·5 cm. long and 1·7 mm. in diameter and the rate of flow of electrolyte was 0·8 c.c. per min. When a current was passed through the thread in the field of an electro-magnet the thread was deflected; the current was varied from 0·0016 to 0·0025 amp., and the deflection was approximately proportional to this and was of the order of 0·5—1 cm. A jet of the electrolyte in air was similarly deflected, but the deflection was less because the rate of flow of the liquid was necessarily greater. A. G.

Electrokinetic and Thermodynamic Potentials. H. FREUNDLICH and G. ETTISCH (*Z. physikal. Chem.*, 1925, **116**, 401—419; cf. Borelius, A., 1916, ii, 512; Freundlich and Rona, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, **20**, 397).—The streaming potential method was used to study the effect of varying the concentrations of dilute solutions of salts on the electrokinetic potentials at glass surfaces. In the typical electrokinetic potential–concentration curve the potential rises to a maximum with increasing concentration, then falls, and finally changes its sign. The maximum may, however, be suppressed, and the inversion point may be approached only asymptotically. The form of the curve is explained by the opposing influences of the two ions adsorbed on the glass. In this connexion, Hardy's rule is shown to hold. The thermodynamic potentials were also measured. Here the curves have none of the above characteristics, and follow courses which can be explained on the usual thermodynamic grounds. L. F. G.

Phase Boundary Forces at Gas–Liquid Interfaces. III. Electrical Properties of Unimolecular Films of Insoluble Substances. A. FRUMKIN (*Z. physikal. Chem.*, 1925, **116**, 485—497; cf. A., 1924, ii, 462; this vol., ii, 109).—A method is described similar to that of Guyot (this vol., ii, 403) for measuring potential differences at gas–liquid interfaces, which allows the potential

difference at the interface air–unimolecular adsorbed film of insoluble substance to be easily determined, and, in the case of soluble substances, gives results which agree with those determined by Kenrick's method. Films of fatty acids and allied substances, in most cases on 0·01*N*-hydrochloric acid, have been studied. The observed effects are ascribed to orientation of the molecules according to Langmuir's theory, but the effect per molecule is less for higher members of homologous series than for lower. This is due to closer packing of the molecules in the former case. L. F. G.

Electrochemical Relation of Free Radicals to Halochromic Salts. J. B. Conant, L. F. Small, and B. S. Taylor (*J. Amer. Chem. Soc.*, 1925, **47**, 1959—1974).—Measurements of the *E.M.F.* of a cell consisting of platinum electrodes immersed in tetrachlorobenzoquinone–tetrachloroquinol and triphenylmethyl–triphenylmethyl sulphate mixtures, respectively, dissolved in a solvent made by mixing glacial acetic acid (15 c.c.), bromobenzene (26 c.c.), and 98% sulphuric acid (15 c.c.), indicate that mixtures of triphenylmethyl and its sulphate give reproducible potentials in accordance with the usual electrochemical equation. The same result is obtained when triphenylcarbinol is titrated with vanadous sulphate in aqueous acetone solution against the above tetrachlorobenzoquinone electrode, and the single electrode potentials of triphenylmethyl, phenylxanthyl, and phenyldimethoxyxanthyl have been evaluated. When the hydrolysis of the halochromic salt is negligible, the potential is independent of the hydrogen-ion concentration. When hydrolysis is complete, the potential is a linear function of the latter, a bend in the potential–p_H curve occurring at the range of decreasing acidity over which the colour of the salt solution fades. Whilst reduction of carbinols to dissociable ethanes is thus reversible, reduction to the non-dissociable ethanes was found to be irreversible.

Reduction of carbinols with vanadous sulphate or chloride, in acetone or acetic acid solution, affords a convenient method for the preparation of the corresponding substituted methyls or ethanes. *Dianisyldi-α-naphthylethane* crystallises with 1 mol. of acetone. The compound melts at 226° when slowly heated, but when heated rapidly it melts at 180°, then solidifies, and finally melts at 226°. F. G. W.

Critical Increment of Chemical Reactions. C. N. Hinshelwood (*Phil. Mag.*, 1925, [vi], **50**, 360—361).—The value of the factor P in the expression $k=2\times$total number of collisions$\times e^{-Q/RT}\times P$ for the velocity constant of a bimolecular reaction in a gaseous system is discussed. The author differs from Garner (this vol., ii, 552) in regarding P as independent of temperature. A. B. M.

Influence of Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air. IV. Influence of Dichloro- and Trichloroethylene on the Limits of Inflammability of Carbon Monoxide–Air Mixtures. W. P. Jorissen and J. H. A. P. van der Valk (*Rec. trav. chim.*, 1925, **44**, 810—813; cf. this vol., ii, 53, 307).—In a slightly modified apparatus, the limits of inflammability of mix-

tures of carbon monoxide and air at 14° were 15·35—72·75%. With various proportions of dichloroethylene vapour, the following limits of inflammability were obtained at this temperature: 5%, 6·65—50·25%; 8%, lower limit 3·2%; 10%, below 1·8—27·8%; 11%, lower limit below 0·5%; 12%, below 1·95—16·5%; 13%, upper limit 12·55%; 14%, 0·75—7·6%; 15%, upper limit 5·65%; 16%, 1·75—3·7%; 17 and 18%, no explosion with 0·5% of carbon monoxide; 20%, no explosion with 0·1%. With 2·5% of carbon monoxide, explosion did not occur with a dichloroethylene concentration greater than 16·6%. Dichloroethylene itself (b. p. 50·6—52·7°/759 mm.) has explosion limits 3·25—15·25%, whilst a specimen of low b. p. (48·2—49°/755·5 mm.) and one of high b. p. (57·5—59·5°/758 mm.) gave limits 8·5—13·5% and 10·5—23%, respectively. With trichloroethylene at 14°, the following limits were obtained: 2%, 18·95—52·75%; 3%, upper limit 43·55%; 4%, lower limit 21·45%; whilst the trichloroethylene itself showed no explosion at 14° with 5% (air saturated with the vapour contains 5·7% by volume).

J. W. B.

Influence of Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air. V. Influence of Trichloroethylene on the Limits of Inflammability of Hydrogen–Air Mixtures. W. P. Jorissen and B. L. Ongkiehong (*Rec. trav. chim.*, 1925, **44**, 814—817; cf. preceding abstract).—Both the upper and lower explosion limits of mixtures of hydrogen and air are lowered by the addition of trichloroethylene vapour. At 14°, the explosion limits of mixtures of hydrogen and air (explosion limit 6·3—61·3% in the apparatus used) in the presence of varying quantities of trichloroethylene were as follows: 3%, 5·9—43·3%; 5%, lower limit 5·4%; 6·05% (saturated), 4·9—25·9%. At 25°, 0%, 5·9—62·3%, 3%, upper limit 45·7%; 5%, 5·1—42·9%; 10·84% (saturated), 5·1—20·8%. At 35°, 0%, 6·1—63·1%; 3%, upper limit 47·2%; 6%, 4·7—41·1%; 8%, upper limit 38·3%; 10%, 4·2—34·9%; 14%, lower limit 6·7%; 15·7% (saturated), no explosions with quantities of hydrogen varying from 4 to 20%. The ratios of hydrogen to oxygen at the various explosion limits are also calculated and confirm the deduction made above.

J. W. B.

Combustion of Carbon Monoxide Mixtures. J. H. Crowe and A. H. Newey (*Phil. Mag.*, 1925, [vi], **49**, 1112—1131).—Mixtures of carbon monoxide and air were ignited at the centre of a spherical explosion vessel. For any completely diffused mixture of air and carbon monoxide at any pressure the flame travels at a uniform velocity. The curve time–distance is a wavy line and a mean straight line can be passed through the points. The wavy line corresponds with a true oscillation of the flame front. The flame reaches the walls before combustion is completed. The velocity of the flame is a function of flame temperature. Convection currents are unimportant, even in the weaker mixtures. The maximum velocity, pressure, and temperature occur with a rich mixture containing about 40% of carbon monoxide. These

phenomena are explained by dissociation. Combustion does not take place instantaneously at any spherical shell of mixtures of carbon monoxide and air, and probably does not do so with any other gas.

The percentage cooling loss is lowest when the mixture contains 45% of carbon monoxide. The values of Pier (A., 1910, ii, 1031) for the volumetric heat are low compared with those of the authors (6·32 compared with 6·92, 60% CO, 2066° Abs.; 7·21 compared with 7·32, 60% CO, 2713° Abs.). The agreement is better at higher temperatures. It is assumed that chemical equilibrium is nearly complete at the time of maximum pressure. The amount of dissociation can be calculated from the temperature curve, since two mixtures which give the same temperature must have the same carbon dioxide content at equilibrium. On the rich side, this composition is known, and hence for any dissociated mixture the amount of carbon dioxide formed can be calculated. The values of the equilibrium constants are slightly higher than those found by Bjerrum (A., 1912, ii, 540). The lower limit of inflammability of carbon monoxide and air is raised by increasing the initial pressure. Nitrogen as an inert diluent slows down the flame velocity and subsequent combustion. R. A. M.

Rate of Thermal Decomposition of Sulphuryl Chloride. A First-order Homogeneous Gas Reaction. D. F. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 1862—1875).—The decomposition, $SO_2Cl_2=SO_2+Cl_2$, at 320° is a reaction of the first order proceeding entirely in the gas phase. At lower temperatures, there appears to be some wall-reaction. It is suggested that the high rates of decomposition of sulphuryl chloride obtained by Hinshelwood and Prichard (T., 1923, **124**, 2725) in presence of glass wool are due to spurious effects. None of the theories of reaction rate as yet put forward has a general application. J. S. C.

Theory of Catalysis. I. Kinetics of Mutarotation. H. von Euler, A. Örlander, and E. Rudberg (*Z. anorg. Chem.*, 1925, **146**, 45—68).—The velocities of mutarotation of α- and β-dextrose have been determined at 5·2° in solutions of different p_H value. Both acids and alkalis accelerate the reaction. In acid solution, the mutarotation is not proportional to the hydrogen-ion concentration, but in alkaline solution it is directly proportional to the concentration of hydroxyl ions. Between p_H 2 and p_H 8, the velocity is little affected by the acidity and sinks to a flat minimum at p_H 5, corresponding with the isoelectric point of dextrose, which can act either as an acid or as a base. The velocity constant $(k_1+k_2)=1/t\,.\log a/(a-x)$, where x is the amount transformed after time t. If K_a and K_b are the acidic and basic dissociation constants of dextrose, and r_{q_1} and r_{q_2} the specific reactivities of the dextrose anions and cations, the results can be expressed in the form $(k_1+k_2)=k_0+A[H^+]+B/[H^+]$, where $A=r_{q_2}K_b/K_w=3{\cdot}83\times10^{-12}$ at 5·2°, $B=r_{q_1}K_a=3{\cdot}78\times10^{-2}$, and $k_0=0{\cdot}00119$. At 5·2, $K_b=2\times10^{-18}$, and on the assumption that $r_{q_1}=r_{q_2}$, the specific reactivity of the dextrose ions is $r_q=40$. W. H.-R.

Kinetics of the Thermal Decomposition of the Permanganates. E. MOLES and M. CRESPI (*Anal. Fís. Quím.*, 1925, **23**, 198—216; cf. A., 1923, ii, 642).—The kinetics of the thermal decomposition of permanganates are discussed, with special reference to the work of Hinshelwood and Bowen (A., 1921, ii, 443), and of Sieverts and Theberath (A., 1922, ii, 360). From their experiments, the authors conclude that these reactions are positive and autocatalytic, and may be represented by the equation $dx/dt=(k_1+k_2x/a)(a-x)$. The decompositions are shown to be made up of two reactions, namely, a simple decomposition and an autocatalytic decomposition which is negligible at first and then passes through a maximum. Comparing the values of the different constants for the decomposition of the permanganates of silver, cadmium, potassium, sodium, cæsium, rubidium, barium, and lithium, respectively, it is seen that there is a correlation between the values for total velocity and the heats of formation of the corresponding oxides. G. W. R.

Velocity of Decomposition of Esters and the Relation to the Hydrogen-ion Concentration. K. G. KARLSSON (*Z. anorg. Chem.*, 1925, **145**, 1—57).—The velocity constants of the hydrolysis of methyl acetate, ethyl acetate, and monoacetin have been determined at 25° and at various p_H values, the method used being similar to that previously described (A., 1922, ii, 42). The desired p_H values were obtained by the addition of hydrochloric acid, acetic acid, or an acetate buffer mixture, and were determined electrometrically at the beginning and end of each experiment; the maximum concentration of sodium acetate in the buffered solutions was $0{\cdot}05N$. Measurements with methyl acetate were also made in the presence of $0{\cdot}5N$ concentrations of sodium, calcium, strontium, and barium chlorides, and of sodium sulphate. In the absence of salts the velocity constant for methyl acetate is a minimum at p_H 5·2, and for ethyl acetate and acetin at 5·4 and 5·0, respectively. When the velocity constants are plotted against the p_H values, the curves are symmetrical about a line vertical to the p_H axis and passing through the minimum value of the constant, and, except in the neighbourhood of the minimum, the curves are straight lines. The asymmetry of the curves previously obtained at higher temperatures was due to experimental errors unavoidable at such temperatures. In acid solutions the velocity constants are nearly independent of the nature of the ester (cf. A., 1894, ii, 274; 1895, ii, 107), the curves for methyl and ethyl acetates being identical; on the alkaline side of the minimum, there are greater differences. The action of neutral salts is positive, although sodium chloride is practically without influence in the concentration used. The anions of the salts have most influence on the acid side of the minimum and the cations on the alkaline side, and the salt action increases with increasing charge on the ions. In the presence of calcium, strontium, and barium chlorides, the minimum is shifted to a slightly lower p_H. Comparison with previous results at 85·45° shows that the neutral salt action is much greater at higher temperatures.

It is shown mathematically that the suggestion of von Euler and

Laurin (A., 1921, ii, 498), that carboxylic acid esters are amphoteric electrolytes and that it is only the ions that take part in the hydrolysis, leads to a symmetrical curve of the form found, and that velocity constants calculated on this basis agree approximately with the experimental values. It is also shown that the action of neutral salts can be explained on the assumption that they cause an actual or apparent increase in the dissociation constants, and that the required values of these increases, viz., sodium sulphate, 0·20, strontium and barium chlorides, 0·25, and calcium chloride, 0·40, are close to the values found by Michaelis and Krüger (A., 1922, ii, 157) for the displacement of the dissociation constant of acetic acid, viz., sodium chloride, 0·18, barium chloride, 0·28, and calcium chloride, 0·40.

Similar determinations were also made with ethyl benzenesulphonate, the hydrolysis being, in this case, carried out in the presence of excess of the liquid ester, and separate determinations made of the solubility of the ester in each of the solutions used. The desired p_H values were obtained by the addition of sodium acetate, sodium hydroxide, or benzenesulphonic acid. The relation between the velocity constant and the p_H is entirely different from that of the carboxylic esters, in agreement with the fact that it is not an amphoteric electrolyte. The constant remains unchanged in acid solutions, but rises with increasing alkalinity proportionally to the concentration of sodium hydroxide. This is in agreement with the results of Wegscheider and Furcht (A., 1903, i, 342), and Praetorius (A., 1905, i, 186; 1907, i, 835), according to whom the velocity constant for methyl benzenesulphonate is given by the equation: $dx/dt=kC_{\text{ester}}+k'C_{\text{ester}}C_{\text{NaOH}}$. The value of the constant k is nearly the same for the two esters (methyl 7·015, ethyl 6·46), but that of the constant k' is much lower for the ethyl ester (0·05275 and 0·0070). Sodium chloride increases the velocity constant in acid and alkaline solutions. A. G.

Velocity of the Reaction $2NO+Cl_2 \longrightarrow 2NOCl$ in the Condensed State. M. Trautz and W. Gerwig (*Z. anorg. Chem.*, 1925, **146**, 1—41).—The solubility of nitric oxide in liquid nitrosyl chloride, pentane, and toluene has been determined at temperatures from 20° to −78°, and the partial pressures for the solutions in nitrosyl chloride have been calculated on the assumption that the method of Dolezalek can be applied below the critical point. The freezing-point diagram has been determined for mixtures of nitric oxide and chlorine from pure chlorine to the composition corresponding with that of nitrosyl chloride. Mixtures kept for some time show a normal eutectic freezing-point diagram with nitrosyl chloride and chlorine as solid constituents, but freshly-prepared mixtures show a break in the liquidus at the composition of an unstable intermediate compound, $NOCl_2$. The velocity of absorption of nitric oxide by liquid chlorine has been determined at −58°, whence a complex method permits the calculation of the velocity constants of the reactions involved, which are (1) $2NO+Cl_2 \longrightarrow 2NOCl$, for which the velocity constant k is of the order 10^7,

(2) $NO+Cl_2 \longrightarrow NOCl_2$, and (3) $NOCl_2+NO \longrightarrow 2NOCl$, for which k (mol./c.c. and secs.) is of the order 10^2. Within the limits of error of the method, the velocities of the pseudo-bimolecular reaction (1) and of the termolecular decomposition of $NOCl_2$ (2) are the same if the reaction takes place in the gaseous state or in liquid nitrosyl chloride as solvent, in contradiction to the methods of calculation of van't Hoff. W. H.-R.

Reactivity of Silver with Oxygen. N. PARRAVANO and G. MALQUORI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 622—626).—Silver prepared by precipitation with dextrose and with hydrogen sulphide was heated slowly in a closed vessel in contact with oxygen, originally at 675 mm. pressure. The pressure–temperature curves showed at 280° and 250°, respectively, evidence of reaction extending over a range of about 50°. Crystals of electrolytic silver and massive silver gave no sign of reaction. The above temperatures do not represent equilibrium states, since the vapour pressures of silver oxide at those temperatures are 5·1 and 8·3 atm., respectively. At lower temperatures, the oxygen absorption is greater but slower. The maximum absorption recorded was 0·228% in 5 hrs. by 15 g. of precipitated silver at 213°. F. G. T.

Action of Dilute Acid Solutions on Ferrous Metals. R. GIRARD (*Compt. rend.*, 1925, **181**, 215—218).—The action of solutions of sulphuric, hydrochloric, and carbonic acids and of phenol, of concentrations less than 0·1*N*, on polished steel and cast-iron plates is investigated. For a given acid, the two plates are always attacked to equal extents. Below a certain concentration (about 0·001*N*), the acid is the more active the less it is dissociated; above this concentration, the reverse holds. The results for carbonic and hydrochloric acids agree with those of Whitman, Russell, and Altieri (*Ind. Eng. Chem.*, 1924, **16**, 665). Sulphuric and hydrochloric acids react similarly to each other. [Cf. *B.*, 1925, 723.] S. K. T.

Rapid Corrosion of Metals by Acids within Capillaries. L. MCCULLOCH (*J. Amer. Chem. Soc.*, 1925, **47**, 1940—1942).—If a rubber band be wrapped rather tightly round a piece of soft iron and the whole left in dilute hydrochloric acid for some weeks, the iron is found to have been pitted beneath the rubber, the acid acting more rapidly within the capillary spaces between metal and rubber than on the exposed surfaces. An explanation of this is put forward. J. S. C.

Induced Oxidation. W. P. JORISSEN and C. VAN DEN POL (*Rec. trav. chim.*, 1925, **44**, 805—809).—Further details of investigations previously described (cf. this vol., ii, 52) are given in support of a criticism of the work of Mittra and Dhar on induced oxidations (this vol., ii, 576). A study of the simultaneous oxidation of sodium sulphate and sodium oxalate or nitrite in aqueous solution is carried out by adding periodically 10 c.c. of the reaction mixture to a standard solution of permanganate and titrating the excess of permanganate with ferrous sulphate or sodium oxalate solutions,

respectively. The end titration of the nitrite or oxalate solutions is uninfluenced by the presence of sodium sulphite, and hence this salt does not induce the oxidation of sodium oxalate or sodium nitrite by atmospheric oxygen under ordinary conditions. The method previously described (*loc. cit.*) for the investigation of the oxidation of sodium antimonite solutions in the presence of sodium sulphite is employed to determine the influence of sodium carbonate on the oxidation of sodium arsenite–sodium sulphite–sodium hydrogen carbonate solutions, the results showing that sodium sulphite does not induce the oxidation of sodium arsenite solution when the alkalinity passes a certain limit (cf. Reinders and Vles, this vol., ii, 567). J. W. B.

Influence of Water on certain Chemical Reactions. I. Effect of Various Concentrations of Water Vapour on the Reaction between Chlorine and Potassium Iodide or Bromide. L. B. PARSONS (*J. Amer. Chem. Soc.*, 1925, **47**, 1817—1820).—The minimum partial pressure of water necessary for any appreciable reaction to occur between chlorine and potassium iodide or bromide is approximately the vapour pressure of a saturated aqueous solution of the components present during the reaction. J. S. C.

Influence of Water on certain Chemical Reactions. II. Reaction between Hydrogen Sulphide and Iodine in Ethereal Solution. L. B. PARSONS (*J. Amer. Chem. Soc.*, 1925, **47**, 1820—1830).—The reaction between hydrogen sulphide and iodine is complete in absence of water and incomplete in presence of water, the equilibrium point reached depending on the water content of the solvent. In anhydrous ether the reaction proceeds according to the equation $H_2S+I_2=2HI+S$. In presence of water, a series of consecutive reactions occurs, which may be formulated into a single equation, $H_2S+3H_2O+3I_2 \rightleftharpoons H_2SO_3+6HI$. The changes in the course of the reaction in presence of atmospheric oxygen are ascribed to the formation of ether peroxide which oxidises hydriodic acid to iodine and water, but does not oxidise hydrogen sulphide. J. S. C.

Influence of Water on certain Chemical Reactions. III. Reactions between certain Metals and Iodine. L. B. PARSONS (*J. Amer. Chem. Soc.*, 1925, **47**, 1830—1835).—Investigations of systems of various metals with iodine in presence of a number of liquids show that there is a close connexion between the ability of the liquid to bring about reaction and the solubility in the liquid of the metallic iodide. The solvent does not act as a true catalyst, but merely dissolves the thin film of iodide and allows more iodine to come into contact with the metallic surface. J. S. C.

Sorption of Iodine and Catalytic Decomposition of Hydrogen Peroxide Solution by "Norit" Charcoals. J. B. FIRTH and F. S. WATSON (*J. Physical Chem.*, 1925, **29**, 987—993).—"Norit" charcoals of grades 1, 2, 3, and 7 shows a very high sorption activity towards iodine in chloroform solution. The percentage of ash does not materially affect the sorption capacity. Charcoals 1 and 2 show feeble catalytic activity towards hydrogen peroxide

solutions, and 3 and 7 show only a moderate activity. A charcoal of high sorptive capacity is not of necessity highly catalytic towards hydrogen peroxide. Results with other active charcoals support this conclusion. J. S. C.

Catalysis. Active and Inactive Iron Oxide. O. Baudisch and L. A. Welo (*Chem.-Ztg.*, 1925, **49**, 661—662).—When synthetic magnetite is heated in oxygen at 330°, it is converted into a magnetic, catalytically active form of ferric oxide, which has a cubic structure like that of magnetite. When this form of ferric oxide is heated at 550°, it changes to a catalytically inactive, rhombohedral form with the same structure as that of hæmatite. Both active and inactive forms have identical composition and give no blue colour with ferricyanide. Magnetite and the active ferric oxide absorb oxygen, whereas the inactive ferric oxide does not. Both magnetic and catalytic properties depend on the arrangement of atoms in space, and this arrangement plays an important part in catalysis. The catalytic actions studied were (1) the formation of a blue colour in a solution of benzidine hydrochloride and hydrogen peroxide and (2) the growth of *Bacterium lepisepticum*. W. H.-R.

Effect of Poisonous Substances and Mixed Vapours on Catalytic Activity. F. H. Constable (*Proc. Camb. Phil. Soc.*, 1925, **22**, 738—750).—A quantitative study of the dehydrogenation of ethyl and amyl alcohol vapours (alternately or mixed) has been made with copper as catalyst. Both alcohols have the same rate of dehydrogenation. The poisoning of the catalyst by amyl alcohol (from fusel oil) has been followed, and the temperature coefficient of the dehydrogenation of ethyl alcohol has been measured during the poisoning and found to be constant. The temperature coefficient was also unchanged during sintering. The activity of the catalyst poisoned by amyl alcohol decreases in accordance with the logarithmic expression $\log v = -kt + c$. An equation is deduced for the rate of poisoning on the assumption that the distribution of the centres of activity is exponential and that the poison attacks the more active centres selectively. The resulting expression cannot usually be distinguished from the simple logarithmic relation. An equation is given showing the reaction velocity as a function of the temperature of the surface and the time. The expression accounts for the heating and cooling curves obtained with "poisonous" alcohols. Except in special circumstances the temperature coefficient remains unaltered after poisoning. R. A. M.

Catalytic Decomposition of Acetic Acid by Wood Charcoal. N. V. Kultaschev and N. A. Kudrjascheva (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 383—396).—In contact with wood charcoal, the decomposition of acetic acid proceeds appreciably at 300° and then increases rapidly as the temperature is raised. Under these conditions, the aqueous acid is decomposed to a greater extent than the anhydrous acid at the same temperature. When pure acetic acid is used, about 50% of it undergoes decomposition with formation of methane and acetone, and with dilute solutions of the acid, more than 50% is decomposed according to these reactions.

Under the catalytic influence of the charcoal acetone is decomposed slightly at 400°, this decomposition being retarded by dilution of the acetone with water. Messinger's volumetric method for the determination of acetone gives satisfactory results if certain modifications are made in the procedure. T. H. P.

Noble Metals as Catalysts of Hydrogenation and Dehydrogenation. N. D. ZELINSKI and M. B. TUROVA-POLLOK.—(See i, 1052.)

Electrochemistry of Non-Aqueous Solutions. VI. Electrodeposition of some Metals from Anhydrous Solutions in Amyl Alcohol, Acetonitrile, Aniline, and Quinoline. R. MÜLLER, E. PINTER, and K. PRETT (*Monatsh.*, 1924, **45**, 525—534).—Electrolysis of solutions of lithium nitrate or magnesium bromide in acetonitrile and of calcium nitrate in amyl alcohol with mercury or platinum cathode did not yield the respective metals, decomposition occurring at voltages below those found for the metal against such solutions. On the other hand, crystalline silver was deposited when solutions of silver nitrate in amyl alcohol, acetonitrile, quinoline, or aniline were electrolysed, the potential differences being constant and easily reproducible, so that the reversibility of the silver electrode is proved with these solvents. Values of the potential differences for various current densities in each case are tabulated and represented graphically. The decomposition potential of silver nitrate is 1·0 volt in amyl alcohol, 1·15 volts in acetonitrile, 2·15 volts in quinoline, and 0·5 volt in aniline solution. G. M. B.

Production of Antimony Hydride (Stibine) at an Antimony Cathode in Alkaline Solution. E. J. WEEKS (*Rec. trav. chim.*, 1925, **44**, 795—797; cf. A., 1924, ii, 606; this vol., ii, 415).—The yields of stibine obtained when sodium carbonate and sodium sulphate solutions are electrolysed using an antimony cathode are determined. The yield may be calculated approximately from the formula $\gamma=12{\cdot}6h-8{\cdot}2$, where γ is the percentage yield of stibine, and h the p_H voltage (cf. Sand and Weeks, A., 1924, ii, 152). The following relationships are also deduced: $\omega=-0{\cdot}0282\gamma+C_1$, $\gamma+20=C'/T$, $\gamma=C_1-C_2\log[OH]$, where ω is the overvoltage, [OH] the hydroxyl-ion concentration, T the absolute temperature, and C_1 and C_2 are constants. J. W. B.

Potassium Dichromate as Depolariser. G. P. VINCENT (*J. Physical Chem.*, 1925, **29**, 875—881; cf. Bancroft, *ibid.*, 1924, **28**, 831).—The depolarising action of saturated potassium dichromate solution on hydrogen liberated at a smooth platinum electrode has been studied in the presence of varying amounts of sulphuric acid. About 0·28% by volume of concentrated sulphuric acid is necessary before appreciable depolarisation occurs. With a clean mercury cathode, the neutral solution shows 100% depolarisation of the hydrogen set free. Neutral $M/40$-potassium permanganate has a distinct depolarising effect on hydrogen at a platinum cathode and also causes appreciable corrosion of zinc, iron, and copper. Corrosion of these metals is only shown by saturated potassium

dichromate solution when acidified, different amounts of acid being required in each case. No corrosion occurs in saturated potassium dichromate solutions when copper is short-circuited with mercury or platinum, or when iron is short-circuited with mercury. Zinc when short-circuited with mercury corrodes slightly and more rapidly in 0·02% acetic acid than in 0·02% sulphuric acid (cf. Bengough and Stuart, *J. Inst. Metals*, 1922, **28**, 89). F. G. S.

Periodic Phenomena in Photochemistry. J. PLOTNIKOV (*Z. Physik*, 1925, **32**, 942—947).—Konigsberger ("Tropismus und Wachstum," 1922) had observed that plants, when allowed to grow at constant temperature and under monochromatic light, increased at a steady rate; when, however, light of two or more different wavelengths was used, the growth was periodic. Other instances of periodicity are the decrease in concentration of chlorine and bromine in carbon tetrachloride solution and the bleaching of dyes. Further work is necessary before any satisfactory explanation can be given. E. B. L.

Action of Radiation on Gas Mixtures. H. SENFTLEBEN (*Z. Physik*, 1925, **32**, 922—932).—Dissociation of a gas is accompanied by a change in conductivity for heat. A wire in one arm of a Wheatstone's bridge was maintained at a constant temperature in a tube the walls of which were kept at a different temperature. The tube was of silica and contained mercury at the ordinary temperature and hydrogen at about 10 mm. pressure. On exposure to the light from the mercury arc, an immediate fall in the resistance of the wire was observed and shown to be due to the increase in thermal conductivity of the gas and hence to the dissociation of the hydrogen, brought about by collisions of the second type with mercury atoms excited by the line 2537 Å. With a mixture of neon and helium or with the aluminium spark, there was no effect. The method can be used for determining the heat of dissociation of a polyatomic gas and also as an indication of the state of excitation of a gas. E. B. L.

Photochemical Decomposition of Chlorine Monoxide. M. BODENSTEIN and G. KISTIAKOVSKI (*Z. physikal. Chem.*, 1925, **116**, 371—390; cf. T., 1923, **123**, 2328, 2730).—An improved method of preparing chlorine monoxide is described. The decomposition of the gas by light of 405 and of 436 mμ was investigated; 1 quantum of absorbed light decomposes 2 mols. It is immaterial whether the energy is absorbed by the monoxide or by the chlorine formed during the reaction. The reaction is unaffected by admixed air. The temperature coefficient is 1·09 per 10°. Small amounts of chlorine dioxide are formed during decomposition by light or by gentle warming. L. F. G.

Mechanism of the Photochemical Reaction between Hydrogen and Chlorine. A. L. MARSHALL (*J. Physical Chem.*, 1925, **29**, 842—852; cf. Bodenstein, A., 1916, ii, 422; Nernst, A., 1919, ii, 208; Chapman and Chapman, T., 1923, **123**, 3079; Weigert and Kellermann, A., 1924, ii, 8; Bowen, J., 1924, **125**, 1233).—The reaction between hydrogen and chlorine has been studied by intro-

ducing a mixture of atomic and molecular hydrogen into chlorine, and determining the ratio of the concentration of the hydrogen chloride produced to that of atomic hydrogen present. The concentrations of atomic hydrogen and molecular chlorine were approximately constant and that of molecular hydrogen was progressively increased. The ratio of hydrogen chloride to atomic hydrogen increased from unity at a total gas pressure of 0·004 cm., measured on a McLeod gauge, to 7 mols. per atom at a pressure of 0·60 cm. The concentration of atomic hydrogen was determined by control experiments involving admixture of the hydrogen with bromine. One mol. of hydrogen bromide results from 1 atom of hydrogen. It is difficult to interpret the observed increase of the hydrogen chloride formed except by a mechanism involving an excited chlorine molecule (cf. Bodenstein, *loc. cit.*), collision of which with hydrogen before re-radiation of its energy occurs being more probable at higher hydrogen pressures. The Nernst theory is discussed and a number of objections are advanced. F. G. S.

Light-sensitiveness of Potassium Ferrocyanide. E. Baur (*Helv. Chim. Acta*, 1925, **8**, 403—405).—The author confirms the observation of Baudisch (A., 1922, i, 993) that alkaline solutions of potassium ferrocyanide become discoloured on exposure to light in absence of oxygen. In addition, he obtains under these conditions a deposit of ferric hydroxide and concludes that the discoloration is due to the latter in colloidal form. Acid solutions are similarly discoloured, giving a precipitate of Prussian blue instead of hydroxide. Failure to detect formaldehyde or ammonia indicates reduction of the cyanide ion, as a counterbalance to the oxidation of the ferrous ion in the ferrocyano complex. Only free hydrocyanic acid is found.

With potassium ferrocyanide freed from ferricyanide by Treadwell and Chervet's method (A., 1922, ii, 786), the production of ferric hydroxide is almost completely eliminated; hence perfectly pure ferrocyanide solutions, whether acid or alkaline, would be entirely insensitive. The sensitiveness must therefore be ascribed to the establishment of an equilibrium in the ferri- and not the ferro-cyano complex: $[Fe(CN)_6]''' \rightleftharpoons Fe''' + 6CN'$. M. J.

Photosynthesis in Tropical Sunlight. N. R. Dhar and R. P. Sanyal (*J. Physical Chem.*, 1925, **29**, 926—934; cf. Baly and others, T., 1921, **119**, 1025; 1922, **121**, 1078; 1923, **123**, 185).—The statement that the light effective for the formation of formaldehyde has very short wave-length and that no such rays are present in sunlight is held to be incorrect. Experiments carried out in glass vessels in tropical sunlight, the spectrum of which is shown to contain no line of wave-length less than 290 $\mu\mu$, afford definite proof of the synthesis of formaldehyde from carbon dioxide and water, with or without the use of any catalyst. Experiments on the polymerisation of formaldehyde were not so successful, traces of sugars only being obtained when formaldehyde solutions were exposed to the sunlight in presence of ferric chloride and methyl-orange.

Tropical sunlight is effective in promoting oxidation. Alcohols

are oxidised to the corresponding aldehydes. When air or oxygen is passed into solutions of ammonia, tests for nitrites are obtained. Exposure of ammonia and oxygen results in the formation of nitrogen. The reducing action is considerable; solid iodic acid gives iodine, potassium chlorate shows traces of chloride, and nitrates are converted into nitrites.

Ultra-violet light is more effective in certain photosyntheses, but tropical sunlight contains a number of rays which can effect the synthesis of complex compounds from simple substances. Methylamine, which is formed in about 12 hrs. when ammonia and formaldehyde are exposed to tropical sunlight, passes into a number of complex substances of the alkaloid type. Experiments with ultra-violet light show that nitrogen and oxygen combine to form nitrogen oxides. The difference between the action of sunlight and ultra-violet light in promoting photosynthesis is one of degree rather than of kind. J. S. C.

Active Hydrogen. A. Bach (*Ber.*, 1925, **58**, [*B*], 1388—1393).—Recently-melted platinum contains adsorbed sulphur compounds and evolves hydrogen sulphide when heated in hydrogen; according to experimental conditions, this power is more or less rapidly lost. Passage of the evolved hydrogen over powdered sulphur does not increase the amount of hydrogen sulphide produced from the fresh metal and does not cause formation of hydrogen sulphide after the metal has become "tired." Treatment of the "tired" metal with ordinary laboratory air restores its ability to give hydrogen sulphide when heated in hydrogen; under similar conditions, no trace of hydrogen sulphide is produced after treatment with carefully purified air. The phenomenon of "resting" depends therefore on the adsorption of sulphur compounds from the air. Palladium-sponge behaves similarly to platinum. Reduction of nitrate to nitrite, methylene-blue to the leuco-base, or of tungsten trioxide to dioxide by active hydrogen could not be observed. H. W.

Displacement of Metals from Solutions of their Salts by less Electro-positive Elements. II. Reaction between Amides of the Alkali and Alkaline-earth Metals and Elements more Electro-positive than Tin. F. W. Bergstrom (*J. Amer. Chem. Soc.*, 1925, **47**, 1836—1841; cf. A., 1924, ii, 106, 607).—The initial reaction involves a partial replacement of the more electro-positive metal by the less electro-positive: $Al+3NH_2K \rightleftharpoons Al(NH_2)_3+3K$. Equilibrium is displaced by secondary reactions with formation of ammono salts, the mechanism being analogous to that of the reaction between solutions of strong aquo bases (*e.g.*, potassium hydroxide) with zinc or aluminium. Impure specimens of potassium ammonolanthanite, $La(NHK)_3,2-3NH_3$, and potassium ammonocerite, $Ce(NHK)_3,2-3NH_3$, have been prepared by the action of an excess of potassamide on the corresponding metal or metallic halide. Potassamide slowly reacts with gallium to form an extremely soluble ammonogallate. Cadmium, chromium, iron, cobalt, molybdenum, tungsten, and thallium either

fail to react or react extremely slowly. In general, the more electropositive a metal is, the more readily does it react with potassamide. Solutions of amide react readily with liquid amalgams of magnesium, zinc, and cadmium to form precipitates approximating in composition to the corresponding amides, but contaminated with varying quantities of potassium. Amalgamated aluminium in contact with mercury is less readily, and a dilute iron amalgam very slowly, attacked. J. S. C.

Complex Compounds of Beryllium. I. R. FRICKE and F. RUSCHHAUPT (*Z. anorg. Chem.*, 1925, **146**, 103—120).—By the crystallisation of hot solutions of anhydrous beryllium chloride in dry acetonitrile, benzonitrile, pyridine, or acetone, in the complete absence of water, complex compounds of beryllium are formed of the general type $BeCl_2,2X$, where X is a molecule of the organic solvent. These correspond with a co-ordination number 4, but the number 8 is also found in the *compound* $BeCl_2,2CH_3{\cdot}CO{\cdot}CH_3,4C_6H_6$, which is formed when a solution of beryllium chloride in acetone is treated with benzene and then allowed to crystallise. The *compound* $BeCl_2,2C_5H_5N$ is best prepared by the addition of beryllium chloride to a mixture of benzene and pyridine instead of pyridine alone. All these compounds form colourless crystals and are at once decomposed by water. The *compounds* $BeCl_2,2MeCN$ and $BeCl_2,2CH_3{\cdot}CO{\cdot}CH_3$ and the compound $BeCl_2,2PhCN$ are described. A *compound*, $BeSO_4,en,H_2SO_4,4H_2O$, is obtained by the crystallisation of an aqueous solution of beryllium sulphate, ethylenediamine, and sulphuric acid in equimolecular proportions. W. H.-R.

Complex Compounds of Beryllium. II. R. FRICKE and L. HAVESTADT (*Z. anorg. Chem.*, 1925, **146**, 121—131; cf. preceding abstract).—The *compounds* $BeCl_2,2Ph{\cdot}NO_2$, $BeCl_2,2Ph{\cdot}CHO$, $BeCl_2,2Ph{\cdot}NH_2$, and $BeCl_2,2Et_2O$ are formed by the crystallisation of hot solutions of anhydrous beryllium chloride in the dry organic compound, the last named requiring special details for which the original must be consulted. The *compound* $BeCl_2,4NH_2Me$ and the compound $BeCl_2,4NH_3$ are precipitated quantitatively when a dry ethereal solution of beryllium chloride is treated with excess of dry methylamine or ammonia, respectively. The above compounds correspond with a co-ordination number 4, whilst the number 8 is shown in the *compound* $BeCl_2,2NH_3,4CH_3{\cdot}CO{\cdot}CH_3$, prepared by the action of gaseous ammonia on a solution of beryllium chloride in acetone; this compound resembles the benzene–acetone complex previously described (preceding abstract). In addition, the co-ordination number 6 is shown in the *compound* $BeCl_2,3Ph{\cdot}NH{\cdot}NH_2$, prepared by the crystallisation of a dry ethereal solution of beryllium chloride and phenylhydrazine. These compounds form white crystals with the exception of $BeCl_2,2Ph{\cdot}NO_2$, which is pale yellow. All are decomposed by water, but with $BeCl_2,2Ph{\cdot}NH_2$ and $BeCl_2,3Ph{\cdot}NH{\cdot}NH_2$ the action is very slow. Beryllium chloride also form a complex of unknown composition with nitromethane, whilst impure beryllium phenoxide is formed when beryllium chloride and phenol are heated to the b. p. W. H.-R.

Spectrographic Study of the Formation of Mercury Complexes. P. JOB (*Compt. rend.*, 1925, **180**, 1932—1933; cf. this vol., ii, 471).—The method developed for the detection of complexes in aqueous solution by spectrographic means has been extended to the systems $HgCl_2$—KCl; $HgCl_2$—KBr; $HgCl_2$—KI. Experiments failed to indicate the existence of mercury–chlorine complexes, but the existence of the tetrabromo-mercury complex was established; it is formed by double decomposition from potassium bromide and mercuric chloride. Potassium bromide reacts with mercuric nitrate or sulphate to give mercuric bromide, which then reacts with excess of bromide to give the tetrabromo complex. The tetraiodo complex is similarly formed. Mass action constants are given. R. A. M.

Origin of Natural Aluminium Hydrosilicates. R. SCHWARZ and R. WALCKER (*Z. anorg. Chem.*, 1925, **145**, 304—310).—Aluminium hydroxide sol and silicic acid sol in neutral aqueous medium in the proportion $1Al_2O_3 : 6SiO_2$, precipitate a substance of the composition $Al_2O_3,2SiO_2,2H_2O$, which on keeping becomes similar to kaolin. The theory is advanced that the primary process in the transition of felspar to kaolin consists in a decomposition of the felspar into its components: $K_2O,Al_2O_3,6SiO_2 \rightarrow 2KOH + 2Al(OH)_3 + 6SiO_2aq.$; and that then, under special conditions, the products reunite to form kaolin or an intermediate product. The connexion between coagulation and hydrogen-ion concentration is investigated by means of the reaction $2AlCl_3+6Na_2SiO_3+6HCl=Al_2O_3+6SiO_2+12NaCl+3H_2O$. By varying the amount of free acid present, it is found that complete precipitation only takes place in a feebly acid medium, p_H 4·5—5·2. The optimal zone is at p_H 4·8—5·0. In each case, a large excess of silicic acid remains in the sol form, since the ratio $Al_2O_3 : SiO_2$ in the precipitate is 1 : 2. An investigation of the influence of the anion on the composition of the precipitation product shows that, by using aluminium acetate instead of the chloride, no difference is to be observed. Some experiments with a salt of the composition $Na_4Si_3O_8$, instead of sodium metasilicate, give a value somewhat greater than 2 for the molecular ratio of SiO_2, whereas with sodium metasilicate, it is somewhat less than 2. Possibly with the acid $H_2Si_2O_5$ the exact ratio 1 : 2 would be obtained. Experiment appears to confirm the view that the natural formation of kaolin is not due to an ionic reaction, but to the mutual coagulation of aluminium hydroxide sol and silicic acid sol. L. L. B.

Thermal Analysis of the Systems Thallous Sulphide–Arsenic Trisulphide and Thallous Sulphide–Lead Sulphide. G. CANNERI and L. FERNANDES (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 671—676).—Thermal analysis of the former system indicates the existence of the compounds Tl_3AsS_3, $Tl_4As_2S_5$, $Tl_6As_4S_9$, and $TlAsS_2$, m. p., respectively, 295°, 278°, 317°, and 300°. The ortho- and pyro-thioarsenites, Tl_3AsS_3 and $Tl_4As_2S_5$, occur at transition points and decompose on fusion. Thallous sulphide and lead sulphide, completely miscible in the liquid state, are only partly so in the solid state, conjugate solid solutions containing

respectively 3 and 75% of lead sulphide separating at 290°. This system possesses a eutectic mixture, containing 40% of lead sulphide, m. p. 290°. Lead sulphide precipitated from slightly acid solutions containing thallium contains up to 4% of thallous sulphide. The results indicate the probable occurrence of thallium in arsenic minerals as thio-salts in solid solution in the corresponding lead salts, whilst in galena the thallium occurs as sulphide in isomorphous mixture with lead sulphide. F. G. T.

Combustion of Carbon. I. H. F. SMITH and W. C. EBAUGH (*Ind. Eng. Chem.*, 1925, **17**, 694—695).—From tests conducted in an experimental producer in which the oxidising and reducing zones were clearly defined, it is concluded that at a bright red heat carbon monoxide is the principal, if not the primary, product of combustion, and that the oxidising zone is very thin indeed. [Cf. *B.*, 1925, 657.] D. G. H.

Germanium. XI. Germanium Glasses. L. M. DENNIS and A. W. LAUBENGAYER (*J. Amer. Chem. Soc.*, 1925, **47**, 1945—1947).—Germanium glasses of four types have been prepared and compared with the corresponding silicate glasses. Replacement of silicon by germanium raises the refractive index. Owing to their much lower m. p., homogeneous, air-free germanium glasses can be prepared much more easily than the corresponding silicates. J. S. C.

Complex Sulphites and Thiosulphites of the Rare-earth Metals. G. CANNERI and L. FERNANDES (*Gazzetta*, 1925, **55**, 440—453).—Metals of the cerium group, by virtue of their high basicity, combine with complex acid radicals to form compounds analogous to those of the alkali and alkaline-earth metals. In these compounds the individuality of the complex is not destroyed by the physical and chemical characteristics of the rare earths. *Uranylsulphites* of the rare earths of the type

$$(UO_2)_5,(SO_3)_8R_2^{III},15H_2O,$$

where R=La, Ce, Nd, and Pr, were obtained by crystallising in a vacuum at the ordinary temperature, a solution, saturated with sulphur dioxide, containing the rare-earth hydroxide and uranyl sulphate. The products obtained were microcrystalline and of constant composition. By saturating a very concentrated solution of ammonium paramolybdate with sulphur dioxide, and adding a solution of the rare-earth acetate, *molybdosulphites* of the rare earths were obtained as minute prisms. The composition of these crystals varied on fractional crystallisation, the rare-earth content falling. It was not possible to assign rational formulæ to them, and it is suggested that this is due to the partial miscibility in the solid state of ammonium molybdosulphite with the corresponding rare-earth compounds. *Cuprosulphites* of the rare earths were obtained as minute crystals by crystallising under reduced pressure a warm solution of copper carbonate and the rare-earth hydroxide, saturated with sulphur dioxide. These compounds are darker in colour and much less stable than the corresponding alkali metal compounds.

The general formula of these compounds was $RCu(SO_3)_2,8H_2O$, where R=Ce, La, Pr, or Nd. *Cuprothiosulphates* of the formulæ $RCu(S_2O_3)_2,8H_2O$ (R=Ce, La, Pr, Nd, Th) and $ZrCu_2(S_2O_3)_3,30H_2O$ were obtained as yellow, microcrystalline precipitates, by mixing solutions of copper sulphate and a soluble rare-earth salt, each previously saturated with sulphur dioxide. In the cases of thorium and zirconium, the solutions must be neutral before the addition of the thiosulphate. F. G. T.

Mechanism of the Fixation of Nitrogen as Sodium Cyanide. E. W. GUERNSEY and M. S. SHERMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1932—1940).—The formation of sodium cyanide in the system, sodium carbonate–carbon–iron–nitrogen at high temperatures is represented by the reaction scheme: $Na_2CO_3 \rightleftharpoons Na_2O+CO_2$; $CO_2+C \rightleftharpoons 2CO$; $Na_2O+C \rightleftharpoons 2Na+CO$; $2Na+2C \rightleftharpoons Na_2C_2$; Na_2C_2 (gaseous)$+N_2 \rightleftharpoons 2NaCN$. The absorption of nitrogen by sodium carbide is the only one of the series of reactions which is catalysed by iron. The existence of such intermediates as sodium nitride, sodium cyanamide, or cyanogen is improbable. J. S. C.

Composition and Stability of Complex Metal–Ammonium Ions. (MISS) H. J. DE WIJS (*Rec. trav. chim.*, 1925, **44**, 663—674).—The composition of complex metal–ammonium ions was examined by determining the pressure of the gas over a solution of these ions by a dynamic method. The composition of the ion $M_m(NH_3)_n^{\cdot\cdot}$ is given by $n/m=(b-b_1)/a$, where a is the concentration of the metallic salt, b that of ammonia, and b_1 that of free ammonia. This equation can be applied only if the solution contains no free metallic ion or other complex ion. The existence of the ions $Ag(NH_3)_2^{\cdot}$, $Cu(NH_3)_4^{\cdot\cdot}$, $Cd(NH_3)_4^{\cdot\cdot}$, $Zn(NH_3)_4^{\cdot\cdot}$, and $Ni(NH_3)_6^{\cdot\cdot}$ is indicated. The values of the constants ${}_2K_c$ and ${}_4K_c$ for the equilibria $M(NH_3)_2^{\cdot\cdot} \rightleftharpoons M^{\cdot\cdot}+2NH_3$ and $M(NH_3)_4^{\cdot\cdot} \rightleftharpoons M^{\cdot\cdot}+4NH_3$ were found to be $2{\cdot}7\times10^{-5}$ and $2{\cdot}5\times10^{-7}$, respectively, for cadmium and $1{\cdot}4\times10^{-5}$ and $9{\cdot}3\times10^{-10}$ for zinc. For nickel, ${}_2K_c=2{\cdot}4\times10^{-5}$, ${}_4K_c=4{\cdot}8\times10^{-8}$, ${}_6K_c=2{\cdot}1\times10^{-8}$. L. L. B.

Action of Phosphorus on Salts containing Oxygen [Nickel Nitrate]. I. W. SCHMOSS (*Bul. Soc. Chim. România*, 1925, **7**, 32—35).—On boiling with yellow phosphorus in an atmosphere of carbon dioxide an alcoholic solution of nickel nitrate, saturated at 20°, for 36 hrs., a pale green precipitate of nickel triphosphate is produced. After washing with benzene and drying at 20°, this compound has the composition $NiH_3P_3O_{10},3H_2O$ and d_4^{15} 2·159. It loses $3H_2O$ at 100—110° and is slightly soluble in water and readily soluble in ammonia and in mineral acids. A. R. P.

High-melting Lower Oxides. E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **145**, 127—140).—A series of lower oxides has been prepared by reducing the corresponding higher oxides with hydrogen or carbon. From titanium and zirconium dioxides and from tantalum pentoxide no lower oxides of definite composition could be obtained, and it is doubtful whether the previously recorded oxides, Ta_2O_4 and Ta_2O_3, exist (cf. this vol., ii, 374). From

vanadium pentoxide a sesquioxide, V_2O_3, m. p. 1970°, and a tetroxide, V_2O_4, m. p. 1640°, were obtained by reduction with hydrogen and carbon, respectively; the former was not further reduced by hydrogen, even at 1700°. From niobium pentoxide and cerium dioxide sesquioxides, Nb_2O_3, m. p. 1780°, and Ce_2O_3, m. p. 1690°, were prepared by reduction with hydrogen. The oxides WO_2, m. p. 1230—1330°, W_2O_5, MoO_2, and Mo_2O_5, were obtained by reducing the trioxides with carbon or with metallic tungsten and molybdenum, respectively. The oxide, U_3O_8, formed when uranium trioxide was heated in air, yielded the blue and brown forms of the dioxide, UO_2, when heated in nitrogen and hydrogen, respectively; both forms melt at 2230—2330°.

These lower oxides differ widely in electrical resistance, but the temperature coefficients are all negative. Tungsten and molybdenum pentoxides have lower resistances than the corresponding dioxides, and the two forms of uranium dioxide differ in specific resistance. A. G.

Action of certain Reagents on Ozone. L. I. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 1850—1853).—The destruction of ozone on passing through dilute or concentrated sulphuric acid or acid permanganate solution is so slight as to be negligible. Considerable destruction is produced by 5% sodium hydroxide solution and by ordinary specimens of phosphorus pentoxide. Phosphorus pentoxide after sublimation in a current of oxygen loses its ability to destroy ozone. J. S. C.

Sulphur Sesquioxide. I. Vogel and J. R. Partington (*J. Chem. Soc.*, 1925, **127**, 1514—1524).—Sulphur sesquioxide, S_2O_3, is prepared by adding liquid sulphur trioxide to finely-powdered sulphur in the absence of moisture. After 30 secs. a violent reaction takes place and a bluish-green solid is deposited. The supernatant liquid is poured off and adherent sulphur trioxide removed by warming in a vacuum. Sulphur sesquioxide is at once decomposed by water, a complex reaction taking place in which sulphur is deposited and a mixture of sulphuric, sulphurous, tri-, penta-, and possibly tetra-thionic acids are produced. It reacts violently with ether and alcohol, whilst with sodium ethoxide in alcoholic solution it forms sodium ethyl sulphoxylate, $NaEtSO_2$, which hydrolyses to form sodium sulphoxylate. The sesquioxide soon decomposes at the ordinary temperature with evolution of sulphur dioxide and deposition of sulphur, but it may be preserved unchanged in a completely dry oxygen-free atmosphere at a pressure of less than 1 mm. of mercury. It dissolves in fuming sulphuric acid to form a blue solution which is a true and not a colloidal solution. W. H.-R.

Additive Products of Selenium Dioxide with the Halogen Acids. C. W. Muehlberger and V. Lenher (*J. Amer. Chem. Soc.*, 1925, **47**, 1842—1844).—The compounds $SeO_2,2HCl$ and $SeO_2,2HBr$ are identical with the hydrates $SeOCl_2,H_2O$ and $SeOBr_2,H_2O$, respectively. The former has d^{25} 2·246, a surface tension at 25° of 55 dynes/cm.^{2}, an electrical conductivity $2{\cdot}7\times10^{-2}$

mho, and n^{20} 1·642. The m. p. is below −100°. Dissociation begins at 94°, the b. p. rising to 179° without indication of any constant-boiling mixture. Metals react to form chlorides and selenites, there being also a simultaneous reduction to selenium monochloride and elementary selenium. The substance readily reacts with sulphur, phosphorus, arsenic, selenium, tellurium, and the halogens.

Selenium oxychloride is conveniently prepared by mixing 4 parts of SeO_2,2HCl with 1 part of sulphuric acid (d 1·84). The oxychloride prepared in this way has b. p. 176°, m. p. 10·9°; d^{22} 2·424.

The compound SeO_2,2HBr, d^{22} 3·077, is prepared as a red-brown oil on passing hydrogen bromide over selenium dioxide. At 115°, it begins to decompose, producing bromine, selenium monobromide, tetrabromide, and oxybromide, selenium dioxide, water, and hydrogen bromide. On cooling to −10°, crystals of selenium tetrabromide separate. An excess of selenium dioxide causes the separation of yellow needles (m. p. 40°) of the oxybromide, $SeOBr_2$. The existence of SeO_2,4HBr is verified, but no evidence was obtained as to the existence of the compound SeO_2,5HBr. J. S. C.

Dichromates of Ter- and Sexa-valent Metals. G. CALCAGNI (*Gazzetta*, 1925, **55**, 396—406).—A highly hygroscopic, amorphous paste of *chromium dichromate*, $Cr_2(Cr_2O_7)_3$, was obtained by evaporating a solution of chromium oxide in chromic acid, and the less hygroscopic basic ferric dichromate, $Fe_2O(Cr_2O_7)_2$, from a solution of ferric hydroxide in chromic acid. A *basic aluminium dichromate*, $Al_2O(Cr_2O_7)_2$, and *molybdenum dichromate*, $Mo(Cr_2O_7)_3$, were obtained by analogous methods. Attempts to prepare the corresponding compounds of uranium and tungsten were unsuccessful. F. G. T.

Complex Derivatives of Quinquevalent Molybdenum. G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 676—679).—Klason's salt, ammonium molybdenyl chloride, $(NH_4)_2MoOCl_5$ (A., 1901, ii, 162), may act both as a complex and as a double salt. Pyridine acetate precipitates from a cold saturated solution of Klason's salt a brick-red double compound of pyridine and molybdenyl chloride, $MoOCl_3,C_5H_5N$, whilst from a solution of Klason's salt in aqueous alcohol, hexamethylenetetramine hydrochloride precipitates dark red crystals of the composition

$$2[(NH_4)_2Mo(OH)_4Cl_3],C_6H_{12}N_4,HCl.$$

F. G. T.

Molybdovanadates. II. G. CANNERI (*Gazzetta*, 1925, **55**, 390—396; cf. A., 1924, ii, 118).—The systems NH_4VO_3–MoO_3, KVO_3–MoO_3, and $NaVO_3$–MoO_3 have been investigated at 15°. As at 30°, two kinds of crystals are obtained from solutions containing alkali vanadates and molybdic anhydride: red, well-formed, soluble crystals, rich in vanadium, and colourless or yellow, sparingly soluble crystals, rich in molybdenum. The composition of the crystals is generally related to that of the solution, but an apparent anomaly occurs with the red crystals obtained from the system KVO_3–MoO_3. The molybdic oxide content of these crystals

decreases from 14·62% to 0·34% as the ratio $MoO_3 : V_2O_5$ in the solution increases from 0·5 to 1·125. This apparent contradiction of the hypothesis that the red crystals are isomorphous mixtures is explained by the assumption that the molybdenum is distributed in the solution between a polyvanadate form and that of a complex radical of a heteropoly-anion type, the equilibrium between these being dependent on the amount of molybdenum present and on the temperature. This assumption is supported by the fact that from solutions in which the ratio $MoO_3 : V_2O_5$ is greater than 1·125, a yellow compound, very rich in molybdenum, separates. Comparison of the behaviour of these systems at 30° and 15° shows that the solubility in the solid state of the polymolybdate compounds in the polyvanadates increases with temperature. On fractionation, the red crystals decrease in molybdenum content, approaching the hexavanadates in composition. On the other hand, increase of the temperature of fractionation results in an augmented molybdenum content. The following are reported as definite *compounds*: $2(NH_4)_2O,3MoO_3,2V_2O_5,8H_2O$, long, lemon-yellow prisms; $4(NH_4)_2O,6MoO_3,2V_2O_5,6H_2O$, yellow prisms; $4K_2O,6MoO_3,3V_2O_5,10H_2O$ and $5K_2O,10MoO_3,4V_2O_5,14H_2O$, both yellow; $2Na_2O,3MoO_3,V_2O_5,10H_2O$, yellow micro-crystals. F. G. T.

Complex Compounds of Pyrocatechol and Pyrogallol with Acids of the Molybdenum Group. L. FERNANDES.—(See i, 1061.)

Supposed Isomorphism of Uranyl Compounds with those of Isomorphogenous Metals of the Magnesium Group. G. CAROBBI (*Gazzetta*, 1925, **55**, 406—410).—Isomorphism of the above type is doubtful as a result of unsuccessful attempts to replace metals of the magnesium group by the uranyl radical in a number of double salts. F. G. T.

Hypochlorous Acid and the Alkali Hypochlorites. R. DIETZEL and F. SCHLEMMER (*Z. anorg. Chem.*, 1925, **145**, 381—393).—The reaction $2NaOH+Cl_2=NaOCl+NaCl+H_2O$ has been quantitatively investigated by titrimetric and absorption spectra methods. If the reaction proceeds as above at low temperatures, a *M*-sodium hypochlorite solution should be formed by passing chlorine into sodium hydroxide solution. Actually, titration with thiosulphate, arsenious acid, or silver nitrate did not give values for the hypochlorite or chloride concentration in accordance with the above equation. At the most, only about 0·5*M*-hypochlorite solutions were obtained. Since the total quantity of chlorine is not recovered, it is assumed that part of the chlorine introduced forms compounds in which the chlorine cannot be determined by usual titrimetric methods. Dilute hypochlorite solutions are fairly stable if prepared and kept under suitable conditions. A slight excess of free chlorine or hypochlorous acid causes a rapid change, according to the equation $ClO'+2HClO=ClO_3'+2H^{\cdot}+2Cl'$. The Hartley–Baly

absorption method of investigation has been applied to the systems water–chlorine and sodium hydroxide–chlorine. Salt formation completely changes the character of the hypochlorous acid absorption spectrum, a well-marked band taking the place of an essentially linear curve. On account of the great transparency of sodium chlorate, no decision can be reached as to whether part of the chlorine in the reaction $2NaOH+Cl_2=NaOCl+NaCl+H_2O$ forms sodium chlorate, or whether by stirring a dilute hypochlorite solution, the free hypochlorous acid (always present on account of hydrolysis) leads to a continuous formation of chlorate.

L. L. B.

Arsenates of Tervalent Manganese. I. E. Deiss (*Z. anorg. Chem.*, 1925, **145**, 365—377).—The appearance of a violet colour on oxidation of manganous salts in presence of arsenic acid (Barreswil, *Compt. rend.*, 1857, **44**, 677) is due to the formation of triarsenatomanganic acid, $[Mn(AsO_4)_3]H_6,3H_2O$. Whilst diphosphatomanganic acid is stable and the triphosphato acid unstable (Meyer and Marek, A., 1924, ii, 555), the reverse is the case with the corresponding arsenic compounds. Conditions for the formation of the violet-red crystalline triarsenato-acid are given, and its preparation is described: (i) by dissolving manganic acetate in cold, concentrated arsenic acid solution; (ii) similarly from manganic hydroxide; (iii) by the action of arsenic acid on Christensen's brown "manganic acetate solution" (A., 1884, 398). The brown "manganic acetate" solution of Christensen and crystallised bright red manganic acetate show different behaviour, which is ascribed to their different methods of formation. L. L. B.

Determination of Equilibria between Stages of Oxidation by Potential Measurements. II. Manganese in Phosphoric Acid Solution. G. Grube and M. Staesche (*Z. Elektrochem.*, 1925, **31**, 362—371; cf. Grube and Huberich, A., 1923, ii, 138).—In phosphoric acid solution the reversible reactions $2Mn^{III} \rightleftharpoons Mn^{II}+Mn^{IV}$ and $4Mn^{IV} \rightleftharpoons 3Mn^{III}+Mn^{VII}$ take place, the equilibria being slightly affected by the manganese concentration and very markedly by the phosphoric acid concentration. Tervalent manganese phosphate shows a maximum of decomposition in highly concentrated acid and a low minimum in 30—35-*N*-acid, whereupon decomposition increases slowly as the acidity decreases. With quadrivalent manganese phosphate the equilibrium shifts continuously and rapidly from left to right as the acidity diminishes, so that the salt can be prepared only in highly acid solutions. Quadrivalent manganese phosphate is a better oxidising agent than permanganic acid and a better reducing agent than tervalent manganese phosphate. W. A. C.

Reactions in the Solid State. V. D. Balarev (*Z. anorg. Chem.*, 1925, **145**, 117—121).—A reply to Hedvall and Heuberger's criticism (this vol., ii, 306) of previous papers (cf. A., 1924, ii, 483, 611, 858). Manganese and tin dioxides do not react with calcium oxide at 950°, but they combine rapidly with strontium and barium

oxides. Barium oxide is more hygroscopic than phosphorus pentoxide and much more so than calcium oxide, and is, therefore, very difficult to free from a surface layer of the low-melting hydroxide. Molybdenum and tungsten trioxides react with calcium oxide, but these reactions are conditioned by the fusion of molybdenum trioxide and calcium tungstate, respectively. Barium oxide and calcium carbonate react to the extent of 90% in the presence of a trace of water because barium hydroxide is continuously re-formed by the dehydration of the calcium hydroxide produced. A moist mixture of manganese dioxide and potassium chlorate reacts at a temperature 12° lower than when carefully dried. A. G.

Osmium Tetroxide. II. Compounds of Osmium Tetroxide. F. KRAUSS and D. WILKEN (*Z. anorg. Chem.*, 1925, **145**, 151—167).—When osmium tetroxide vapour is condensed in a cooled receiver it collects as white needles which are readily soluble and reactive. When heated at 40° the needles are converted into a yellow, sparingly soluble, and non-reactive form, which may be reconverted into the white oxide by cooling in liquid air or by sublimation. The white form melts at 39·5° and the yellow form at 41°, and the former has the higher vapour pressure; the b. p. is 134°. Both forms had the calculated osmium content and liberated the calculated weight of iodine from potassium iodide. The compounds of osmium tetroxide with alkali hydroxides described by Tschugaev (A., 1918, ii, 322) could not be obtained by his method, but by adding saturated solutions of the hydroxides to the solid white tetroxide the following *compounds* were obtained: $OsO_4,2CsOH$, $OsO_4,2KOH$; $OsO_4,2NH_4OH$; $OsO_4,Ba(OH)_2$; $OsO_4,2CsF$; $OsO_4,2RbF$; only the potassium compound has the same composition as Tschugaev's preparation. These compounds form light red-brown or yellow crystals which, however, decompose when separated from the mother-liquor. Complete analysis was, therefore, impossible, but, by washing rapidly with water and then dissolving, solutions were obtained in which the ratio of osmium to alkali metal and to iodine liberated could be determined; the compounds were thus shown to contain octavalent osmium. Similar compounds were not formed with cyanides, thiocyanates, fluorides, or organic bases. A. G.

Molecular Compounds of Halogen-Metal Acids and Acid Amides. R. FRICKE and R. RUSCHHAUPT (*Z. anorg. Chem.*, 1925, **146**, 141—148).—The yellow *compounds*, $HAuCl_4,2Ph\cdot CO\cdot NH_2$ and $H_2PtCl_6,2Ph\cdot CO\cdot NH_2,2H_2O$, are prepared by the crystallisation of aqueous solutions of benzamide and chloroauric or chloroplatinic acids, respectively, in the presence of excess of hydrochloric acid. When heated, the compound $HAuCl_4,2Ph\cdot CO\cdot NH_2$ gradually decomposes even below 100° with the formation of metallic gold, whilst the compound $H_2PtCl_6,2Ph\cdot CO\cdot NH_2,2H_2O$ begins to soften at 100° and is completely melted at 130—140°. The *compound* $HAuCl_4,2Me\cdot CO\cdot NH_2$ is obtained in yellow needles by the crystallisation of a concentrated aqueous solution of chloroauric acid and acetamide. The solid must be separated quickly and no free

hydrochloric acid must be present or hydrolysis of the acetamide takes place. On heating, the compound decomposes liberating metallic gold. When concentrated aqueous solutions of acetamide and chloroplatinic acid are mixed and allowed to crystallise in a vacuum in the presence of phosphoric oxide, the yellow-brown *compound*, $H_2PtCl_6,2Me{\cdot}CO{\cdot}NH_2,2H_2O$, is deposited; it begins to soften at 65° and melts completely at 83—84°. W. H.-R.

Degree of Hydration of Calcium Oxalate. M. Auméras (*Compt. rend.*, 1925, **181**, 214—215).—Calcium oxalate precipitated from 0·1*N*-oxalic acid and calcium chloride solutions in presence of hydrochloric acid (cf. A., 1924, i, 137) has the composition CaC_2O_4,H_2O. S. K. T.

Preparation of Colloidal Gold Solution by the Mellanby–Anwyl–Davies Technique. R. L. Haden (*J. Lab. Clin. Med.*, 1925, **10**, 310—311).—To 1 c.c of 1% potassium oxalate solution in 100 c.c. of boiling water is added, dropwise, a mixture of 1 c.c. of 1% auric chloride solution and 1·3 c.c. of 1% potassium hydroxide solution. Chemical Abstracts.

Preparation of Metal Tellurides from Hydrogen Telluride and Solutions of Salts. A. Brukl (*Monatsh.*, 1924, **45**, 471—484).—A number of tellurides of the metals have been prepared by precipitation of solutions of salts with hydrogen telluride or, in certain cases, with sodium telluride solution. The compounds PdTe, Cu_2Te, PbTe, BiTe, NiTe, CoTe, As_2Te_3 are described in greater detail than hitherto; the following tellurides have been isolated for the first time: *mercuric*, *auric*, *ferrous*, *stannous*, *stannic*, *antimonious*, *thallous*, and *platinic*. Most of these compounds are unstable in air and tend to reduce solutions of substances such as mercuric or cupric salts. They are soluble in dilute acids with the exception of the lead, nickel, cobalt, gold, platinum, arsenic, and antimony tellurides. There is in all cases a progressive deepening of colour from the sulphide to the selenide and the telluride. G. M. B.

Crystal for Wave-length Measurements of Soft *X*-Rays. L. Pauling and A. Björkeson (*Proc. Nat. Acad. Sci.*, 1925, **11**, 445—447).—Hexagonal β-alumina possesses an unusually large grating-constant, rendering it very suitable for measurements of soft *X*-rays. For the line CuK_α, the constant is 11·240 Å. and for AgL_α, 11·225 Å. The difference is a real effect. The crystal gives strong reflection. R. A. M.

Universal *X*-Ray Spectrograph. A. Müller (*J. Sci. Instruments*, 1925, **2**, 312—318).—A compact *X*-ray spectrograph is described, which, by the use of interchangeable parts, permits the employment of the Bragg, Hull, Debye, Laue, and revolving crystal (Schiebold, Polanyi) methods of *X*-ray and crystal analysis. F. G. T.

Potassium as a Mercury-vapour Trap. A. L. Hughes and F. E. Poindexter (*Phil. Mag.*, 1925, [vi], **50**, 423—439).—The efficiency of a bulb lined with metallic potassium as a mercury trap

in a vacuum system has been investigated. Using the first appearance of mercury lines in the helium spectrum as a criterion, it is found that a potassium-lined trap acts as an efficient barrier until the potassium has absorbed at least 150% of its own weight of mercury. A more complete investigation using an ionisation gauge shows that the potassium-lined bulb is at least as efficient as a liquid air-trap for mercury. Dry air can be passed over the surface of the potassium without affecting its trapping power. The method of making the trap is described in detail. A. B. M.

Construction of Nernst Filaments. H. D. GRIFFITH (*Phil. Mag.*, 1925, [vi], **50**, 263—265).—A mixture of 80% of zirconium oxide, 10% of thorium oxide, 5% of calcium oxide, 5% of magnesium oxide, with a trace of boric acid is ground to a thick paste with glycerol or with sugar solution, and forced through a press as threads 1·3 mm. in diameter. These are slowly heated until the sugar chars, and fired by passing through a carbon arc. The negative electrode is a loop of platinum wire, 0·1 mm. in diameter, attached by a layer of the above paste, which is allowed to dry in air. The positive seal is made by setting the end of the filament in a twist of several platinum wires, using a luting of equal parts of the oxides of yttrium, thorium, cerium, and zirconium. As a balancing resistance for such a filament 20 mm. long, two 60-watt, 220-volt lamps in parallel are satisfactory. The light from these filaments is somewhat yellower than that from commercial filaments.

F. G. T.

Filling Mercury Manometers. P. F. WEATHERILL (*J. Amer. Chem. Soc.*, 1925, **47**, 1947; cf. Swan, this vol., ii, 707).—A method of filling mercury manometers is described, mercury being distilled into the apparatus in a high vacuum. Clean mercury surfaces are easily obtained. J. S. C.

Simple Differential Air Thermometer for Use at Low Temperatures. W. A. NOYES (*J. Amer. Chem. Soc.*, 1925, **47**, 1942—1944).—A simple air thermometer for the approximate determination of temperatures between the b. p. of liquid air and 0° is described. Standard temperatures for calibration are those of melting ice, carbon dioxide snow, and alcohol (—78·5° at 760 mm. with a change of 0·1° for 10 mm.) and of fresh liquid air (—191·62°). J. S. C.

Laboratory Ozoniser Yielding High Concentrations of Ozone. L. I. SMITH (*J. Amer. Chem. Soc.*, 1925, **47**, 1844—1850).—An ozoniser for general laboratory use is described. The apparatus is capable of producing concentrations of ozone in ozonised oxygen of 15%, or of making 4 g. of ozone per hour. J. S. C.

Rotating Dialyser. A. ASTRUC and E. CANALS (*J. Pharm. Chim.*, 1925, [viii], **2**, 14—17).—A dialyser is arranged so that it may be mechanically rotated in a vessel containing water, whilst at the same time a stirrer rotates in the opposite direction inside the dialyser. It is shown that the speed of dialysis is increased. The

presence of gum arabic or gum tragacanth in solution, which usually greatly hinders the dialysis of salts, has little or no effect when the dialyser is rotated. B. F.

Simple Laboratory Apparatus for Electrodialysis. W. FUCHS and E. HONSIG (*Ber.*, 1925, **58**, [*B*], 1323—1324).—A small glass cylinder is covered at the bottom with a parchment membrane and provided at the side with a small opening which serves for the introduction of the solution or a stirrer. It is fixed by pieces of cork into a Büchner funnel through which water or other liquid can be continuously circulated. The electrodes are placed between the funnel and the cylinder. H. W.

Simple Apparatus for Extracting Liquids with a Specifically Heavier Solvent. H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1925, [ii], **110**, 37—39).—The solvent (*e.g.*, chloroform) is distilled from a flask, *A*, fitted with a branched delivery tube. The vapour passes through one branch to the condenser, and after condensation streams down a wide connecting tube (into which the two branches are sealed) into a flask, *B*, containing the liquid to be extracted. The second branch bends downward inside the wide tube nearly to the bottom of flask *B*, and serves to return the extract continuously to the flask *A*. Flask *B* may or may not be heated. C. H.

Apparatus for Preparing Vapour–Air Mixtures of Constant Composition. W. P. YANT and F. E. FREY (*Ind. Eng. Chem.*, 1925, **17**, 692—694).—The liquid to be volatilised is fed into a measured air stream by means of a constant drop of water into one arm of a U-tube containing mercury in the bend, over which, in the other arm, is the reservoir of liquid to be volatilised. This is forced up to the volatiliser by the pressure of the mercury, itself caused to rise by the constantly and evenly increasing head of water over it. The air, which is kept at constant pressure, passes into a flow-meter and out at a rate of 3 litres per minute, giving about 9 air changes an hour in a 20-litre bell jar. The calibration of the apparatus is described. D. G. H.

Distilling Flask for Corrosive Liquids. F. E. BROWN (*Ind. Eng. Chem.*, 1925, **17**, 706; cf. this vol., ii, 589).—An ordinary distilling flask is adapted by first sealing on to its neck a tube through which the thermometer will pass, and to that another wider tube. The thermometer is kept in place by a small glass tube, too small to allow the ring of the thermometer to pass, which rests on the join of the two sealed-on tubes, and is so arranged that liquid can drain past it. D. G. H.

Laboratory Apparatus. H. JOHN and V. FISCHL (*J. pr. Chem.*, 1925, [ii], **110**, 279—282).—A description of simple devices for sublimation and distillation. M. J.

Electrodes for the Measurement of Small Bioelectric Potentials. E. J. LUND (*Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 128—129).—The electrode was made up with a 3% pure lead

amalgam and 0·05—0·01 mol. of lead chloride. The copper leads were dipped into copper amalgam in place of mercury. The drift in potential at constant temperature was slow, and small enough to permit measurements of 1·0—0·05 mv. with an error of about 0·01 mv. CHEMICAL ABSTRACTS.

Mineralogical Chemistry.

Presence of the Compound $K_2Mn_2(SO_4)_3$ among the Products of Activity on Vesuvius. F. ZAMBONINI and G. CAROBBI (*Gazzetta*, 1925, **55**, 414—416).—Minute, faint rose-coloured tetrahedra, intimately mixed with thenardite and alite, have been found by microscopical examination of stalactites in the lava cupola formed in 1922. Their chemical and optical properties identify them with the compound $K_2Mn_2(SO_4)_3$, previously synthesised by Carobbi and Caglioti (A., 1924, ii, 685), and the name *manganolangbeinite* is proposed for them. F. G. T.

Analytical Chemistry.

Apparatus for Direct Reading of Conductivity (and Salt Content) of a Salt Solution. TÖDT (*Chem.-Ztg.*, 1925, **49**, 656—657).—An ordinary Wheatstone bridge apparatus is used with a fixed resistance, and the graduations are made to read directly in terms of conductivity or concentration of salts. G. M. B.

Use of the Cornec–Cottet Pipette in the Measurement of Small Volumes in Micro Analysis. M. NICLOUX (*Bull. Soc. Chim. biol.*, 1925, **7**, 750—752).—The pipette is a capillary tube containing a small bulb and is fused on to a tube of wider bore, the liquid rising to the point where the capillary tube ends. Excellent agreement has been obtained in figures for the density of blood (1·060) with pipettes containing 0·1022—0·1246 g. of water and for urinary nitrogen by the micro-Kjeldahl method. H. J. C.

Burette for Gas Analysis in Electrochemical Processes. W. JOFINOV (*Chem.-Ztg.*, 1925, **49**, 657).—The gas burette previously described (A., 1920, ii, 221) is simplified by substituting for the glass tap a pinch-cock on a piece of wide rubber tubing cut off below at an angle. G. M. B.

Apparatus for Ferrous Oxide Determinations. F. MEYER (*Chem.-Ztg.*, 1925, **49**, 622).—The apparatus, which replaces the Bunsen valve, consists of a narrow glass tube with a glass valve

at the top and having a side siphon tube, the latter dipping into a reservoir containing sodium hydrogen carbonate solution. When the solution flask cools, the valve closes, and the solution siphons over into the acid solution. The carbon dioxide evolved temporarily checks the siphon action, which continues intermittently until the flask is cold. W. M. C.

Modification of Duboscq-Pellin Colorimeter for Biocolorimetric Work. H. Wu (*Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 111—114).—An extra cup, movable stage, and vernier are added to one side of the colorimeter; with phenol-red as indicator, the apparatus is specially suitable for p_H determinations.
CHEMICAL ABSTRACTS.

Recommended Specifications for Analytical Reagent Chemicals. W. D. COLLINS, H. V. FARR, J. ROSIN, G. C. SPENCER, and E. WICHERS (*Ind. Eng. Chem.*, 1925, **17**, 756—760).—Recommended specifications are given for hydrochloric, nitric, oxalic, and sulphuric acids, ammonium hydroxide, oxalate, and thiocyanate, barium chloride, iodine, potassium dichromate and hydroxide, silver nitrate, sodium hydroxide and oxalate. [Cf. *B.*, 1925, 695.]
D. G. H.

Explosion Method for Peroxide Fusions. W. F. MUEHLBERG (*Ind. Eng. Chem.*, 1925, **17**, 690—691).—The finely-divided material is well mixed with sugar carbon and sodium peroxide, and ignited in a nickel crucible. The fused mass readily separates from the crucible, and the acidified solution is clear. It is necessary to use rather larger quantities of peroxide by this method, with a corresponding increase in the volume of solution, and a certain amount of unfused residue is left, which may frequently be disregarded, or its weight subtracted, although it may be necessary to re-fuse it. Results appear to be as accurate as those obtained by peroxide fusion over a free flame or with alkali carbonate in platinum. [Cf. *B.*, 1925, 674.] D. G. H.

Potentiometric Hydrogen-ion Measurements with Non-gas Electrodes. H. C. PARKER (*Ind. Eng. Chem.*, 1925, **17**, 737—740).—A large number of metals and combinations of oxides and metals have been tested by various means for suitability in measuring hydrogen-ion concentrations. Amongst the most promising are tungsten–manganese sesquioxide and platinum–manganese sesquioxide electrodes. [Cf. *B.*, 1925, 696.] D. G. H.

Volumetric Determination of the Reaction of a Medium at True Neutrality. G. CHABOT (*Bull. Soc. chim. Belg.*, 1925, **34**, 202—211).—A mixture of equal proportions of 1% alcoholic solutions of neutral-red and phenol-red which independently show colour changes from red at p_H 6·8 to yellow at p_H 8·0 and from yellow at p_H 6·8 to red at p_H 8·4, respectively, forms an indicator which shows a sharp colour change at the point of real neutrality

(p_H 7·07) and is efficient for the titration of very weak acids and bases. If the ordinary method of titration be employed, 1—2 drops of each indicator for each 10 c.c. of liquid are employed, but better results are obtained by using the comparative method of Walpole (cf. A., 1910, ii, 541; 1915, ii, 61), a solution made by adding 50 c.c. of a 0·2*N*-solution of potassium dihydrogen phosphate to 31·51 c.c. of a 0·2*N*-solution of sodium hydroxide and diluting to 200 c.c. (p_H 7·07) being used as the standard. In the latter case 0·25 c.c. of each indicator solution is added to each 10 c.c. of the liquid. The indicator is very sensitive to carbon dioxide, which may be eliminated by any of the usual methods. Full details of technique and examples are given, the results being very satisfactory. J. W. B.

Determination of Chloride in Animal Tissue. R. VLĂDESCU.—(See i, 1113.)

Sodium Arsenite as Reagent for Loosely Combined Reactive Oxygen, Sulphur, and Nitrogen. A. GUTMANN.—(See i, 1059.)

Micro Determination of Nitrogen. A. R. ROSE (*J. Biol. Chem.*, 1925, **64**, 253—256).—The preliminary digestion with sulphuric acid in the micro-Kjeldahl method is hastened by the addition of perchloric acid and hydrogen peroxide; after oxidation is complete the solution is diluted and the nitrogen determined directly by means of Nessler's reagent. C. R. H.

Micro Determination of Ammonia in Urine. A. YOVANOVITCH.—(See i, 1114.)

Colour Reaction for Nitrites. A. NOVELLI (*Anal. Asoc. Quím. Argentina*, 1925, **13**, 13—22).—The reagent is prepared by dissolving 5 g. of resorcinol in distilled water; 5 drops of 26% ferric chloride solution are added. On warming, the violet coloration gradually disappears and the solution becomes yellow. The solution is boiled for a few minutes and allowed to cool. A few drops of the reagent added to a few c.c. of a solution containing nitrites in the presence of acetic acid give an intense green coloration. It is possible to detect 0·001 g. of nitrite in 10 c.c. of water by this reagent. The reaction is indefinite in the presence of vanadates. G. W. R.

Determination of Small Quantities of Phosphorus in Proteins. M. SØRENSEN (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, No. 10, 1—6).—After evaporation, the protein solution is digested with a mixture of sulphuric and nitric acids. It is then diluted and precipitated in the boiling water-bath with ammonium molybdate in presence of ammonium nitrate. After remaining over-night, the precipitate is collected, washed, and dissolved in ammonia. Standard sodium hydroxide is added and ammonia boiled off. Excess of standard sulphuric acid is added, carbon dioxide boiled off, and the excess of acid titrated with standard sodium hydroxide. A control experiment is carried out to allow for traces of impurity in the reagents. C. P. S.

Determination of Arsenic in Organic Compounds. G. NEWBERY (*J. Chem. Soc.*, 1925, **127**, 1751—1752).—The following method gives results correct to 0·2%. The substance is boiled with aqueous ammonium persulphate solution until colourless, oxalic acid is added, and the mixture heated for 2 mins. after carbon dioxide evolution appears to stop. 2*N*-Sulphuric acid and potassium iodide are added, and the whole is vigorously boiled until the solution is of a pale straw colour, which is discharged by the cautious addition of 0·05*N*-sodium thiosulphate. The mixture is at once diluted, sodium hydrogen carbonate added in excess, the mixture is warmed at 35—40°, and titrated with iodine solution. W. H.-R.

Determination of Small Amounts of Boron in Tungsten. D. H. BROPHY (*J. Amer. Chem. Soc.*, 1925, **47**, 1856—1861).—0·5 G. of alloy is fused with 0·7 g. of sodium nitrate and 2·5—3·5 g. of sodium chloride in a platinum crucible. The cooled mass is dissolved in 30 c.c. of water in a porcelain, silica, or platinum dish and boiled with 2 g. of barium hydroxide. To the filtered solution a little potassium iodide is added to reduce any nitrites formed during the fusion, and one drop of methyl-orange. Sufficient 1 : 1-hydrochloric acid is added to make it distinctly acid. After a few minutes free iodine is removed by thiosulphate, and nitrogen oxides are removed by bubbling in air free from carbon dioxide. The solution is neutralised by barium hydroxide free from carbonate and the pink colour just restored with hydrochloric acid. The solution is now filtered, the pink colour just discharged with barium hydroxide, and the solution titrated with barium hydroxide solution in presence of phenolphthalein and glycerol, a blank experiment being also performed. The alloys may alternatively be fused with sodium peroxide and hydroxide. The nitrite difficulty is eliminated, but the manipulations are by no means as easy. J. S. C.

Volumetric Determination of Carbon and Hydrogen in Elementary Organic Analysis. J. LINDNER (*Z. anal. Chem.*, 1925, **66**, 305—370).—The substance is heated in the usual way in a current of pure air or oxygen and the gases are passed through a heated tube containing copper gauze, copper oxide coated with lead chromate, and silver gauze in succession; they are then led through a U-tube packed with lead peroxide and heated gently in an air-bath which finally removes any impurities, leaving only water vapour and carbon dioxide. The former is made to react with heated "naphthyloxychlorophosphine," $C_{10}H_7 \cdot POCl_2$, whereby hydrogen chloride equivalent to the hydrogen in the substance being analysed is evolved. The gases are then passed through a special absorption tube containing only 1—2 c.c. of water, which retains completely the hydrogen chloride, into an absorption apparatus containing a measured amount of standard barium hydroxide solution to absorb the carbon dioxide. Titration of the hydrochloric acid with standard alkali gives the hydrogen content and titration of the excess of barium hydroxide with standard acid and phenolphthalein gives the carbon content of the substance. The original paper contains a detailed description of the

absorption apparatus and of the methods of preparing the reagents and of carrying out an analysis. The results are equally as good as those obtained gravimetrically. A. R. P.

Modification of Laulanié's Apparatus for the Determination of Carbon Dioxide and Oxygen in Air. L. PLANTEFOL (*Bull. Soc. Chim. biol.*, 1925, 7, 638—651).—Modifications have been made (chiefly in the central tap) to overcome the objections previously described (*ibid.*, 590—605). H. J. C.

Application of Electrical Conductivity to Quantitative Analysis in Biochemical Practice. I. Titration of Certain Inorganic Salts with Sodium Hydroxide. S. DEMJANOVSKI.—(See i, 1113.)

Preparation and Analysis of Constant Mixtures of Air and Carbon Dioxide. J. JOHNSTON and A. C. WALKER.—(See ii, 851.)

Modification of the Kramer–Tisdall Method for the Determination of Sodium in Blood. R. L. HADEN.—(See i, 1112.)

Perchloric Acid as an Analytical Reagent. J. H. YOE (*Ann. Chim. Analyt.*, 1925, [ii], 7, 193—197).—For the determination of potassium, the aqueous solution is acidified strongly with hydrochloric acid, sulphates are removed by barium chloride solution (cf. Davis, T., 1915, **107**, 1679), and ammonium salts are removed in the usual manner. After conversion into perchlorates, sodium perchlorate is separated by agitation with 97% ethyl alcohol containing 0·2% of perchloric acid and the potassium perchlorate finally washed on the Gooch crucible with 97% ethyl alcohol (cf. Thin and Cumming, T., 1915, **107**, 365; Baxter and Kobayashi, A., 1920, ii, 388). The crucible is dried at 130° for 45 mins. Errors do not exceed 0·3%. Methods for the determination of silica in felspar, limestone, and cement are discussed; that of Willard and Cake (A., 1921, ii, 60) is accurate. Mears and Hussey's modification (A., 1922, ii, 159) of the Kjeldahl method for the determination of nitrogen is also accurate. W. M. C.

Determination of Small Quantities of Magnesium in Copper–Zinc Alloys. SCHÜRMANN and SCHOB (*Chem.-Ztg.*, 1925, **49**, 625—626).—The alloy is dissolved in nitric acid, the solution evaporated with sulphuric acid, and the copper removed by electrolysis. The electrolyte is then evaporated again until the sulphuric acid is expelled; the residue is dissolved in water and the solution poured into a cold solution of sodium hydroxide. The precipitate is collected, dissolved in the minimum of hydrochloric acid, and the precipitation with sodium hydroxide repeated. The last traces of zinc are removed by hydrogen sulphide from the formic acid solution of the second precipitate and the magnesium is precipitated as magnesium ammonium phosphate. Alternatively, the formic acid solution is evaporated to dryness with a few drops of hydrochloric acid and the magnesium determined colorimetrically with 1 : 2 : 5 : 8-tetrahydroxyanthraquinone. [Cf. Hahn, Wolf, and Jäger, A., 1924, ii, 784, and *B.*, 1925, 724.] A. R. P.

Co-precipitation of Magnesium Hydroxide with Aluminium Hydroxide in Ammoniacal Solution. PARISELLE and LAUDE (*Compt. rend.*, 1925, **181**, 116—117).—The precipitation, by four times the necessary amount of ammonia, of the above hydroxides from a 0·005*M*-solution of the mixed sulphates has been investigated, in the presence of varying amounts of ammonium chloride. An excess of the latter is necessary for complete precipitation of aluminium hydroxide alone. The presence of less than an equimolar amount of ammonium chloride is sufficient to prevent the precipitation of magnesium hydroxide alone. In the absence of ammonium chloride, a mixture of the sulphates of magnesium and aluminium is completely precipitated.

Complete co-precipitation is obtained so long as the ammonium chloride is present in amounts not greater than 8 mols. per mol. of each of the sulphates. The co-precipitation diminishes when this value is exceeded, and practically ceases when 100 mols. of ammonium chloride are present per 2 mols. of mixed salts. The co-precipitation may be due to the formation of an insoluble magnesium aluminate. F. G. T.

Determination of Lead. C. E. RICHARDS (*Analyst*, 1925, **50**, 398—399).—The lead is precipitated from faintly acid solution by means of sulphur dioxide, with which the liquid must be saturated. The precipitate is rinsed into 0·1*N*-iodine solution and completely dissolved in concentrated hydrochloric acid, the excess of iodine being titrated with thiosulphate solution. D. G. H.

Determination of Lead in Minute Quantity. W. W. SCOTT (*Chem. News*, 1925, **131**, 17—20).—To determine minute quantities of lead in baking powder, food, etc., the lead in the material under investigation is generally converted into sulphate, extracted by means of ammonium acetate, converted into sulphide, and the latter determined colorimetrically by comparison with standard solutions. To determine lead in water, aluminium sulphate and sulphuric acid are added, and then ammonia; the lead is occluded in the precipitated aluminium hydroxide, and may be determined as above. [Cf. *B.*, 1925, 654.] B. F.

Inexpensive Method for Determining Lead. W. W. SCOTT (*Ind. Eng. Chem.*, 1925, **17**, 678).—The sample is prepared as for the chromate–iodide method and the liberated chromic acid titrated directly by adding excess of ferrous sulphate solution in the presence of diphenylamine, and determining the excess with potassium dichromate or permanganate solution until the green colour is changed to blue. If lead is precipitated the end point will be navy-blue and in the presence of excess of hydrochloric acid, dark green. D. G. H.

Gravimetric Determination of Copper and its Separation from Cadmium and Zinc. A. JÍLEK and J. LUKAS (*Chem. Listy*, 1925, **19**, 275—277).—Copper (especially in small quantities) may be determined in the presence of cadmium and zinc by adding to the warm, neutral solution of the cupric salt four times its volume

of a 1·4% alcoholic solution of ethyl acetonedioxalate, when there is precipitated only the brown-yellow substance $C_{11}H_{12}O_7Cu$. This precipitate may be weighed as such, or converted into cupric oxide by calcination. B. F.

Volumetric Determination of Copper with Potassium Iodide. M. HERSCHKOVITSCH (*Z. anorg. Chem.*, 1925, **146**, 132—140).—In the reaction between cupric sulphate and potassium iodide, cupric iodide is first produced according to the reversible reaction $CuSO_4+2KI \rightleftharpoons CuI_2+K_2SO_4$. If free iodine is present copper polyiodides are also formed, but both these and normal cupric iodide react with excess of potassium iodide to form cuprous iodide and potassium polyiodides. To obtain accurate results by titration with thiosulphate, 3 g. of potassium iodide should be taken for each 100 c.c. of solution, which should not contain more than 0·5% of copper. Low results are obtained, especially in dilute solutions, if sufficient potassium iodide is not present, owing to some of the cupric iodide remaining unchanged. W. H.-R.

Potentiometric Standardisation of Potassium Permanganate Solution with Sodium Oxalate. C. DEL FRESNO (*Anal. Fis. Quim.*, 1925, **23**, 231—241; cf. this vol., ii, 602).—When potassium permanganate solution is gradually added to an acid solution of sodium oxalate at 70°, the difference of potential between a platinum electrode immersed in the solution and a normal calomel electrode changes gradually until the oxidation of the oxalate approaches completion, when there is a very rapid increase. The critical potential corresponding with the completion of the reaction is +0·74 volt. This rapid increase in potential may be used as the basis for potentiometric standardisation of permanganate solutions. G. W. R.

Colorimetric Determination of Cobalt in the Presence of Nickel. B. S. EVANS (*Analyst*, 1925, **50**, 389—393).—Cobalt may be determined by matching the intense rose-pink colour produced on treating the solution with ammonium chloride solution and excess of ammonia, and adding a small quantity of sodium peroxide, with that from a standard solution of cobalt ammonium sulphate. In the presence of nickel, the blue colour given with excess of ammonia may be stabilised by keeping the proportion of ammonia low and adding sodium citrate, and the determination is then carried out using two pairs of tubes, one above the other, in a Walpole colorimeter. Details are also given for the application of the method to steel analysis. D. G. H.

Use of Liquid Amalgams in Volumetric Analysis. II. Determination of Tungsten etc. by Means of Lead and Bismuth Amalgams. K. SOMEYA (*Z. anorg. Chem.*, 1925, **145**, 168—180).—Liquid lead amalgam reduces ferric and uranyl salts to ferrous and uranous salts, respectively, and molybdic, titanic, and tungstic acids are reduced to the tervalent state; by titrating the reduced solutions with potassium permanganate the metals may be determined. The reduction is usually carried out in an atmosphere of carbon

dioxide, and the solution is made sufficiently acid with hydrochloric acid to prevent the precipitation of lead chloride; to accelerate reduction, the solution is generally warmed at 50°. When iron is to be determined, less acid must be used or the end-point is not sharp; the precipitated lead chloride does not interfere. Tungstic acid is also reduced to the tervalent state by cadmium and zinc amalgams, but the reactions are inconveniently vigorous; bismuth amalgam at 60—70° reduces only to the quinquevalent state. The liquid lead amalgam can be kept indefinitely without deteriorating and reacts only very slowly with dilute sulphuric or hydrochloric acid. A. G.

Volumetric Determination of Small Quantities of Ethyl Alcohol. W. JEROME and F. PEPIN (*Can. Chem. Met.*, 1925, **9**, 65—66).—A modification of Nicloux's method for application to blood, urine, etc. The material is distilled with steam in the presence of picric acid, aliquot portions of the distillate being tested by heating with dilute potassium dichromate solution in quantity sufficient to yield a yellowish-green colour, and the results compared with those given by dilute aqueous alcohol of known concentration.
CHEMICAL ABSTRACTS.

Detection of Benzyl Alcohol as Benzyl Oxalate. A. S. PFAU (*Perf. Essent. Oil. Rec.*, 1925, **16**, 190—191).—Benzyl alcohol is readily converted into benzyl oxalate by warming with ethyl oxalate and anhydrous potassium carbonate. By this means, benzyl alcohol may be detected in mixtures of 25—30% of it with hydrocarbons, alcohols, aldehydes, ketones, etc., unless the mixture contains other primary alcohols, when 50% of it must be present to respond to the test. [Cf. *B.*, 1925, 612.] B. F.

Micro Determination of Methoxyl. J. C. SMITH (*J. Chem. Soc.*, 1925, **127**, 912).—Low results are obtained with a silver nitrate solution of the concentration recommended in the English translation of Pregl's "Die Quantitative Organische Mikroanalyse" (20 g. in 200 g. of 95% alcohol). The concentration given in the German edition (20 g. in 500 g. of 95% alcohol) gives trustworthy results.
M. J.

Detection of Plant Phenols by the Use of Nitrites or Nitric Acid. A. H. WARE.—(See i, 1122.)

Reactions of Picric Acid and of Cignolin [1 : 8-Dihydroxyanthranol]. P. TORTI (*Boll. Chim. Farm.*, 1925, **64**, 259).—Colour reactions for each of these compounds are given. T. H. P.

Modifications of the Ferric Citrate Precipitation Test for Tannins. A. H. WARE (*Analyst*, 1925, **50**, 335—336; cf. A., 1924, ii, 789).—The preliminary addition of boiling sodium sulphite solution to the extractive prevents excessive precipitation of dehydrated or oxidised tannin in the form of phlobaphen. A final violet precipitate indicates tannin, but a brownish-black precipitate may be due to phloroglucinol–pyrocatechol flavones or flavonols, or certain phlobatannins. Tannins and phlobaphens are precipitated

if, after boiling with the iron and ammonium citrate solution and filtering, a second boiling with ammonium chloride is carried out. A further addition of ammonium hydroxide solution (in the absence of tannin) will often indicate the presence of anthoxanthins by formation of a deep brown precipitate. D. G. H.

Determination of Reducing Sugars. L. Pick (*Z. Zuckerind. Czechoslov.*, 1925, **49**, 211—216, 219—225, 235—241, 243—250).—During the reduction of Fehling's solution in the determination of reducing sugars, an error arises from the irregular boiling of the alkaline liquid, differences corresponding with 10 mg. of copper being observed. Superheating may be obviated almost entirely by the addition to the mixture of Fehling's solution and assay liquid of an inert powder to promote regular ebullition, wood charcoal in the gravimetric and talc in the volumetric method being recommended. In gravimetric processes, appreciable errors may be caused by the use of Fehling's solution containing insoluble matter, and also (when dealing with impure products) by the cuprous oxide being formed in colloidal solution, so as to pass the filter, although this latter error would appear generally to be a small one. J. P. O.

Iodometric Determination of Reducing Sugars. L. Pick (*Z. Zuckerind. Czechoslov.*, 1925, **49**, 251—255, 259—263).—A modification of Shaffer and Hartmann's iodometric method (A., 1921, ii, 417) is proposed, Fehling's solution diluted fourfold being used, and a small quantity of talc added to promote regular ebullition during reduction (cf. preceding abstract). This method gives more accurate results than the permanganate process when organic matter is present in the precipitated cuprous oxide.

J. P. O.

Induced Crystallisation in Micro-chemistry. G. Denigès (*Mikrochem.*, 1925, **3**, 33—37).—0·1—0·2 Mg. of a sugar or polyhydric alcohol to be identified is dissolved in 1 drop of water on a slide, the solvent evaporated by gentle heating, and the glassy residue caused to crystallise throughout by scratching with a glass point, preferably bearing one or two tiny crystals of the substance believed to be that under examination. The mass is treated with 1 drop of a mixture of acetone and acetic acid, the solvent allowed to evaporate, and the residue again treated in the same way. Clear, well-formed crystals suitable for microscopical examination and optical measurement are thus obtained. S. I. L.

Effect of Sodium Carbonate Concentration in the Determination of Sugar by Benedict's Method. A. J. Quick.—(See i, 1115.)

Chemical Analysis of Cotton. II. Determination of Copper Number. D. A. Clibbens and A. Geake (*J. Text. Inst.*, 1924, **15**, T, 27—38).—The authors have examined the various methods in use for the determination of copper numbers, and show that Schwalbe's procedure and its modifications, the best of which

is that due to Knecht and Thompson (A., 1920, ii, 712), all fail to fulfil the ideal conditions. These are considered to be: (1) a "blank" as near zero as possible, (2) a very small figure for pure cellulose, (3) high values for slightly modified celluloses, (4) results readily reproducible, and (5) simple technique. The fault in the above methods lies in the use of Fehling's solution, owing to the absorption of copper by the cellulose, the instability of the reagent, and especially to its alteration by auto-reduction. Of other methods described in the literature, the most satisfactory is Braidy's (*Rev. gén. Mat. Col.*, 1921, **25**, 35). The solution of copper sulphate is made alkaline with a mixture of sodium carbonate and sodium hydrogen carbonate, and the cuprous oxide formed is determined by the reduction of acidified ferric alum and subsequent titration with permanganate. A critical examination of the method is reported and a procedure is described which meets the above requirements. Pure cotton cellulose gives very low and constant figures and the effects of slight attacks by acids or oxidising agents are revealed by significantly high values. Results obtained with several raw cottons and bleached cloths are described. J. C. W.

Determination of Pentosans in Wood. W. GIERISCH.—(See i, 1122.)

Determination of Acetaldehyde in the Determination of Lactic Acid. P. LEONE and G. B. TAFURI (*Annali Chim. Appl.*, 1925, **15**, 206—208).—This method, which avoids the use of complicated apparatus or of standard solutions liable to deterioration and is applicable to the determination of quite small amounts of lactic acid, is based on the quantitative formation of the oxime when the distillate from a mixture of lactic acid and 50% sulphuric acid is passed into free hydroxylamine. G. L. R.

Identification of the Alkyl Derivatives of Barbituric Acid. A. ZAMPARO (*Boll. Chim. Farm.*, 1925, **64**, 257—258).—Various reactions are given for distinguishing the different alkyl derivatives of barbituric acid used as hypnotics. [Cf. *B.*, 1925, 651.] T. H. P.

Determination of Benzoquinone by Means of Thiosulphate. J. RZYMKOVSKI (*Z. Elektrochem.*, 1925, **31**, 371—372).—When thiosulphate is added to benzoquinone in acid solution, reaction takes place in three stages and finally the quinone is reduced quantitatively to quinol and quinol derivatives, whilst the thiosulphate is oxidised to compounds of the general formula $R(S_2O_3H)$. Titration may be carried out by colour-indication or electrometrically. W. A. C.

Separation of Aliphatic Amines from Ammonia. P. LEONE (*Gazzetta*, 1925, **55**, 246—252).—The presence of ammonia or ammonium salt in the solution of an amine salt may be detected by addition of excess of an aqueous alcoholic solution of sodium cobaltinitrite and sodium nitrite, this giving a turbidity or precipitate with the ammonia. If the volatile alkali is determined both before and after precipitation in this way, the difference between the two

results represents the amine present. A solution of an amine salt may be freed from ammonia by neutralising with acetic acid, treating with sodium cobaltinitrite and nitrite, filtering, adding sodium hydroxide, and distilling. [Cf. *B.*, 1925, 612.] T. H. P.

Determination of Urea in Dog's Blood. (MLLE.) E. VARTEJEANU.—(See i, 1113.)

Determination of Urea and Sugar in Blood. B. GRUSKIN.—(See i, 1113.)

Determination of Urea in Blood and Urine. T. ADDIS.—(See i, 1113.)

Use of Acetylene for the Determination of Hæmoglobin. H. R. MILLER.—(See i, 1112.)

Iodometric Determination of Methylene-blue. T. SABALITSCHKA and W. ERDMANN (*Chem.-Ztg.*, 1925, **49**, 561).—Excess of iodine–potassium iodide solution precipitates a dark-brown solid approximating to a tetraiodomethylene-blue; the excess is titrated with thiosulphate without addition of starch. When the excess of iodine has been removed from the solution, further thiosulphate reacts with the precipitate, liberating methylene-blue, so that the end-point is easily seen. S. I. L.

Proline and Tryptophan as Factors Influencing the Accuracy of Van Slyke's Method for the Determination of Nitrogen Distribution in Proteins. R. A. GORTNER and W. M. SANDSTROM (*J. Amer. Chem. Soc.*, 1925, **47**, 1663—1671).—Van Slyke's method for the determination of the distribution of nitrogen in proteins (A., 1911, ii, 944) yields accurate results in the absence of tryptophan and of proline if the amino-acids are not boiled previously to analysis. Boiling for 24 hrs. with 20% hydrochloric acid prior to analysis leads to a loss in amino nitrogen of the bases and a gain in the ammonia nitrogen, only 64·5% of the cystine nitrogen being precipitated by phosphotungstic acid. Addition of tryptophan to a similar mixture of 14 amino-acids (containing no proline) leads to appreciable errors in the basic fraction, and in the amino nitrogen and the total nitrogen of the filtrate from the bases, the errors in the basic nitrogen chiefly affecting the arginine fraction. Analysis of the boiled mixture when tryptophan is present shows high results for histidine and low results for cystine (37·9% unprecipitated), and further errors in the ammonia fractions and in the filtrate from the bases. The addition of proline (in the absence of tryptophan) produces errors in the analysis of the unboiled mixture, both in the basic fraction and in the fractions in the filtrates from the bases. Part of the proline appears to be precipitated by phosphotungstic acid with the diamino-acids and distributed between the arginine and histidine fractions. Owing to its entire lack of amino nitrogen, the calculations of Van Slyke's method cause the lysine fraction to show a loss. Analysis of the mixture after 24 hrs.' acid boiling shows that proline produces high results in the basic nitrogen fractions and a corresponding decrease in the filtrate fractions. Ammonia nitrogen is high and only 73·3% of the cystine is precipitated. R. B.

General, Physical, and Inorganic Chemistry.

Structure in the Secondary Hydrogen Spectrum. O. W. RICHARDSON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 553—561; cf. this vol., ii, 469).—Thirty-seven more lines have been arranged in series. Attention is directed to the numerical relations with especial reference to the principle of combination. The causes of the combinations found are discussed. L. F. G.

Structure in the Secondary Hydrogen Spectrum. O W. RICHARDSON (*Proc. Roy. Soc.*, 1925, **A**, **109**, 35—56; cf. A., ii, 1924, 217, also preceding abstract).—A continuation of the reduction of this spectrum into groups of related lines, starting from the lines which are selectively weakened in electron discharges in hydrogen at low pressures. F. G. T.

Wave-lengths of Additional Lines in the Many-lined Spectrum of Hydrogen. T. TANAKA (*Proc. Roy. Soc.*, 1925, **A**, **108**, 592—606; cf. preceding abstract).—Data for 560 weak lines in the secondary spectrum, not previously recorded, are tabulated. The measurements were made on spectrum plates taken by Merton, as the spectral lines were there better resolved than on plates taken, under different conditions, by the author and Richardson. A list is given of lines recorded by other experimenters, but missing from the plates of both Merton and the author. L. F. G.

Secondary Spectrum of Hydrogen at Higher Pressures. I. SANDEMAN (*Proc. Roy. Soc.*, 1925, **A**, **108**, 607—616; cf. Kiuti, *Phys. Math. Soc. Japan*, 1922, [iii], **5**, No. 2).—The lines of the spectrum given by an arc between tungsten electrodes in an atmosphere of hydrogen have different intensities from those recorded by Merton and Barratt (A., 1922, ii, 461). The method suggests the possibility of detecting regularities among the lines. A band has been found with head at 4582·58 Å., shading towards the violet. The value of the initial moment of inertia of the molecule emitting the band agrees with the value deduced by Allen from a static model of triatomic hydrogen (A., 1923, ii, 679). The lines of the *P*, *Q*, and *R* combination discovered by Richardson and Tanaka (this vol., ii, 11) are also present, and the intensity distribution found for them agrees with that found for the new band. L. F. G.

Measurement of the Fine Structure of Hydrogen Lines with the Lummer-Gehrcke Plate. P. H. VAN CITTERT (*Ann. Physik*, 1925, [iv], **77**, 372—380).—In measuring intervals between spectral lines with the Lummer-Gehrcke plate errors other than personal ones must be considered. The reflection coefficient is not uniform, but decreases from the centre of the interference

image towards the edges of the plate. As a result, a line near the edge appears enhanced, has a rather flat intensity maximum, and is evaluated as brighter than a similar line lying nearer the centre. A bright symmetrical line is rendered asymmetric, with its intensity maximum somewhat displaced from its centre. The brightening of an outer line makes the interval between two lines appear smaller than it is, and it is very probable that in all measurements with the Lummer–Gehrcke plate the recorded intervals have been too small because the above effects have been disregarded. For this reason, a decision as to the correctness of Sommerfeld's theory is not possible on the basis of such measurements. A further correction is necessary owing to a transformation of the intensity gradation in a line as a result of a difference of phase of the light in the plate. When the values for the separation of the hydrogen lines obtained by Gehrcke and Lau (A., 1921, ii, 565) are subjected to the above corrections, values are obtained which agree with those calculated by Janicki from Shrum's measurements (this vol., ii, 449). Measurements with the Fabry and Perot interferometer are simpler and more accurate because the distortion of the original intensity gradation is less, the reflection coefficient changes less rapidly, and the relation between the intervals in the photograph and the phase difference in the instrument is less complicated than when use is made of the Lummer–Gehrcke plate. The conditions in order to obtain accurate measurements with an interferometer are summarised. F. G. T.

Behaviour of Some Spark Lines of Carbon in an Electric Field. S. NAKAMURA and Y. FUJIOKA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **3**, 155—162).—The doublets 4267 and 3921 Å. attributed to singly and positively ionised carbon atoms are enhanced and broadened symmetrically in a high electric field. Transverse observations in a discharge tube containing helium show that the amount of broadening of these lines depends chiefly on the field strength and not on either the pressure of helium or the exposure of the plate. Measurements are also recorded for several ultra-violet lines. Longitudinal observations show that the two lines split into sharply defined " components," but the original lines are totally absent. No definite conclusion is drawn as to whether the broadening is due to an unusual Stark effect or not owing to the intrusion of the Döppler effect. R. A. M.

Production of Atomic Nitrogen and its Arc Spectrum. K. T. COMPTON (*Phil. Mag.*, 1925, [vi], **50**, 512—516).—Attempts to dissociate nitrogen thermally into atoms have yielded negative results due to the abnormally high value of the heat of dissociation, 440 kg.-cal./mol. It is suggested that the dissociation might be brought about by inducing collisions of the second kind with excited atoms of helium. The value of the heat of dissociation of the nitrogen molecule corresponds with 19·05 volts, whilst helium has minimum excitation states of 19·73 and 20·56 volts. The conditions for securing the collision of the second kind would then be that the gas mixture should be at a relatively high pressure and

have only a small partial pressure of nitrogen, that a high current density be used in the discharge, and that the gases be very pure. These conditions are those given by Merton and Pilley (this vol., ii, 333) in obtaining a new line spectrum of nitrogen attributed to nitrogen atoms. Failure to produce the spectrum when argon is substituted for helium points to the fact that the heat of dissociation of nitrogen is greater than 280 kg.-cal./mol. and adds support to the value given above. A. E. M.

Series in the Arc Spectrum of Nitrogen. C. C. KIESS (*J. Opt. Soc. Amer.*, 1925, **11**, 1—9).—Merton and Pilley (this vol., ii, 333) have recently found conditions under which the arc spectrum of the nitrogen atom can be observed, unobscured by the molecular band spectra. The lines measured by them, with the addition of others, have now been arranged into doublet and quartet series, the existence of which in the arc spectrum of nitrogen was predicted by the displacement law, as the spark spectrum is known to contain series of odd multiplicity. S. B.

Spectra of Neon and Argon in the Extreme Ultra-violet. T. LYMAN and F. A. SAUNDERS (*Nature*, 1925, **116**, 358).—The spectrum of argon contains a pair of lines at 1048·28 and 1066·73 (±0·2) Å., similar to those observed with neon (*Physical Rev.*, 1925, [ii], **25**, 886) corresponding with Hertz' resonance potential of 11·5 volts, and another pair corresponding with his value of 14·0 volts. The complete argon spectrum is probably like that of neon. The neon line 735 Å. is normally stronger than the line 743 Å., but when a small quantity of neon is present as an impurity in helium the intensities are reversed. It is supposed that the collisions between atoms of neon and helium render the atomic state yielding the line 735 Å. less probable than when neon alone is present. A. A. E.

Line Breadths and Absorption Probabilities in Sodium Vapour. G. R. HARRISON and J. C. SLATER (*Physical Rev.*, 1925, [ii], **26**, 176—188; cf. this vol., ii, 734).—From data recorded previously, the theoretical half-breadths of the lines 2 to 8 are calculated, together with the half-breadths in frequency units $P/2\pi$ which are proportional to the probabilities. The broadening of the first line is 100 times as great as that to be expected from the Stark effect and collision broadening, and the breadths of succeeding lines decrease rapidly with increasing term number at the saturated vapour pressures over the temperature range 450—600°, a result contrary to that found at low vapour pressures. The high pressure broadening is ascribed to diatomic sodium molecules, the perturbation being greater the lower the quantum state. The proportion of diatomic molecules increases with the temperature, suggesting that the energy of dissociation of Na_2 at absolute zero may be negative. R. A. M.

Regularities in the Spectra of the Alkaline Earths. H. N. RUSSELL and F. A. SAUNDERS (*Astrophys. J.*, 1925, **61**, 38—69).—Tabulated data are given of the wave-lengths and wave numbers

of 97 calcium lines, 55 strontium lines, and 95 barium lines, not included in the ordinary series, which have been identified as combinations between known spectroscopic terms and new terms. A number of new lines, mainly of calcium, are also recorded. Calcium affords a new series of five groups of 6 lines each, including the strong groups near 4300 and 3000 Å. and new groups near 2560, 2360, and 2260 Å. There is evidence in favour of other series, and of similar series in the case of strontium and barium. The inner-quantum properties of the new terms are normal; the azimuth-quantum properties are sometimes normal and sometimes correspond with a change of the usual azimuth-quantum number by ± 1. Some of the terms have negative values; apparently a neutral atom can contain more than enough energy to ionise it. Bohr's suggestion that the two valency electrons are both displaced to outer orbits is acceptable. The limit of the new calcium series, which differs from that of the ordinary series, corresponds with an ionised and excited atom in the metastable 1δ state, the normal state being 1σ; apparently all the other new series of calcium, strontium, and barium converge to the 1δ limit. It is assumed that the angular momenta of the two valency electrons are quantised in space with respect to each other, and their resultant is quantised with respect to that of the residue of the atom. Methods of spectroscopic notation are considered, and a tentative scheme is developed in which the series is denoted by Roman capitals, the system by an index on the left, giving the multiplicity, and the component of a multiple term by a subscript figure on the right, giving the inner quantum number. The index position on the right is reserved for indices denoting the "anomalous" terms, and the serial number is denoted by a prefixed integer; thus, the calcium line 5270·3 Å. is denoted by $1^3D_3—1^3P_2''$. A. A. E.

Magnetic Resolution of the Scandium Spectrum. I. S. GOUDSMIT, J. VAN DER MARK, and P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 127—141).—The lines of the scandium spectrum are classified, and the classification is confirmed by an examination of the magnetic resolutions of a number of the lines. A concave Rowland grating was used as spectrograph, and a vacuum trembler as source of light. The spark was formed in hydrogen under low pressure between a tungsten electrode and a specially prepared carbon electrode previously soaked in a solution of scandium chloride. A magnetic field of about 41,000 gauss was produced by a Weiss magnet with water cooling. The magnetic resolutions of a number of lines of the Sc I doublet system and the Sc II triplet system are tabulated. A. B. M.

Interpretation of Complicated Spectra Particularly of the Elements from Scandium to Nickel. F. HUND (*Z. Physik*, 1925, **33**, 345—371).—The author extends the methods which have been found applicable to the short periodic groups to the elements from scandium to nickel and assigns to them quantum numbers for the electrons in the normal state of the atom and for the positive

ion. The relationship between the type of spectrum and the position in the periodic table is established. E. B. L.

Multiplets in the Spectrum of Ionised Vanadium. W. F. MEGGERS (*Z. Physik*, 1925, **33**, 509—528).—Although the spectrum of vanadium II resembles that of titanium I, in accordance with the displacement law, the ground term is a quintuplet *f*-term and not a triplet. Widely separated terms with azimuthal quantum numbers up to six are found. For the vanadium spark spectrum, thirty-three multiplets are ascertained to be combinations of quintuplet and triplet terms. Tables are given containing a list of all the classified lines, their wave-lengths, combinations, and intensities, and the class in which they are placed by King according to their appearance by thermal excitation. E. B. L.

Arc Spectrum of Nickel. K. BECHERT and L. A. SOMMER (*Ann. Physik*, 1925, [iv], **77**, 351—371).—The intensities and combinations are tabulated for 354 lines of the arc spectrum of nickel between the wave-lengths 10530·09 and 2244·5 Å. The ground term of this spectrum, which has odd multiplicities, is an *f*-term belonging to the triplet series, and has an azimuthal quantum number 4. All the terms are inverted, and the magnetic moment in the ground state has the value 5 Bohr magnetons. Jumps in azimuthal quantum number of 2 units are frequent in the nickel spectrum, and occur in the singlet as well as in the triplet series. F. G. T.

Order of Appearance of certain Lines in the Spark Spectra of Cadmium and Magnesium. F. L. BROWN and J. W. BEAMS (*J. Opt. Soc. Amer.*, 1925, **11**, 11—15).—The order in which the various visible lines in the spark spectra of cadmium and magnesium appear after the striking of the spark has been determined. A "shutter" device, consisting of a Kerr cell filled with carbon disulphide, and two suitably disposed Nicol prisms, is placed in the same circuit as the spark, and the light from the latter is observed through the cell. The "shutter" permits the passage of light only when an electric field is applied to the carbon disulphide. By altering the lengths of the leads in the apparatus, the shutter can be "opened" at different intervals, subsequent to the passage of the spark, and the variations in the spectrum observed. The method is being applied to other spectra. Similar observations show that the interval between the appearance of the spark lines of cadmium and that of the arc lines is longer than 3×10^{-8} sec. S. B.

Series Spectrum of Gold. J. C. MCLENNAN and A. B. MCLAY (*Proc. Roy. Soc.*, 1925, **A**, **108**, 571—582; cf. A., 1924, ii, 4).—A method has been developed of obtaining the absorption spectrum of metallic vapours in the Schumann region, and has been applied to the vapours of gold, silver, and copper. The second members of the principal series of doublets in the gold arc spectrum are λ=1646·71 and λ=1665·75. The term scheme for the arc series of gold is discussed. Attention is directed to the similarity that exists between the term systems of Au I, Cu I, and Zn II in respect to their inverted δ terms, and to the similarity of the term

systems of Au I and Cu I in respect to certain π terms. The ionisation potential of the gold atom is 9·25 volts. L. F. G.

Absorption Spectrum of Lead Vapour in the Ultra-violet. R. V. ZUMSTEIN (*Physical Rev.*, 1925, [ii], **26**, 189—194; cf. A., 1921, ii, 474; 1924, ii, 455).—In the region 5000—2000 Å. at temperatures up to 1600° a 3 cm. column of lead vapour exhibited absorption of 34 lead lines. The arc spectrum of lead with a current of 100 amperes was photographed. Between 2255 and 2020 Å. all the 15 recorded lines (A., 1923, ii, 672, 710) were reversed; three new lines were measured. The classification of lead lines given by Grotrian (A., 1923, ii, 710) has been extended and confirmed; the $2p_5$ term, however, is eliminated. Absorption occurs from the normal state $2p_4$ and the metastable states $2p_3$ and $2p_2$. Most of the 20 new lines lie on the short-wave side of 2400 Å. and the only one unclassified (2393·802) is regarded as $2p_3—X_3$, where X_3 is a new term (10232). Values are given for $3p_2$, $3p_3$, $4p_2$, $4p_3$, $3d_1$, $2x$, $3x$, $4x$, $5x$. New lead combination lines are calculated, and a new series $2p_3—mx$ is suggested. R. A. M.

Effect of Chemical Constitution on the *X*-Ray Spectrum of Sulphur. B. RAY (*Phil. Mag.*, 1925, [vi], **50**, 505—511).—Measurements of the wave-lengths of the *K*-lines of sulphur and a large number of sulphur compounds have been made. Within the experimental error, the wave-lengths are the same for sulphur and sulphide compounds, but for sulphite and sulphate compounds the lines $K\alpha_1$ and $K\alpha_2$ are shifted to shorter wave-lengths and have their distance apart considerably diminished. For sulphur and sulphides, the distance between $K\alpha_1$ and $K\alpha_2$ is 3*X*-units, whilst for sulphites and sulphates the value is 2·4*X*-units, the shift of $K\alpha_1$ being 3·0*X*-units toward the shorter wave-lengths. No such displacements occur with the lines $K\alpha_3$ and $K\alpha_4$. The results are discussed in connexion with the theory of the origin of doublets. A. E. M.

New $K\beta_1$ Doublet of the Elements Manganese and Chromium. N. SELJAKOV and A. KRASNIKOV (*Z. Physik*, 1925, **33**, 601—605).—Photographs were obtained showing the separation of the doublets into $K\beta_1$ and $K\beta'$, the latter having only half the intensity of the former as measured by a Koch microphotometer. The wave-lengths for $K\beta'$ were : Mn 1910·24, Cr 2085·01 *X*-units. E. B. L.

Doublet $K\alpha_{1,2}$ of the Lighter Elements and the Dependence of the *X*-Ray Spectra on Chemical Combination. E. BÄCKLIN (*Z. Physik*, 1925, **33**, 547—556).—The distance between the two lines was measured for the elements from aluminium to calcium, using a very large angle of incidence. The lines for aluminium oxide are displaced towards shorter wave-lengths relative to aluminium metal; similarly for sulphur in sulphates as compared with the element, and for phosphorus compared with the pentoxide. The effect is much more pronounced with barium sulphate than with calcium sulphate. E. B. L.

Energies of Multiple *X*-Ray Ionisation of Light Atoms. L. A. TURNER (*Physical Rev.*, 1925, [ii], **26**, 145—149).—Wentzel (A., 1924, ii, 368, 434) considers that the weak lines accompanying the K emission lines of some light elements are due to multiply ionised atoms. The author assumes that the removal of a K electron exerts the same effect on the energies of the outer electrons as an increase in the nuclear charge of one unit. The energy required for the successive removal of a K and an L electron is calculated for elements of atomic numbers 11—19 (Na—K) and thence by means of Wentzel's theory multiple ionisation terms are calculated from the ordinary K and L terms and the α_3, α_4, α_5, and α_6 lines. The square roots of the energies for the successive removal of the first, second, and third L electrons plotted against atomic numbers give three parallel straight lines, indicating that the screening constant is reduced from 7·27 to 6·65 and then to 6·0. The lines obtained for the two K electrons are similar. The results are extended to show that the experimental value for the K absorption limit of phosphorus is in error. R. A. M.

Quantum Number Relations in Series Spectra. R. B. LINDSAY (*J. Opt. Soc. Amer.*, 1925, **11**, 17—30).—A theoretical paper in which the effective quantum numbers corresponding with the entire series of stripped atoms in the third group of the periodic system (Bohr's arrangement) are calculated. It is further shown that if a spectrum of a given atom is compared with that of another atom one unit greater in atomic number, but at a higher stage of ionisation (*e.g.*, Mg^+ with Al^{++}), the ratio of the quantum defects for corresponding orbits is nearly the same for different pairs of atoms as one passes along a group in the periodic system. This fact, it is suggested, may be used in the prediction of unknown spectral terms. S. B.

Fine Structure of Optically Excited Spectrum Lines. E. GROSS and A. TERENIN (*Nature*, 1925, **116**, 280).—The spectrum lines emitted by mercury vapour illuminated by an intense mercury lamp have a much simpler fine structure than is usual. The absence of some of the satellites suggests that these are not due to isotopy. A. A. E.

Measurement of Intensity Ratios of Doublets of Alkali Metals in the Principal Series. F. W. OUDT (*Z. Physik*, 1925, **33**, 656—657).—The ratio of the lines in the rubidium doublet in the Bunsen flame is 1 : 2. For cæsium, the ratio in the arc is 1 : 2, but in the blow-pipe flame the results were not constant, varying from about 1 : 5 to 1 : 2. E. B. L.

Intensity Ratios of Some Inter-combination Lines. T. BOUMA (*Z. Physik*, 1925, **33**, 658—659).—The inter-combination lines show a more rapid decrease in intensity with increasing series number than the diminution found for the singulets. E. B. L.

Intensity of Multiple Spectral Lines. L. S. ORNSTEIN (*Proc. Physical Soc.*, 1925, **37**, 334—347).—A review of the experimental and theoretical investigations of the author and collaborators.

F. G. T.

***pp'* Groups in Atoms of the Same Electronic Structure.** I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **26**, 150—164).—It is shown that two electrons may simultaneously change their energies within an atom and integrate their joint energy-change into a monochromatic emission. By the methods of hot spark spectroscopy and high dispersion applied to the two series of atoms (*a*) Mg I, Al II, Si III, P IV, S V, Cl VI; (*b*) Be I, B II, C III, N IV, O V, a quintuplet of nearly equally spaced lines has been observed for all these atoms. The group is really a sextuplet, but the two middle lines are not separated. The *pp'* group arises from an electron jump from the lowest p to the lowest s orbit, combined with a simultaneous jump of the other electron between the p_1, p_2, p_3 orbits. The frequency differences between the groups of successive atoms obey the irregular doublet law, showing that the jumps are between levels of the same total quantum number. A new quadruplet *pp'* group is found in the three-valency electron atoms Al I, Si II, P III, S IV, Cl V, and C II, N III, O IV. The relative intensity increases with the effective nuclear charge from Al I to Cl V. These quadruplet *pp'* groups are due to the return of one of the s electrons after displacement to a p position combined with the simultaneous interchange of the p electron between the p_1, p_2 orbits. The groups also obey the irregular doublet law.

The earlier work of Wentzel (A., 1924, ii, 434) and of Russell and Saunders (A., 1924, ii, 800) on *pp'* groups in calcium led to negative term values. Bohr (*Physikal. Z.*, 1922, **24**, 106) first suggested the simultaneous jump of a second electron as an explanation. The present work supplies a rigorous proof, although the mechanism of the integration of complex vibrations remains unknown. It follows from the work that the ionisation potential must depend on the state in which the ionised atom is left after removal of an s electron. There will thus be several ionisation potentials differing according as the p electron is left in the p_1, p_2, p_3, or P orbit. R. A. M.

Excitation of Forbidden Spectral Lines. P. D. FOOTE, T. TAKAMINE, and R. L. CHENAULT (*Physical Rev.*, 1925, [ii], **26**, 165—175).—The following lines which are forbidden on the selection principles of Bohr have been observed in the positive column of a hot-cathode low-gradient discharge at low pressure: $1S-2p_1$ ($\Delta j=2$) for mercury, cadmium, and zinc at 2270·0, 3141·1, and 3039·8 Å., respectively, and $1S-2p_3$ for cadmium at 3320·0 Å. A cadmium *pp'* multiplet has also been measured. The general applicability of the azimuthal-quantum number rule and the inner-quantum rule is not questioned, but the increasing number of forbidden lines observed makes an investigation of the effects of varying electric and magnetic fields necessary. R. A. M.

Joining the Infra-red and Electric-wave Spectra. E. F. NICHOLS and J. D. TEAR (*Astrophys. J.*, 1925, **61**, 17—37).—The spectrum of a quartz mercury arc, when examined in the long wave region, exhibits radiation at wave-lengths approximately 228, 292, 412, 420, and possibly 685 μ, as predicted by the quantum theory, when the moment of inertia of the source (HgH molecules) is assumed to be $5{\cdot}7\times10^{-40}$. A. A. E.

Anomalous Electrical Double Refraction of Sodium Vapour. R. LADENBURG and H. KOPFERMANN (*Sitzungsber. Preuss. Akad. Wiss. Berlin.* 1925, 420—424; cf. this vol., ii, 79).—Electrical double refraction of the D_2-line of sodium vapour has been observed. Passage of light through a layer of sodium vapour 2·8 cm. thick at a pressure of 10^{-5} mm. causes a phase difference of the components of the D_2-line, parallel and transverse to the field, of 6° for a field strength of 30,000 volt/cm. No electrical double refraction of the D_1-line was observed and it is certainly less than one-tenth of that of the D_2-line. The electrical double refraction causes the D_2-line to light up under crossed Nicols and a quarter wave-length plate on switching on the field, whilst the D_1-line remains invisible. The difference in the electrical displacements of the parallel and transverse components of the D_2-line is evaluated, the parallel component being 10 times as much displaced as the transverse. On the basis of Kramers' theory, the electrical separation of the levels of the p- and s-terms of sodium is calculated. F. G. S.

Intensity of Multiplets and their Zeeman Components. II. R. DE L. KRONIG (*Z. Physik*, 1925, **33**, 261—272; cf. this vol., ii, 458).—An extension of the former treatment to more complicated cases. The effect of inter-combinations on the spacing of the multiplets is considered, and also the case in which the magnitude of the effect of the core on the outer electrons is comparable with that of mutual action of these electrons. For neon, the calculations agree satisfactorily with experimental data. E. B. L.

Intensities of the Zeeman Components. S. GOUDSMIT and R. DE L. KRONIG (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 418—422).—A mathematical paper in which, employing Ornstein and Burger's rule, $2i_+ + i_0 + 2i_- = C$ (this vol., ii, 340; *Z. Physik*, 1924, **29**, 241), formulæ for the intensities of the Zeeman components for small quantum numbers are deduced corresponding with similar formulæ obtained for large quantum numbers by Sommerfeld and Heisenburg (*ibid.*, 1922, **11**, 131). J. W. B.

Zeeman Effects Contrary to the Rule for Multiplets of the First Stage. E. BACK (*Z. Physik*, 1925, **33**, 579—600).—The influence of magnetic fields on the spectrum of calcium has been studied and a relation found to exist between the terms which do and those which do not conform to Landé's rule. The application of the principle of correspondence is considered for magnesium and a modification introduced. A partial Paschen–Back effect was

observed for sodium using a vacuum arc and a field of 38,782 gauss. E. B. L.

Zeeman Effect in Strong Magnetic Fields. P. KAPITZA and H. W. B. SKINNER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 224–239; cf. *ibid.*, 1924, **A**, **105**, 691; **A**, **106**, 602).—Details are given of a method of utilising for the study of the Zeeman effect transient magnetic fields up to 130,000 gauss, produced by accumulator discharges of about 3000 amp. through a coil. The magnetic constant of the field was determined from the force exerted by it, under standard conditions, on a specially constructed solenoid. The field strength was obtained from oscillograms of the current passing through the magnet coil. As the field was not constant for more than 1/300 sec., the spectrum was photographed with a high-dispersion quartz spectrograph, by using a localised spark obtained by the use of a large condenser battery. The method of synchronising the spark with the occurrence of the field is described. The results of photometric measurements of the Zeeman separations indicate that in most cases the splitting is approximately proportional to the field strength, but for the triplet p–s combinations of zinc and mercury evidence was obtained that the splitting was not strictly proportional to the field strength between fields of 70,000 and 130,000 gauss, being 10% greater than was anticipated for the latter field. The total separations in a field of 120,000 gauss were from 0·3 to 0·15 mm. on the plates, the maximum separation (for Zn 4680) corresponding with 5·8 Å. In most cases, lines in the longitudinal effect split into two components, the intensities of these and of the unaffected line showing that both complex and simple splitting may occur. The splitting in some cases appears not to occur exactly about the position of the unaffected line, but to show a slight shift, non-reproducible, and apparently of secondary origin, towards the red. Reasons are given for attributing this shift to pressure changes. The splitting of the s–p combinations in doublet and singlet spectra seems to be normal. Three examples of the Paschen–Back effect were observed, namely, the Ca II diffuse doublet (3159, 3179, 3181), the Mg pp' group (2783·0, 2781·5, 2779·8, 2778·3, 2776·8), and the Be pp' group (2650·88, 2650·81, 2650·75, 2650·72, 2650·66, 2650·57). In the last case, the splitting is normal, exhibiting the complete Paschen–Back effect. The first example is of an incomplete Paschen–Back effect, and an intermediate stage of the effect is observed in the case of the Mg pp' group, a field of 120,000 gauss causing the appearance in the longitudinal effect of six components, the positions of which are susceptible to small changes in the field strength. F. G. T.

Ionisation Potential of Ionised Manganese. D. R. HARTREE (*Nature*, 1925, **116**, 356).—Two independent estimates of terms from some triplets of the spectrum Mn II, one from the position of a line of the triplet and the other from triplet separations, are in satisfactory agreement and indicate that the 1s term of the Mn II septet system lies within the limits 118,000±3000, whence the ionisation potential corresponding with the removal of the 4_1 electron is 14·5±0·4 volts. A. A. E.

Ionisation of Mercury Vapour by Ultra-violet Light. G. F. ROUSE and G. W. GIDDINGS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 514—516).—The work of Steubing (*Physikal. Z.*, 1909, **10**, 787) has been repeated with an improved technique. The hot mercury arc does not produce ionisation of mercury vapour. With a water-cooled arc and high vapour pressures true ionisation of the vapour is indicated. According to the quantum relation, $Ve=h\nu$, there is no single wave-length of sufficient energy to cause ionisation and hence some cumulative action occurs. Various possibilities regarding this cumulative effect are considered. J. S. C.

Ionisation Produced in Gaseous Reactions. A. K. BREWER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 512—514; cf. A., 1924, ii, 745).—When ethyl alcohol and oxygen react between gold electrodes below the ignition temperature, the current flowing is proportional to the applied voltage (the mean potential gradient varied between 0 and $\pm$ 2400 volts/cm.) and increases exponentially with the temperature. With aluminium electrodes, the current is almost zero. Glass electrodes give a current for both positive and negative applied potentials; copper electrodes give a current only when the hot outer electrode is negatively charged. No approach to a saturation current is observed. Ions are formed in the gas layer in immediate contact with the conducting surface and not in the gas space between the electrodes. Positive and negative ions are formed in equal amounts on the same surface. The currents observed are due to the ions removed by the field against the attractions in the neighbourhood of the conducting surface. J. S. C.

Relative Ionisation in Different Gases for Slow-moving Electrons. W. P. JESSE (*Physical Rev.*, 1925, [ii], **26**, 208—220).—A uniform beam of electrons in a thermionic tube was made to ionise the gas to be studied. Secondary effects were eliminated by low pressures. With increasing electron energies, the ionisation reached a maximum at the following voltages: helium 140, neon 220, argon 100, carbon monoxide 120, nitrogen 100. For 200 volts, the relative ionisations at 1 mm. pressure, taking that of neon as unity, are hydrogen 0·91, helium 0·48, methane 3·5, nitrogen 3·2, carbon monoxide 3·45, argon 4·1. The results, except for argon, are in agreement with those of Hughes and Klein (A., 1924, ii, 375). A second maximum at 350—400 volts appeared in each case, but it is not completely understood. R. A. M.

Photo-electric Ionisation of Cæsium Vapour. P. D. FOOTE and F. L. MOHLER (*Physical Rev.*, 1925, [ii], **26**, 195—207).—A sensitive method has been devised for the measurement of photo-electric ionisation in gases. A small cathode is almost enclosed by the anode and the imprisoned ions increase the current in a filament. Changes in thermionic current with unresolved light have been measured as functions of applied voltage, filament temperature, and vapour pressure. The photo-electric effect has been studied as a function of wave-length, using a quartz monochromator. The ionisation increases with increasing wave-length to a sharp maximum

at the limit $1s$=3184 Å. of the principal series as required by the Bohr theory. The ionisation decreases to 10% at 3400 Å. The data support the view that radiation on the long-wave side of 3184 Å. produces excited atoms which acquire sufficient energy to become ionised by collisions with other atoms. Hence the photo-ionisation is not sharply discontinuous at the true threshold for direct ionisation as postulated in the simple theory. R. A. M.

Saha's Ionisation Formula, and the Theoretical Value of the Photo-electric Absorption Coefficient. E. A. MILNE (*Phil. Mag.*, 1925, [vi], **50**, 547—550).—As modified by Fowler, (*ibid.*, 1923, [vi], **45**, 21), Saha's formula for the degree of ionisation is correct only when the ionised atom possesses no energy other than translational and requires a factor which is a partition function of the weights of the various stationary states of the ionised atom. The formula for the photo-electric absorption coefficient requires also a similar factor for the weight of the lowest state of the ionised atom in addition to that for the neutral as given by Kramers (*ibid.*, 1923, [vi], **46**, 843), Becker (A., 1923, ii, 820), and the author. A. E. M.

Passage of Electrons through Photo-electrically Active Crystals. H. LENZ (*Ann. Physik*, 1925, [iv], **77**, 449—476).—Measurements of the Hall effect have been made with diamond and zinc sulphide crystals. In agreement with the theory of the Hall effect developed by the author, the Hall potential was found to be proportional to the strength of the applied magnetic field, and independent of the photo-electric current strength. Calculations of the electron free-path, time of collision, and electron velocity in the case of a diamond, with an electric field of 400 volts, Hall potential 62 volts, and magnetic field of 4000 gauss, gave, respectively, $3{\cdot}4\times10^{-6}$ cm., 10^{-12} sec., and $6{\cdot}8\times10^{-6}$ cm./sec. The dependence of the primary photo-electric current on temperature was determined between −191° and 80°; with both diamond and zinc sulphide, the temperature coefficient at first increases with temperature, but later becomes constant, with diamond at about −90°, and with zinc sulphide at about −35°. Experiments are described showing that the electron stream through unilluminated crystals cannot be attributed to diffuse reflected light, and that no change of diamagnetism through irradiation is detectable. F. G. T.

Thermionic Effect from the Point of View of the Phase Rule. N. VON RASCHEVSKY (*Z. Physik*, 1925, **33**, 606—612).—The emission of electrons cannot strictly be regarded as a simple evaporation; the evaporation of molecules and the existence of positive ions must also be considered. A purely thermodynamical formula of the thermionic current is deduced which contains Richardson's formula as a special case. A relation between electron emission, vapour pressure, and specific heat of a body is obtained. E. B. L.

Kinetic Theory of the Thermionic Effect. N. P. RASHEVSKY (*Physical Rev.*, 1925, [ii], **26**, 241—246).—Theoretical. Different assumptions are made regarding the behaviour of electrons inside a

solid body and statistical deductions are drawn for the thermionic currents in each case. All the expressions are of the type $i=AT^{a}e^{-b/T}$ and differ only in the values of the constants A and a. The experimental results are not accurate enough to decide which assumptions are correct. R. A. M.

Sodium by Electrolysis through Glass. R. C. Burt (*J. Opt. Soc. Amer.*, 1925, **11**, 87—91).—It is possible to introduce pure metallic sodium into the high vacuum of an electric light bulb by using the thermionic emission from the filament. The exterior of the bulb is partly immersed in a bath of molten sodium nitrate, between which and the filament a potential difference is maintained, the filament being negative. Currents up to 0·3 amp. may be passed through the glass, and 0·3 g. of sodium per hour deposited in the bulb. Sodium lamps may be prepared in this way, giving a sodium spectrum free from impurity lines, even those of potassium. Ions other than those of sodium will not pass through the glass, and if potassium nitrate or lithium nitrate is substituted in the bath of molten salt, the bulb breaks after passage of a current for a short period. S. B.

Apparent Transmission of Low-velocity Electrons through Aluminium Foil. H. E. Hartig (*Physical Rev.*, 1925, [ii], **26**, 221—231).—Aluminium foil 0·0003 cm. thick shows apparently a transparent atom effect for slow electrons similar to that observed in rare gases. The effect was reduced to 10^{-4} of the original by a second foil, and was then probably largely photo-electric. A promising method for the determination of critical potentials from the photo-electric effect of soft X-rays from a metal foil is described. R. A. M.

Electric Discharge in Gases at Low Pressure. B. N. Banerji (*Nature*, 1925, **116**, 429—430).—Polemical and explanatory (cf. McCurdy, A., 1924, ii, 808; Compton, Turner, and McCurdy, this vol., ii, 86). The phenomenon of discharge is intermittent, the conditions at the anode and cathode being of the same kind but different intensity. An alternative explanation of the selective reduction of the oxide W_2O_3 is put forward. A. A. E.

Recent Researches in Positive Rays. W. Wien (*Proc. Physical Soc.*, 1925, **37**, 324—333).—A lecture, reviewing the author's work on this subject. F. G. T.

Isotopic Composition and Atomic Weight of Chlorine in Meteorites. W. D. Harkins and S. B. Stone (*Nature*, 1925, **116**, 426).—The atomic weight of meteoric chlorine is identical with that of terrestrial chlorine, *e.g.*, from wernerite, apatite, and commercial hydrochloric acid. A. A. E.

Isotopes of Uranium. O. Hahn (*Z. anorg. Chem.*, 1925, **147**, 16—23).—The possibility of the existence of unknown isotopes of uranium is discussed and the difficulties of extending knowledge on this subject are pointed out. J. S. C.

Elements which are "Electron-Isomerides." R. SWINNE (*Z. Elektrochem.*, 1925, **31**, 417—423; cf. Meyer, this vol., ii, 173).—A discussion of the structure of the rare earths in terms of the Bohr atom. When the inner orbits are fully occupied by electrons, a relation between elements becomes possible to which the name "electron-isomerism" is given, differing from isotopy in that the nuclei remain the same. W. A. C.

Electric Charge Carried by Thorium-X and Thorium Emanation Recoil Atoms in Gases. G. H. BRIGGS (*Phil. Mag.*, 1925, [vi], **50**, 600—612).—Two simple, satisfactory methods for obtaining thorium-*X* by recoil are described. In helium, oxygen, hydrogen, nitrogen, carbon dioxide, nitrous oxide, and acetylene, all the thorium-*X* recoil atoms are positively charged at the end of their recoil path. In ethyl ether, methyl acetate, ethyl acetate, acetone, methylol, and hexane vapours, and ammonia from 84 to 94% of the recoil atoms were positively charged. It is concluded that in these gases also all the recoil atoms are initially positively charged. Atoms of thorium emanation recoiling from thorium-*X* in air, oxygen, hydrogen, and carbon dioxide are all neutral. The factors determining the probability of a recoil atom being positively charged or neutral at the end of its recoil path are discussed and a mechanism is suggested. A. E. M.

Capture and Loss of Electrons by α-Particles. G. H. HENDERSON (*Proc. Roy. Soc.*, 1925, **A, 109**, 157—165; cf. *ibid.*, 1922, **A, 102**, 496).—The ratio of the number of doubly charged to the number of singly charged α-particles in equilibrium has been found quantitatively, by an ionisation method, under various conditions. With α-particles of initial velocities of $1{\cdot}922\times10^9$—$0{\cdot}769\times10^9$ cm./sec., it was found that the above ratio at any velocity was independent of the material (gold, mica, aluminium, silver, or copper) through which the α-particles have passed. The variation of the ratio with the velocity of the α-particles was determined and is given approximately by $n=6{\cdot}4-4{\cdot}2V/V_0$, where V is the velocity of the α-particle, and $V_0=1{\cdot}922\times10^9$ cm./sec. F. G. T.

β-Ray Spectra of Thorium Disintegration Products. D. H. BLACK (*Proc. Roy. Soc.*, 1925, **A, 109**, 166—176).—An analysis of the β-ray spectra of thorium-*B* and thorium-*C*+*D* has been made by separating the β-rays into a spectrum by a magnetic field, using a focussing method. For thorium-*B*, 17 lines were measured, that at $H\rho$ 1398 being of extremely high intensity. Of these lines, 4 are ascribed to the conversion of the ordinary *K X*-radiation of thorium-*B*. For thorium-*C*+*D* 16 lines were measured, the strongest being at $H\rho$ 541. A group of lines of energies more than $2{\cdot}5\times10^6$ volts was recorded, probably due to thorium-*D*, and arising from the conversion of a single γ-ray in the *K* and *L* levels of the atom. The analysis of these spectra affords strong support for the hypothesis that the lines of the β-ray spectra are due to the conversion of γ-rays in the various absorption levels of the atoms concerned. F. G. T.

Absorption and Scattering of γ-Rays. N. AHMAD (*Proc. Roy. Soc.*, 1925, **A**, **109**, 206—223; cf. A., 1924, ii, 440, 582).—Experiments have been made to test the hypothesis suggested by Compton (*Physical Rev.*, 1923, [ii], **21**, 483) and by Debye (*Physikal. Z.*, 1923, **24**, 161) by comparing the theoretical total absorption due to scattering with that given by the general absorption relation characterising each beam. A further test was made by comparing direct measurements, obtained by means of a conical ionisation chamber capable of rotation about the middle of the radiator, of the intensity of rays scattered within a small cone with that given by theory. The results of these experiments were in general agreement with the formulæ obtained by Compton on a classico-quantum basis. The γ-rays from a radium standard were hardened by filters of iron, lead, or mercury, and their absorption by aluminium, copper, tin, and lead investigated by a modified form of balance method. In every case the atomic absorption coefficient, μ_a, is closely represented by the expression $\mu_a=AZ+BZ^4$, where A and B are constants for a particular beam, although decreasing steadily as the rays become harder, and Z is the atomic number. The right-hand terms represent the scattering and fluorescence absorptions, respectively. The γ-rays, in their absorption by the elements investigated, thus obey the same general law as X-rays of much lower frequency. By assuming the validity of the λ^3 law, the mean effective wavelengths of the beams were calculated, values being obtained only slightly less than those deduced on Compton's theory from the scattering terms. Determinations of the spectral distribution of energy indicate that the homogeneous γ-rays are superimposed on a background of general radiation which contains a considerable fraction of the total γ-ray emission, with a maximum near 0·02 Å. Measurements of the intensities of the rays scattered within a definite cone for two positions of the revolving ionisation chamber gave results one-third to one-fifth of those predicted by classical theory, but only about 10% lower than those calculated from Compton's formula for the angular distribution of the scattered rays.

F. G. T.

Heating Effects of the γ-Rays of Radium-*B* and Radium-*C*. C. D. ELLIS and W. A. WOOSTER (*Phil. Mag.*, 1925, [vi], **50**, 521—536).—In an apparatus automatically compensated for the heating due to α-particles, the heating effect of the total γ-rays emitted by one curie of radium-*B* and radium-*C* has been found to be $8{\cdot}6\pm0{\cdot}4$ cal./hour. From the value of the ratio of the γ-ray energies 0·10 determined from the absorption coefficient measurements of Ahmad (A., 1924, ii, 440, 582) 0·86 cal./hour is attributed to radium-*B* and 7·7 cal./hour to radium-*C*, corresponding with $1{\cdot}85\times10^5$ and $16{\cdot}6\times10^6$ volt per disintegrating atom, respectively.

A. E. M.

Atomic Disintegration by α-Particles. G. KIRSCH (*Physikal. Z.*, 1925, **26**, 457—465).—In amplification of the "explosion" theory, it is suggested that atomic disintegration by means of α-particle bombardment occurs in two steps. The first is the

assimilation of the α-particle into the nucleus, and the second the immediate expulsion of the H-particle. These two processes are nearly simultaneous; the life of the intermediate product, which, in the case of a nitrogen nucleus, is a fluorine isotope, is of the order of 10^{-10} second. The energy with which the H-particle is emitted is regarded as independent of its direction, and the impulse law is assumed to hold in each stage of the process. Calculations are made of the differences of energy content of fluorine isotopes formed by the assimilation into the nitrogen nucleus of α-particles of various initial velocities. Comparison of these differences with those of the energy contents of H-particles emitted by the disintegration of these fluorine isotopes shows that the emission is accompanied by just as much energy as was contributed by the α-particle, so that, in all circumstances, the final product has the same energy content. These assumptions are supported by a study of the absorption curves of the H-particles from nitrogen under various conditions of bombardment by α-particles. The absorption curves of H-particles from aluminium differ markedly from those from nitrogen, in that some particles of very long range are emitted, the energy of which, in some cases, is double that predicted by theory. Several reasons are suggested for this fact, and the conclusion is reached that the emitted H-particles are not derived from protons situated in a single energy level, but that an innermost level, of maximum energy, exists which can receive energy only from those α-particles which have a maximum velocity and which strike the nucleus centrally. The emission of H-particles from nitrogen, aluminium, and other elements is considered on the basis of the structure of the kernel suggested by the author (A., 1921, ii, 150; 1924, ii, 380), and the existence of the group of four protons and two electrons as a subsidiary unit is supported. It is further suggested that in building up the kernel from such units ("quasi H-particles") and free electrons, levels of energy exist in the nucleus equal in number to the electron shells external to the nucleus, so that the periodicity of the elements is a property directly related to the kernel-structure. In considering the forces which bind the kernel together, it is shown that if the charges in the nucleus are regarded as rotating with an impulse moment $mvr=h/2\pi$, the field-energy of negative charges becomes many times greater than that of stationary electrons, and that, in such circumstances, a proton in a one-quantum orbit of 10^{-12} cm. radius may be in equilibrium with an attracting point-charge of magnitude $2{\cdot}88e$. F. G. T.

Atomic Weight of the Gold obtained from Mercury by Miethe and Stammreich. O. Hönigschmid and E. Zintl (*Z. anorg. Chem.*, 1925, **147**, 262—264; cf. Miethe and Stammreich, A., 1924, ii, 874; *Naturwiss.*, 1924, **12**, 597, 1211).—The atomic weight of the gold so obtained was determined by the authors' potentiometric method and agrees with that of ordinary gold. J. S. C.

Transformation of Mercury into Gold. A. S. Russell (*Nature*, 1925, **116**, 312).—Theoretical considerations lead to the

suggestion that the transformation of lead into thallium is as possible as that of mercury into gold. If the masses of the thallium isotopes are 203 and 205, and its atomic weight, as recently determined, is 204·4, that element is an exception to the rule whereby, when any element of odd atomic number possesses two isotopes, the heavier is never in excess. Possibly, therefore, the excess of the isotope 205 may be due to a natural process involving absorption of an electron by the nucleus of the lead isotope 205. A. A. E.

Transmutation of Uranium into Uranium-*X*. A. GASCHLER (*Nature*, 1925, **116**, 396—397).—Priority is claimed against Miethe for the transmutation of mercury into other elements. The behaviour of uranium and thorium and their salts in the electric arc and in the glow discharge in evacuated tubes has been examined, but no alteration in the radioactivity or chemical activity could be observed. When, however, strong rushes of momentary high-tension currents are passed, during 30 hrs., between tungsten electrodes in a silica tube containing mercury and uranium oxide, increasing radioactivity was observed, due to the production of uranium-*X*. A variation of the experimental conditions allows of the production of relatively large quantities of uranium-*X* in 30 mins. A. A. E.

Occurrence of Helium and Neon in Vacuum Tubes. R. W. RIDING and E. C. C. BALY (*Proc. Roy. Soc.*, 1925, **A**, **109**, 186—193).—By bombardment of a hollow anticathode coated with the nitride of magnesium or of aluminium and placed in the focus of a concave cathode in a tube containing oxygen, the nitrogen atoms are disintegrated, helium, hydrogen, and neon being found as products. Previous failures to repeat the results of Collie and Patterson (T., 1913, **103**, 419) are attributed to the strong occlusion of the rare gases in the electrode splash. By heating the powdered discharge tubes, after 60 hrs'. discharge, at 800° in a vacuum a considerable amount of helium was obtained. With a single induction coil giving a 6-inch spark, the rare gases were always obtained, only minor variations in their amounts being observed when the hammer break was replaced by a mercury break and when a condensed discharge was used. Negative results were obtained when a larger coil was used. F. G. T.

Chemical Activity of Helium. E. H. BOOMER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 198—205; cf. Manley, this vol., ii, 144).—When helium is subjected to an intense electronic bombardment (1000 volts, 5—10 milliamp.) at low pressures in the presence of a heated tungsten filament, both helium and tungsten disappear and a black deposit is formed. In general, the atomic ratio between the loss in weight of the filament and the loss of helium was 1 : 2, but the proportion of tungsten was increased when a large amount of mercury was present in the discharge tube. In nitric acid or potassium hydroxide, the black deposit was decomposed with the evolution of helium, and the formation of tungstic oxide or a clear solution. If the ratio of tungsten to helium which had disappeared

was greater than 1 : 2, only the amount of tungsten necessary to form WHe_2 was dissolved from the black deposit in potassium hydroxide, the tungsten in excess of this ratio remaining in the metallic state. The rate of disappearance of helium was greatest in the pressure range 0·1—0·45 mm., reaching a value 4—5 mm.^{3} helium at *N.T.P.* per minute. The velocity of the reaction decreased as the discharge voltage was decreased, and was markedly affected by the material composing the leads, or by the presence of mercury vapour. Strong evidence has been obtained for the existence of the distinct and stable compound WHe_2, *tungsten helide*, and less certain evidence, by analogous methods, that helium unites with the vapours of mercury, iodine, phosphorus, and sulphur to form compounds which are stable at the temperature of liquid air, and decompose at slightly higher temperatures. F. G. T.

Nature of Radiation. J. C. SLATER (*Nature*, 1925, **116**, 278).—Discussion. A. A. E.

Equilibrium between Matter and Radiation. O. STERN (*Z. Elektrochem.*, 1925, **31**, 448—449).—On the basis of the fundamental relativistic equation $U=mc^2$ and of Nernst's heat theorem, an expression is developed for the number of atoms per cm.^{3} in equilibrium with black radiation at a given temperature. W. A. C.

Equilibrium between Radiation and Matter. W. WESTPHAL (*Z. Physik*, 1925, **33**, 557—562).—The distribution of energy is calculated for an enclosed space containing stationary radiation and molecules of a perfect gas in a stationary state and possessing a single specific frequency. E. B. L.

Theory of Atomic Structure. P. JORDAN (*Z. Physik*, 1925, **33**, 563—570).—Pauli's arrangement (this vol., ii, 339) of the complex terms of the spectrum of an atom in weak and strong magnetic fields and of the multiplicity of states of the atom, leads to more definite grouping of the valency electrons than was previously possible. E. B. L.

Equilibrium Principle of G. N. Lewis. M. LEONTOVICZ (*Z. Physik*, 1925, **33**, 470—474).—Lewis' principle is investigated in connexion with Einstein's derivation of Planck's formula for black body radiation and is found to lead to Wien's formula, unless it is assumed that there is association of quanta. E. B. L.

Serious Difficulty in the Determination of the Number of Vibrations Radiated from a Bohr Atom. R. K. CHATURVEDI (*Z. Physik*, 1925, **33**, 660—663).—The difficulty is to account for the emission of a coherent train of waves in the time allowed by the leap from one Bohr orbit to another. E. B. L.

Structure of Zinc. H. COLLINS (*Chem. News*, 1925, **131**, 145—149).—Speculative. From the laws of relative volume and of heats of formation the structure of zinc is deduced as KCN. A. R. P.

Absorption Spectra of Mixed Metallic Vapours. II. Spectra of Volatile Compounds of Magnesium and the Alkali Metals. S. BARRATT (*Proc. Roy. Soc.*, 1925, **A**, **109**, 194—197; cf. A., 1924, ii, 138).—Measurements have been made, at about 1000°, of the absorption of the mixed vapours magnesium–sodium, magnesium–potassium, magnesium–rubidium, and magnesium–cæsium. The magnesium–sodium spectrum consists of a single band in the green region, degraded towards the blue, and with a head at 5290·8 Å. Magnesium–potassium vapours of moderate density exhibit two bands, one in the red, degraded towards the long-wave side, with the head at 6549·7 Å., and the other in the blue, degraded towards the short-wave region, with the head at 4611·6 Å. In much denser vapours a third band appears in the green, degraded towards the blue, with the head at 5150·4 Å. The magnesium–rubidium spectrum has a band at 4728·1 Å., degraded towards the blue. Magnesium–cæsium vapours show two bands, one shading off on either side of a maximum at 5706 Å., the other, with a head at 4839·2 Å., degraded towards the blue. Reasons are advanced for attributing these bands to the molecules of volatile compounds of magnesium and the alkali metals. F. G. T.

Absorption of Light by Vapours of Lead, Tin, Bismuth, Antimony, and Magnesium. A. L. NARAYAN and K. R. RAO (*Phil. Mag.*, [vi], 1925, **50**, 645—649).—The absorption spectrum of non-luminous lead vapour shows, in addition to the fundamental line at 2833 Å., a faint banded spectrum, appearing at about 1100°, extending from 3100 to 3400 spaced at intervals of about 32 Å. That of tin vapour showed a faint reversal of the line 2706·6 Å. That of bismuth at 800° showed the typical line at 3067 Å., a banded spectrum extending from 2600 to 2900 with a spacing of 15 Å., and fine lines at 2721·5, 2730, and 2745 Å., and at 1200° a further banded spectrum extending from 6500 to 4500 with the spacing varying from 90 to 35 Å. in passing from the red to the blue. That of antimony shows fine lines at 2312 and 2306 Å., and a banded spectrum extending from 2305 to 2250, with an interval of about 15 Å.; with increasing temperature a band spectrum in the region 2830 to 3000 and a fine line at 2770 Å. appear. That of magnesium at high temperatures shows a line at 4571 Å. corresponding with the change in energy level $1S-2p_2$. A. E. M.

Structure of the Ultra-violet Bands of Water Vapour. G. H. DIEKE (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 174—181).—The lines of the water vapour bands at 3064 and 2811 are classified. By making use of Watson's measurements of the band 2811 (this vol., ii, 349) and a modification of Heurlinger's arrangement of the band 3064 ("Untersuchungen über die Struktur der Bandenspektra," Lund, 1918), a complete analysis of the bands is shown to be possible. The question of the origin of the bands, whether due to H_2O or to OH molecules, is still open. A. B. M.

Band Spectra Associated with Carbon. F. BALDET (*Nature*, 1925, **116**, 360).—A claim for priority. A. A. E.

Flame Spectra of Carbon Monoxide and Water-gas. I. F. R. WESTON (*Proc. Roy. Soc.*, 1925, **A**, **109**, 176—186).—The flame spectrum of carbon monoxide, and the effect on it of admixture of hydrogen in varying proportions, have been determined. The spectrum of pure undried carbon monoxide consists of a banded radiation extending from 5000 to 2200 Å., on which a continuous spectrum and some steam lines are superimposed. As the carbon monoxide in the burning gas is progressively replaced by hydrogen, both the banded and continuous parts of the spectrum fade away until, at an equimolecular mixture of the gases, they nearly disappear, only steam lines remaining visible. The intensity of these lines increases with the amount of hydrogen, reaching a maximum in the spectrum of pure hydrogen. At the same time, a rapid shortening of the ultra-violet end of the continuous spectrum occurs. The spectrum of carbon monoxide burning in various supporting atmospheres (air, "argon air," dried, undried, and 6% ozonised oxygen, nitrous oxide) was photographed. With undried air, the continuous part of the spectrum is intensified and prolonged. Dried oxygen has the effect of diminishing the intensity of the steam lines. By burning carbon monoxide in oxygen at various pressures it was found that as the pressure is reduced the banded spectrum becomes more distinct and the continuous part less intense, without any alteration of the positions of the bands. Measurements are given of the intensity and distribution of the band spectrum of carbon monoxide burning in air. It is concluded that in the flame of undried carbon monoxide two sets of independent reactions occur simultaneously, (*a*) direct combination of carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum and to the blue colour of the flame, and (*b*) reaction between carbon monoxide and oxygen molecules giving rise to steam lines in the spectrum. Addition of hydrogen causes the second reaction to predominate. F. G. T.

Red Cyanogen Spectrum in Daniel's Comet (1907). F. BALDET (*Compt. rend.*, 1925, **181**, 331—333).—Re-examination of plates taken in 1907 shows that the red band of the comet originates in the red group of bands due to cyanogen which are observed in the carbon arc. In the comet the bands are very intense and are superimposed on a fairly intense continuous spectrum. R. A. M.

Infra-red Absorption Spectra of Organic Derivatives of Ammonia. I. Aniline and some Mono- and Di-alkyl-anilines. F. K. BELL (*J. Amer. Chem. Soc.*, 1925, **47**, 2192—2207).—The absorption spectra of aniline, methyl- and dimethyl-, methyl-ethyl-, ethyl- and diethyl-, *n*-propyl- and di-*n*-propyl-, *n*-butyl- and di-*n*-butyl-, and *iso*amyl-anilines between 1·0 and 12·0μ have been measured and plotted, the accuracy of the absorption curves being within 0·05μ. The main conclusions are as follows: ammonia shows a single deep band at 2·98μ (Coblentz, *Carnegie Inst. Pub.*, 1905, **35**, 53), whilst in aniline this shifts to 2·8μ and the 3·25μ band of benzene appears. In the monoalkylanilines, the 2·8μ band becomes shallower and the 3·25μ band shifts to 3·3μ and is con-

sistently deeper than the 2·8μ band, whilst in the dialkylanilines the latter almost disappears and the 3·3μ band becomes deeper. Thus with progressive substitution in ammonia the specific influence of tervalent nitrogen on absorption in the region 2·8μ progressively diminishes. In the region 2·7—3·4μ, therefore, the absorption permits a pronounced qualitative differentiation between aniline, mono- and di-alkylanilines. J. W. B.

Absorption Spectra of Pyruvic Acid. Existence of Tautomeric Forms. V. HENRI and C. FROMAGEOT (*Bull. Soc. chim.*, 1925, [iv], **37**, 845—853).—The study of absorption spectra gives a ready method of proving the presence of tautomeric forms, since the ultra-violet absorption by a molecule with a double bond between two carbon atoms is much stronger than that by a molecule with a double bond between a carbon and an oxygen atom. In concentrated solutions of pyruvic acid the acid is almost entirely in the keto form, but the intensity of absorption increases with dilution, and the presence of a double bond between two carbon atoms is indicated. A formula is given for calculating the growth of the enol form with dilution, from which it appears that the growth of the enol form increases tenfold when the concentration drops from 0·1N to 0·01N, and is only increased one and a half times on dropping from 0·01N to 0·002N. A study of the influence of the p_H of the medium shows that the amount of the enol form increases with the alkalinity of the solution. The biological significance of these results is pointed out. L. L. B.

Ultra-violet Absorption Spectra of Mono- and Di-derivatives of Benzene. F. W. KLINGSTEDT (*Acta Acad. Aboensis Math. Phys.*, 1924, **3**, 1—82; from *Chem. Zentr.*, 1925, i, 2286; cf. A., 1923, ii, 48).—The absorption of ultra-violet radiations up to 1944 Å. has been examined quantitatively for toluene, phenol, aniline, the xylenes, cresols, toluidines, and dihydroxybenzenes. All compounds which show narrow absorption bands in the vapour state give also in indifferent solvents spectra with narrow (10—30 Å.) bands similar to the spectra of their vapours. The characteristics of the absorption spectra of the compounds mentioned are described, Substitution in the benzene nucleus by methyl, hydroxyl, or amino groups results in a displacement of the selective absorption towards the red, an increased total absorption in the inner ultra-violet, an increase in the molecular absorption coefficient of the strongest inner bands, and a change in the number, form, and distribution of the different bands. Similar effects are observed in substituted toluene derivatives. The selective absorption of para derivatives is distinguished, apart from the nature of the substituent, by a large number of sharply defined narrow bands, begins at longer wavelengths, and is more marked in the extreme ultra-violet than is the case with the other isomerides. Ortho and meta derivatives are similar in the middle ultra-violet and to a certain extent in the outer ultra-violet. The absorption spectra of the hydrocarbons examined have no definite benzene character. The absorption spectra of the phenols, apart from those parts of the spectra of para derivatives

which contain numerous bands, are generally similar. The amines are generally similar in their absorption spectra up to the outer ultra-violet, except that aniline and *p*-toluidine have narrow bands in the inner ultra-violet. G. W. R.

General Nature of Band Spectra. J. W. NICHOLSON (*Phil. Mag.*, 1925, [vi], **50**, 650—662).—A theoretical discussion of band spectra, directing attention to the relationships between line and band spectra. A formula is suggested which contains as a fundamental constant a Rydberg constant only. Some terms arise from ordinary quantum theory as applied to electronic orbits, whilst others arise from the quantising of the degrees of freedom of the nuclei. A. E. M.

Complementary Researches on the Structure and Distribution of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1925, **181**, 265—271; cf. this vol., ii, 736).—The infra-red bands of the simple gases oxygen, carbon monoxide, hydrogen cyanide, ammonia, water, and methane can be expressed by the relation $\nu=qd_1/rs$, where d_1 is a universal constant 1062·5 and q, r, and s are integers. The data for ammonia are examined in detail and are found to agree with the relation very well. Hydrogen fluoride, chloride, and bromide also exhibit bands related to the universal frequency. Although the data are incomplete, a tentative analysis is put forward suggesting that the constant frequency-differences characteristic of sub-groups are also small sub-multiples of the constant. The author agrees with Baly ("Spectroscopy," vol. I, 1924) that the infra-red region is of primary importance for radiation theories of reaction. R. A. M.

Experimental Determination of the Critical Excitation Frequency for the Production of Fluorescent *X*-Radiation. S. K. ALLISON and W. DUANE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 485—489; cf. *Physical Rev.*, 1925, [ii], **25**, 581).—Experiments in which the fluorescent radiation was excited in a silver plate by primary radiation from a tungsten target show that to produce a fluorescent line spectrum the primary radiation must contain *X*-rays of frequency at least as great as that of the corresponding critical absorption, this frequency being the same for all lines in the series. The wave-lengths of the $K\alpha_1$ and $K\alpha_2$ lines in the fluorescent silver spectrum are 0·55834 and 0·56266 Å., respectively. J. S. C.

Photographic Sensitometry with Fluorescent Oils. G. R. HARRISON (*J. Opt. Soc. Amer.*, 1925, **11**, 113—123).—The changes in sensitivity and contrast produced in several brands of photographic plates by coatings of fluorescent oils have been studied through the wave-length range 2200—3800 Å. Characteristic curves are given for the coated plates. Some plates show a maximum sensitivity increase with a thick coating of oil, others with a thin coating. Clear paraffin oil gives the maximum sensitivity increase, whilst light lubricating oil has more effect on the contrast. The exposures required may be cut down 400-fold by oil treatment. With some oils, a gain in sensitivity is achieved only when the

intensity of the incident light is above a certain value, below which the sensitivity is diminished. The sensitivity is generally decreased for wave-lengths longer than 2500 Å. Contrast improvement may be obtained even up to 3800 Å. The sensitivity of a plate uniformly oiled is constant over its surface to within 1%. S. B.

Activating Element in Luminescent Boron Nitride. E. TIEDE and H. TOMASCHEK (*Z. anorg. Chem.*, 1925, **147**, 111—122; cf. A., 1921, ii, 74; *Z. Elektrochem.*, 1923, **29**, 303).—Experiments are described which show that specimens of boron nitride exhibit luminescence only when small quantities of carbon are present. J. S. C.

Economy Coefficients of Phosphorescent Substances. F. SCHMIEDER (*Ann. Physik*, 1925, [iv], **77**, 381—416).—The economy coefficient, defined as the ratio of the energy of the emitted to that of the exciting light, has been measured for three phosphorescent calcium sulphide preparations, employing exciting light of wave-lengths 365 and 435 μμ. A method is described, based on Lenard's differential equation for the light emission of phosphorescent substances, in which the total transmitted and phosphorescent light emerging from a monochromatically illuminated layer of a phosphorescent substance is measured by a photo-electric cell. The transparency of the layer is determined by measuring the transmission of light of the non-exciting wave-length 546 μμ. Measurements were made of the intensity of the phosphorescent bands of the preparations CaBiα, ZnCuα, CaCuα, at a series of temperatures. The possible sources of error in the method are investigated in detail, and all assumptions subjected to experimental tests. For the above phosphorescent substances, in the order given, the mean economy coefficients for exciting light of wave-length 435 μμ are 0·97, 0·835, 0·75, and for light of wave-length 365 μμ, 0·82, 0·731, 0·63, respectively. The results confirm Lenard's conclusion that for each quantum of exciting light absorbed, one quantum of emitted light appears. Evidence was obtained that some of the emission centres are able under certain conditions to emit more light energy than they absorb, the excess energy arising possibly from the kinetic energy of the atoms composing the emission centre, or from the thermal energy of the centres. F. G. T.

Dependence on Temperature of the Internal Friction and Electrical Conductivity of Aqueous Solutions. M. WIEN (*Ann. Physik*, 1925, [iv], **77**, 560—586; cf. *Physikal. Z.*, 1924, **25**, 559).—A review of data for the effect of temperature on the electrical conductivity of aqueous solutions supports the view that the initial temperature coefficient comprises the two effects of a change of viscosity of the solvent, which occurs in an imperceptibly short time, and of a second effect, which is not instantaneous, and is dependent on the ions in solution. The temperature coefficient of the fluidity of water and of aqueous solutions can be expressed by the formula $\alpha=1/(a+bt)$, where a and b are constants. The temperature coefficients of the electrical conductivity of these solu-

tions, plotted against temperature, lie on curves which are parallel to those for the temperature coefficients of the fluidity, so that in the range 0—100°, the expression $\beta=\alpha+\gamma$ holds, where β and α are the temperature coefficients of the conductivity and the fluidity, respectively. With the exception of sodium carbonate solutions, γ is negative. It has values for neutral salts between −0·2 and −0·3, for bases between −0·5 and −0·7, and for acids between −0·8 and −1·6; it is a characteristic of a given ion. For most solutions, γ is, within the limits of experiment, independent of temperature, and only slightly, if at all, dependent on the concentration. Except with phosphoric and hypophosphorous acid solutions, the constancy of γ holds over the range 0·0001—0·05*M*-solutions. The chief deviations from constancy of γ with temperature change are shown with solutions of sulphuric and hydrochloric acids, and of copper sulphate. The significance of γ is discussed, and it is shown that most theories of solution afford simple explanations for it. By integration of the expression $\beta=\alpha+\gamma$, the expression $\lambda_t=\lambda_\tau\{1+q_\tau(t-\tau)\}^p e^{\gamma(t-\tau)}$ is obtained for the conductivity of the solution, where $\{1+q_\tau(t-\tau)\}^p$ represents the dependence of the fluidity of the solution on temperature, and the term $e^{\gamma(t-\tau)}$ depends on the nature of the ions. This expression accords extremely well with experimental data, for such diverse solutions as 0·00097*M*-sodium chloride and 1·014*M*-hypophosphorous acid.

F. G. T.

Dependence of Dielectric Constant of Aqueous Solutions on Temperature. L. KOCKEL (*Ann. Physik*, 1925, [iv], **77**, 417—447).—A sensitive apparatus is described by which measurements may be made of the dielectric constants of liquids with conductivities up to 5×10^{-5} mho. Numerous measurements were made with water, and with sucrose solutions containing up to 40% of sucrose at temperatures between 0° and 100°, and with carbamide solutions containing up to 15% of carbamide between −4·3° and 63°. The following values were obtained for the mean temperature coefficients of sucrose solutions between 0° and 100°: 10%, 0·392%; 20%, 0·395%; 30%, 0·403%; 40%, 0·412%. The values for water between 0° and 100° may be represented by the expression $\epsilon=87\cdot9e^{-0\cdot0047t}$. A more accurate value of the coefficient in this expression is 0·00481 between 0° and 50°, and 0·00445 between 50° and 100°. The behaviour of carbamide is abnormal in that its presence raises the dielectric constant of water, and the alteration of dielectric constant of its solutions on heating above 35° is irreversible, although no decomposition can be detected in the solution. The results for water show no agreement with Debye's theory (*Verh. phys. Ges.*, 1913, **15**, 777) and only an approximate one with that of Gans (*Ann. Physik*, 1921, [iv], **64**, 498). The variation of dielectric constant with concentration is in qualitative agreement with the results of other workers.

F. G. T.

Molecular Fields and their Volumes. A. BATSCHINSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 11—22; from *Chem. Zentr.*, 1925, i, 2528).—The volume of an atom is only accounted for to a small extent

by the nucleus and the electrons, the greater part consisting of electrical fields. Similarly, the volumes of molecules consist largely of interstitial spaces. Molecular volume is thus rather the sum of the volumes of the linkings than of the volumes of constituent atoms. The following mean values in c.c. are given for the molecular volumes of different linkings at the b. p. of compounds in which they occur: C—C and C—H, 7·37; double linkings, twice the value for single linkings; benzene linkings, 51·2; C—Cl, 25·2; C—Br, 31·1; C—I, 41·9. G. W. R.

Contraction Regularities in the Formation of Solid Chemical Compounds. I. I. Saslavsky (*Z. anorg. Chem.*, 1925, **146**, 315—323).—The molecular volumes MV of a large number of compounds are compared with the sums of the atomic volumes ΣAV. The quantity $C=MV/\Sigma AV$, the "contraction," is calculated in each case. When similar salts are compared, this quantity C is seen to exhibit regularities which lead to the rule: each metal and each acid radical which enters into a compound has its own specific effect on the contraction. The observed regularities are illustrated graphically. A. B. M.

Refractive Power of Atoms for X-Rays. H. Mark and S. Tolksdorf (*Z. Physik*, 1925, **33**, 681—687).—Anhydrous strontium chloride crystallises in the cubical system of the type of fluorite, the length of the edge of the unit cube being 7·00 Å. The intensities of the interferences indicate that the deflection produced by the ions is not simply proportional to the number of electrons they possess. E. B. L.

Critical Potentials and the Refractive Indices of Elements and Compounds. B. Davis (*Physical Rev.*, 1925, [ii], **26**, 232—240).—The Lorentz dispersion formula involves terms of the type $N_1/(\nu_1^2-\nu^2)+N_2/(\nu_2^2-\nu^2)+\cdots$, where ν is the frequency of the light and ν_1 and ν_2 are natural frequencies characteristic of the refracting atom or molecule; ν_1 and ν_2 are identified with critical resonance frequencies. For hydrogen, the observed refractive index is obtained if the critical resonance potential is accepted as 16·4 volts. The observed values are 16·0 and 16·9. Unexcited molecular hydrogen should therefore have an absorption band at 760 Å. For the vapours of zinc, cadmium, and mercury the observed refractive indices are reproduced if the following critical resonance potentials at the outer levels are assumed: 4·77, 4·38, and 5·21 volts, respectively. These values in each case lie between values corresponding with two strong absorption lines. For other gases, the potentials observed and those assumed in order to fit the theoretical work are given below:—

	Carbon.	Nitrogen.	Oxygen.	Sulphur.	Chlorine.	Bromine.	Iodine.
Observed:	11·5, 35	17, 29·9	15·5, 52	12·2, 35	13·2, 46	11·3, 32	10, 21
Calculated:	15, 35	17, 29·9	18·5, 52	12·2, 16·2	13·2, 35·3	11·3, 25·8	10, 13·8

The experimental values for carbon, nitrogen, and oxygen cannot all be correct. The values assumed lie on a straight line in a Moseley diagram. For helium, neon, and argon, the observed potentials

cannot be used to calculate the refractive index correctly with the equation of Lorentz and Lorenz.

The calculations are extended to compounds. It is assumed that the heat of formation is associated with an equal energy-change of the valency electrons. For water and ice if the heats of formation are added to the critical potentials of hydrogen, the calculated values of the refractive index are within 0·5% of the observed values. A number of inorganic and organic compounds has been studied in this manner and excellent agreement between observed and calculated values found. R. A. M.

Tests on the Accuracy of Measurement with the Rotatory Dispersion Colorimetric Photometer. K. S. GIBSON (*J. Opt. Soc. Amer.*, 1925, **11**, 75—79).—The rotatory dispersion photometer previously described by Priest (A., 1924, ii, 247) has been subjected to tests of its performance, chiefly in the determination of intensities from incandescence lamps etc. The results are highly satisfactory. S. B.

Rotatory Dispersion Power of Organic Compounds. XVI. β- and π-Sulphonic Derivatives of Camphor. E. M. RICHARDS and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 1503—1514).—The rotatory dispersion and absorption spectra of a series of β- and π-sulphonic derivatives of camphor have been determined in the visible and ultra-violet regions. As in previous cases, there is a discrepancy of nearly 100 Å. between the characteristic frequencies deduced for the low-frequency term by the two series of observations. The rotatory dispersion of these camphor derivatives can be expressed in general by a two-term Drude equation containing a high-frequency and a low-frequency term, the former being identified with the fixed asymmetric atoms and the latter with the induced asymmetry (A., 1924, ii, 373) of the ketonic group. In the π-derivatives the high-frequency term is suppressed or becomes negligible in comparison with the enhanced low-frequency term. In camphor-β-sulphonanhydramide the elimination of the ketonic group results in the suppression of the low-frequency term together with the selective absorption with which this term has been correlated. An explanation of these and other related facts is sought in a critical examination of the symmetry of the camphor molecule and of its derivatives. The rotation for light of any wave-length between the limits mentioned can be calculated from the Drude equation $[\alpha]_{\lambda}^{20}=k_1/(\lambda^2-\lambda_1^2)+k_2/(\lambda^2-\lambda_2^2)$, in which the first term represents the partial rotation due to the low-frequency absorption and the second that due to the high frequency. The numerical values of the constants follow ($\lambda_1-\lambda_a$ is the difference between the wave-length of the low-frequency band as determined from the Drude equation and the absorption data respectively, expressed in Å.). Ammonium α-bromocamphor-π-sulphonate in water: $C=13{\cdot}936$, $k_1=22{\cdot}015$, $\lambda_1^2=0{\cdot}09668$, $\lambda_1-\lambda_a=90$ Å. (λ=6708 to 4010); ammonium α-chlorocamphor-π-sulphonate in water: $C=20{\cdot}440$, $k_1=17{\cdot}677$, $\lambda_1^2=0{\cdot}09946$, $\lambda_1-\lambda_a=120$ Å. (λ=6708 to 4055); α-bromocamphor-π-sulphonethylchloroamide in chloroform: $C=14{\cdot}287$, $k_1=25{\cdot}889$,

λ_1^2=0·09969 (λ=6708 to 4358); α-bromocamphor-π-sulphondichloroamide in chloroform: C=10·872, k_1=23·897, λ_1^2=0·10719 (λ=6708 to 4358); camphor-β-sulphonic acid in water: C=28·636, k_1=22·17, λ_1^2=0·08515, k_2=−18·32, λ_2^2=0·04945, $\lambda_1-\lambda_a$=70 Å. (λ=6708 to 3969); potassium α-chlorocamphor-β-sulphonate in water: C=12·386, k_1=12·060, λ_1^2=0·09768, k_2=5·1354, λ_2^2=0, $\lambda_1-\lambda_a$=125 Å. (λ=6708 to 3952); potassium α-bromocamphor-β-sulphonate in water: C=16·206, k_1=18·78, λ_1^2=0·09517, k_2=5·569, $\lambda_1-\lambda_a$=55 Å. (λ=6708 to 4041); camphor-β-sulphonanhydramide in acetone: C=4·941, $k_1=\lambda_1^2=\lambda_2^2=0$, k_2=−10·696 (λ=6708 to 4220). E. E. W.

Calculation of Rotatory Power of a Tetrahedral Molecule. R. DE MALLEMANN (*Compt. rend.*, 1925, **181**, 298—300).—An expression for the rotatory power of an asymmetric compound is derived. Atoms are assumed to be situated at the apices of a trirectangular tetrahedron. J. S. C.

Production of Optical Activity in Silver by Circularly Polarised Light. H. ZOCHER and K. COPER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 426—431).—A layer of silver chloride, about 0·15μ thick, was formed on a glass plate by the action of chlorine on a silver film. The plate was exposed to circularly polarised light for 1 hr. and after this treatment exhibited permanently circular asymmetry. The source of light was a very powerful arc lamp and the light was circularly polarised by Nicol prisms and a Fresnel total reflection epiped. The film not only rotated the plane of linearly polarised light to the extent of 0·25°, but also caused the light to become elliptically polarised. The rotation of the plane of polarisation was unaffected by rotation of the plate through 90°. Circularly polarised light in nature is considered a possible cause of the asymmetry of organic structure. F. G. S.

Thermal Expansion of Crystals and Chemical Constitution. F. A. HENGLEIN (*Z. Elektrochem.*, 1925, **31**, 424—428).—The expansibilities of alkali halides have been measured in the ranges 0° to −79° and −79° to −184°. All decrease with temperature. For a given cation, the expansibility increases as the atomic weight of the anion rises; for a given anion it diminishes as the atomic weight of the cation rises. Fluorides, however, do not obey this rule. W. A. C.

Chemical Constitution and *K* Absorption Spectra. II. Investigation of certain Compounds of Phosphorus. O. STELLING (*Z. physikal. Chem.*, 1925, **117**, 161—174; cf. A., 1924, ii, 139).—The *X*-ray *K* absorption spectra of a number of quinquevalent and tervalent compounds of phosphorus and also of additive compounds of tervalent phosphorus compounds were studied. A systematic connexion between constitution and the positions of absorption bands is shown to hold in most cases. L. F. G.

Chemical Constitution and *K* Absorption Spectra. III. O. STELLING (*Z. physikal. Chem.*, 1925, **117**, 175—193; cf. preceding abstract).—Lindh's data of the *X*-ray *K* absorption spectra of

elements and compounds are correlated with chemical constitution (cf. *Z. Physik*, 1925, **31**, 210). The wave-lengths of the absorption bands of elements are higher than those of their compounds; sulphur is an exception. With the same element, the absorption bands become shorter-waved as the valency rises, provided that the successively attached atoms or radicals are the same. With constant valency, the position of the absorption bands of an atom depends on the atoms or radicals directly combined with it. The results are discussed from the point of view of the deformation theory (Fajans, *Z. Kryst.*, 1925, **61**, 18), and the use of *X*-ray absorption spectra in the solution of problems in chemical constitution is considered. The experimental methods of Lindh and of the author are compared. L. F. G.

Chemical Constitution and *K* Absorption Spectra. IV. Constitution of Phosphorous Acid and Some Derivatives. O. Stelling (*Z. physikal. Chem.*, 1925, **117**, 194—208; cf. preceding abstracts).—Previous investigations of the constitution of the phosphorous acids are reviewed, and it is shown that the hypothesis of Rosenheim, Schapiro, and Italiener (A., 1924, ii, 51) that these acids exist in double molecules in aqueous solution is based on an incorrect interpretation of their results. A study of the *X*-ray *K* absorption spectra leads to the conclusion that structural formulæ may be ascribed to derivatives of phosphorous acid as follows: $(RO)_2PH{:}O$ for phosphorous acid, its diesters, triphenylmethylphosphorous acid, and ferric monopropyl phosphite (cf. A., 1918, i, 479); $(EtO)_2PNa{:}O$ for sodium diethyl phosphite; $(EtO)_2P{\cdot}OAg$ for silver diethyl phosphite; $(HO)_2PAc{:}O$ for monoacetylphosphorous acid. It is probable that the diesters and metal esters form tautomeric mixtures in solution. L. F. G.

The Parachor and Chemical Constitution. I. Polar and Non-polar Valencies in Unsaturated Compounds. S. Sugden, J. B. Read, and H. Wilkins (*J. Chem. Soc.*, 1925, **127**, 1525—1540). —The parachor (A., 1924, ii, 662) is calculated from the orthobaric densities and the surface tension and affords a means of comparing molecular volumes under equal surface tensions. The parachor is an additive function of certain atomic and structural constants. It has been found that there are two values for the double bond; the one contributes 23·2 (mean value) to the molecular parachor and the other reduces this quantity by 1·6 (mean value) units. The former is characteristic of the groups $>C{=}C<$ and $>C{=}O$, and the latter of the groups $>P{\rightleftharpoons}O$, $>S{\rightleftharpoons}O$, $>S\overset{\rightleftharpoons O}{\underset{\rightleftharpoons O}{}}$, in which $\rightleftharpoons$ represents what the authors call a semi-polar bond (Lowry's "mixed" or "ionised" double bonds, cf. A., 1923, ii, 480). The nature of the double linking in a number of compounds containing carbon, nitrogen, phosphorus, and sulphur has been investigated. In all the cases examined by the authors, semi-polar bonds (as detected by the parachor) are formed only when each atom, except hydrogen, has attained a complete octet. The octet is never exceeded and semi-polar bonds are not found when their existence would necessitate the presence of a

sextet around one or other of the atoms concerned. New measurements of the surface tension and density of sixteen substances have been made, using for the former the method of maximum bubble pressure (cf. Sugden, A., 1924, ii, 154). E. E. W.

The Parachor and Chemical Constitution. II. Geometrical Isomerides. S. SUGDEN and H. WHITTAKER (*J. Chem. Soc.*, 1925, **127**, 1868—1874).—By means of the parachor, a distinction can be drawn between the non-polar and semi-polar double bond (cf. A., 1924, ii, 662, and preceding abstract). To determine the type of linking in geometrical isomerides, measurements have been made of the surface tension and density of methyl cinnamate, methyl *allo*cinnamate, methyl α-bromocinnamate, methyl α-bromo-*allo*cinnamate, methyl β-bromocinnamate, methyl β-bromo-*allo*-cinnamate, methyl mesaconate, methyl citraconate, methyl fumarate, and methyl maleate. All the substances examined contain a non-polar double bond, adding 23·2 units to the molecular parachor. In each case, the *cis*-compounds, in which two bulky groups are adjacent, give values for the parachor closely approximating to the theoretical figure, whilst the *trans*-compounds give values which are lower by from one to four units. L. L. B.

Theories of Polar and Non-polar Free Affinities. Reply to some Recent Criticisms and Comparisons. G. N. BURKHARDT and A. LAPWORTH (*J. Chem. Soc.*, 1925, **127**, 1742—1750).—The contention of Ingold and his co-workers (A., 1924, i, 322, 323, 1116), that the results of their recent studies of certain reactions of nitrosobenzene provide evidence in favour of the Thiele–Flürscheim non-polar theories of valency, and against the polarity theories, is freely criticised. It is contended that Ingold and Weaver have given a ring formula to the product of the interaction of nitrosobenzene and ethyl methylenemalonate without sufficient evidence. The same compound has now been prepared from ethyl hydroxymethylenemalonate and β-phenylhydroxylamine in cold methyl alcohol. The compound is thus dicarbethoxymethyl-*N*-phenylnitrone, O:NPh:CH·CH(CO_2Et)$_2$, or the enolic form of this compound. It is claimed that the formation of this substance is in accordance with the prediction of the polarity theories of Lapworth and Robinson, but quite contrary to the predictions of the Werner–Flürscheim theory. E. E. W.

Valency Relations of Boron, Carbon, and Nitrogen from the Standpoint of the Bohr Atomic Model. W. A. WAHL (*Z. anorg. Chem.*, 1925, **146**, 201—224).—The valency relations of boron, carbon, and nitrogen are explained by a development of the Bohr theory. It is assumed that different arrangements of the orbits of the electrons outside the stable inert gas kernel can exist, corresponding with the different possible valencies of the atoms, that the atom can pass from one of these arrangements to another under suitable conditions, and that in some cases two such arrangements can exist together in dynamic equilibrium; *e.g.*, the orbits of tervalent nitrogen are arranged thus: two 1_1, two 2_1, three 2_2. This

arrangement is shown to be in accordance with the spectroscopic evidence. In quinquevalent nitrogen, the orbits become two 1_1, one 2_1, four 2_2. Both nitrogen and boron tend to form the especially stable electron configuration of carbon, and this tendency is shown to lead to the formation of the stable complex ions of quinquevalent boron and quinquevalent nitrogen. Thus the addition of KF to BF_3 is explained by the boron atom taking up a fourth electron with the consequent production of the complex ion $[BF_4]^-$. Nitrogen, on the contrary, forming a stable four-electron arrangement, forces the fifth electron to move in an eccentric outer orbit similar to that of the outer electron in the atoms of the alkali group, so that a positive quinquevalent ion is readily produced. The theory is applied to other valency phenomena of these three elements. A. B. M.

Problems of Boron Chemistry. W. A. WAHL (*Z. anorg. Chem.*, 1925, **146**, 230—238).—The quadrivalency of boron cannot be assumed from the existence of such compounds as B_2H_6 and B_4H_{10}. These compounds are more closely related in their chemical behaviour to the hydrides of nitrogen than to those of carbon. This comparison leads to a suggested structure for these compounds, which does not need the assumption of quadrivalent boron, but to substantiate which requires further experimental evidence.
A. B. M.

Regularity in the Rare Earth and Titanium Groups. G. VON HEVESY (*Z. anorg. Chem.*, 1925, **147**, 217—232).—The properties of the rare earth elements are considered from the point of view of the quantum theory of atomic structure. The molecular volumes of the isomorphous octahydrated sulphates of praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, ytterbium, and lutecium decrease with increasing atomic number, from which it is concluded that the binding forces of the valency electrons increase as the series is ascended.
J. S. C.

Distribution of Intensity in the *X*-Ray Spectra of certain Long-chain Organic Compounds. G. SHEARER (*Proc. Roy. Soc.*, 1925, **A, 108**, 655—666).—The carbon chain with its attached hydrogens is regarded as a uniform distribution of scattering material for *X*-rays. A methyl group at the end of the chain will result in a low scattering power at the end of the molecule on account of the small mass of the hydrogen atoms. A carboxyl group will have a scattering power in excess of the average scattering power of the chain. In esters and ketones the ketonic oxygen attached to one of the carbons of the chain will result in an increase in scattering power at this point. On the basis of the above assumptions and of ideas previously developed regarding the spacing of molecules (this vol., ii, 366, 367), the theoretical distribution of intensities in the spectra of a number of organic compounds is calculated; the calculated values agree fairly well with those observed. Attention is directed to the possibility of using such methods to elucidate problems in chemical constitution. L. F. G.

Dimensions of the Molecule and Molecular Weight of Crystalline Egg-albumin. P. L. DU NOÜY (*J. Biol. Chem.*, 1925, **64**, 595—613).—The author's surface tension method (this vol., ii, 109) for the study of molecular dimensions has been applied to crystalline egg-albumin; the two most prominent groups of surface tension minima were observed at concentrations of 1/140,000 and 1/190,000; from these, the dimensions of the "phantom shape" of the molecule are calculated as $41{\cdot}7\times10^{-8}$ cm. and $30{\cdot}8\times10^{-8}$ cm., which, assuming the shape to be that of a parallelepiped with a square base and the specific gravity to be a property of all the space occupied by the molecule, gives for the volume occupied by a molecule $39{\cdot}6\times10^{-21}$ c.c. and for its weight $51{\cdot}3\times10^{-21}$ g. Taking the constant of Avogadro, N, to be $6{\cdot}004\times10^{23}$ this leads to a molecular weight of 30,800, which agrees well with the figure (31,406) obtained by doubling the minimal molecular weight as determined by analysis. The figures receive further support from the fact that the volume occupied by one carbon atom (vol. of molecule ÷ number of carbon atoms) calculated from them is $28{\cdot}45\times10^{-24}$ c.c., which is in close agreement with the mean value obtained similarly from eight compounds of which the molecular dimensions have been determined by Langmuir (A., 1917, ii, 525). C. R. H.

Two New Elements of the Manganese Group. W. NODDACK, I. TACKE, and O. BERG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 400—409).—From theoretical considerations, it was concluded that the missing elements of the manganese group, of atomic numbers 43 and 75, respectively, occur in platinum ores and in the mineral earths. Examination of platinum ores led to the separation of a volatile oxide, probably the highest oxide of element 75. Its identity was established by examination of its X-ray spectrum. Both elements occur in columbite, and a product was obtained containing 5% of element 75 and 0·5% of element 43. The sublimate from this product gave the lines of the new elements. Small amounts of element 43 occur in sperrylith, gadolinite, fergusonite, and zircon, and traces of element 75 in tantalite and tungstite. The following lines have been measured in the X-ray spectrum of element 43: $K\alpha_1=0{\cdot}672$, $K\alpha_2=0{\cdot}675$, $K\beta_1=0{\cdot}601$ Å.; those measured for element 75 are $L\beta_2=1{\cdot}2048$, $L\beta_3=1{\cdot}216$, $L\beta_1=1{\cdot}2352$, $L\alpha_1=1{\cdot}4299$, $L\alpha_2=1{\cdot}4407$ Å. The positions of these lines agree well with the calculated values, and their relative intensities are as expected from those of the neighbouring elements.

The names "masurium" (Ma) for element 43 and "rhenium" (Re) for element 75, have been chosen. Their estimated total amount is between 10^{-12} and 10^{-13} of the earth's crust. F. G. S.

X-Ray Investigation of the Structure of Alloys. A. SACKLOVSKI (*Ann. Physik*, 1925, [iv], **77**, 241—272; cf. A., 1923, ii, 519; 1924, ii, 110).—The Bohlin–Seeman method (A., 1920, ii, 214) of investigating powdered materials using a cylinder has been employed with alloys. The technique is described and its advantages and disadvantages fully discussed. The crystallographic results for the

following sets of alloys, silver–copper, lead–magnesium, tin–magnesium, copper–nickel, fully confirm the conclusions based on phase diagrams, and in particular the non-existence of the compounds Ag_3Cu_2 and NiCu is reaffirmed.

The rule given by Vegard (A., 1916, ii, 405) that the lattice constants in mixed crystals are purely additive is found to be valid for the silver–copper and copper–nickel systems. Bain has advanced the view that the lattices of inter-metallic compounds exhibit lower symmetry than those of their components. Becker and Ebert have already denied the validity of this generalisation, and the author shows that the compounds $PbMg_2$ and $SnMg_2$ are also in conflict with Bain's rule. These compounds both exhibit a regular face-centred structure, $a_{PbMg_2}=6{\cdot}76$, $a_{SnMg_2}=6{\cdot}75$ Å. From the densities ($PbMg_2$ 5·542, $SnMg_2$ 3·591) the calculated values are 6·75 and 6·77 Å., respectively. R. A. M.

Application of X-Rays to the Study of Alloys. H. Weiss (*Proc. Roy. Soc.*, 1925, **A**, **108**, 643—654).—The α-bronzes and the silver–gold alloys were examined by the powder-photograph method. The spectra of the α-bronzes follow the same laws of position and intensity as the spectrum of pure copper, the side of the cell increasing, however, with increase of tin until the limiting solid solution is reached (about 10% Sn). The results suggest that one atom of tin takes the place of several atoms of copper. With the silver–gold alloys all the results are again in accordance with a face-centred cubic lattice. From silver to gold the size of the cell varies continuously, the sudden increases recorded by McKeehan (A., 1923, ii, 428) not being observed. L. F. G.

Determination of Intensity Ratios in Systems of Debye–Scherrer Rings. Application to the Investigation of the Photographic Process. R. Blunck and P. P. Koch (*Ann. Physik*, 1925, [iv], **77**, 477—494).—An *X*-ray camera of the Debye–Scherrer type is described, with a photometer device consisting of a sectional cylinder rotating against the lower half of the film, so that the illumination of that portion of the film may be proportionately reduced, compared with that of the upper half. A series of measurements with *X*-rays of wave-length 0·71 Å. showed that the density of the image was proportional to the intensity of the *X*-rays. *X*-Ray analysis of the silver in a photographic plate which had been developed in artificial daylight indicated a face-centred cubic lattice with an elementary cell of edge 0·403 Å., agreeing with the value for massive silver. Measurement of the intensity-distribution in individual rings of the *X*-ray photograph gave values, by Scherrer's method (A., 1919, ii, 274), of 1—2μ for the diameter of individual silver crystals in the exposed photographic film. Comparison was made of the measured intensity-distribution in single rings with that calculated from the geometry of the instrument. The measured intensities were slightly higher than the calculated. *X*-Ray absorption measurements of an exposed photographic film corresponded with a silver content of 0·00065 g./cm.^{2} F. G. T.

Separation of Silver from Silver Halides through Intense Irradiation. P. P. Koch and H. Vogler (*Ann. Physik*, 1925, [iv], **77**, 495—502).—The assumption that the formation of the latent photographic image, if due to the passage of an electron from the bromine ion to the silver ion, and the separation of free silver, should be associated with a derangement of the crystal lattice of silver bromide has been investigated by the photometric *X*-ray analysis method of Blunck and Koch (cf. preceding abstract). Measurements with silver bromide prepared in red light from a dry plate or by precipitation, indicated a cubic lattice, with lattice-constant $a = 2{\cdot}89 \times 10^{-8}$ cm., agreeing with previous measurements. Slight but definite differences in the intensity-distributions were found in the Debye–Scherrer rings for these two preparations. The ratio of the intensity of the innermost (001), to that of the second (011) ring was 0·99 for the technical silver bromide and 1·16 for the gelatin-free product. With specimens of silver bromide exposed to sunlight for a day, or under 5% sodium nitrite for 1½ hrs., a second series of rings, corresponding with the silver lattice, was superimposed on the silver bromide rings in the *X*-ray photograph.

An *X*-ray photograph of a dry plate, exposed in sunlight, undeveloped, but fixed in an acid fixing bath, showed the rings corresponding with the silver lattice with great clearness. Measurements of the absorption of *X*-rays by a plate so treated, corrected for the absorption by the gelatin, gave a free silver content in the plate of 0·00024 g./cm.^{2} Similar results were obtained with silver chloride, but no development of the rings of the silver lattice was observed with silver iodide, even after 4 months' daily exposure to sunlight.

F. G. T.

Compton's Theory of *X*-Ray Scattering. H. Fricke (*Nature*, 1925, **116**, 430—431).—Two methods are briefly described whereby, for very hard *X*-rays ($\lambda < 0{\cdot}15$ Å.), Compton's theory of scattering has been verified within an experimental error of about 10%.

A. A. E.

Crystal Structure of Thallium Chloride and Thallium Bromide. G. Lunde (*Z. physikal. Chem.*, 1925, **117**, 51—56).—Debye–Scherrer diagrams for these substances were obtained. The data for thallium chloride obtained by Davey and Wick (*Physical Rev.*, 1921, [ii], **17**, 403) are corroborated. The thallium bromide unit cell contains about 1 mol.; the side is 3·968 Å.; the structure is cubic body-centred, as found by Niggli (A., 1922, ii, 36).

L. F. G.

Permutoid Structure. H. Kautsky and G. Herzberg (*Z. anorg. Chem.*, 1925, **147**, 81—90).—The concept of permutoid structure is considered in relation to the siloxen derivatives (A., 1924, ii, 674), graphitic acid (Kohlschütter and Haenni, A., 1919, ii, 152), and silicic acid from biotite. These substances behave as if the molecules are arranged in a series of surfaces. They all show the same structure and consist of a series of lamellæ of thickness of the order of molecular magnitudes. In the several cases, the original

substances for the preparation of these compounds possess a structure of this type. The reaction between calcium silicide and hydrochloric acid takes place exclusively along the basal surfaces, the side surfaces being unattacked. Rapid diffusion occurs only within the spaces between the lamellæ. J. S. C.

The Molecule in Crystals. R. O. Herzog and K. Weisenberg (*Kolloid-Z.*, 1925, **37**, 23—24).—The name "dynad" is given to a unit within which each atom is held by forces stronger than those between the atom and any atom outside the unit. Two broad groups are recognised: microdynes, which are never larger than the elementary cell, and macrodynes, which may be of the order of a whole crystal. Determination of the dynads should replace at present attempts to define the molecule in crystals. E. M. C.

Crystallography of Methyldiphenylmethyldichloroamine. D. J. Fisher (*Amer. J. Sci.*, 1925, [v], **10**, 201—203).—The crystals (from light petroleum and from alcohol) are monoclinic-prismatic, $a:b:c=0{\cdot}402:1:0{\cdot}365$; $\beta=67°\ 16'$. They are acicular along the *c*-axis and have a strong cleavage along (010). They are optically positive, with refractive indices approximately $\alpha=1{\cdot}64$, $\beta=1{\cdot}68$, and $\gamma=1{\cdot}74$. W. A. C.

Dissolution Velocity and Etched Figures on Crystals. G. Tammann (*Z. anorg. Chem.*, 1925, **146**, 413—419).—The kinetics of the dissolution of a crystal is considered in relation to the figures produced by etching. A theory of the phenomena observed is briefly outlined. A. B. M.

Orientation of Etched Figures and the Distribution of the Atoms in the Space Lattice. G. Tammann and W. Krings (*Z. anorg. Chem.*, 1925, **146**, 420—432; cf. preceding abstract).—The etched figures produced on a number of crystals are compared in the light of our knowledge of the structure of the crystals. It is shown that the crystal surface is first attacked along the lines of the crystal lattice in which the atoms entering into the reaction are most closely packed. On continued etching, figures appear the outlines of which are parallel to the primary grooves. A. B. M.

Theory of Metallic Conductivity. H. Cassel (*Z. Physik*, 1925, **33**, 477—478).—The specific conductivities of the elements are multiplied by the atomic volume raised to the power $\frac{2}{3}$ and the results exhibited in connexion with the periodic table of elements. E. B. L.

Theory of Electrical Conduction in Metals. A. Wolf (*Physical Rev.*, 1925, [ii], **26**, 256—260; cf. Frenkel, this vol., ii, 479; Højendahl, A., 1924, ii, 647).—The electrons are assumed to have kinetic energy corresponding with the thermionic work function W and to move in orbits which form a space lattice with a constant δ of the same order as that of the positive ions δ_I. At each critical point of an orbit, each of the six directions is taken as equally probable. It is then deduced that σ, the specific conductivity, is

given approximately by $0{\cdot}6Ne^2(\delta^2/h)eW/E^1$, where E^1 is the mean heat content of one degree of freedom of the metal. Fair agreement between observed and calculated values is obtained. R. A. M.

Electron Conduction in Crystals. B. GUDDEN and R. POHL (*Physikal. Z.*, 1925, **26**, 481—483).—Lenz (*ibid.*, 365) found that the stationary photo-electric current in zinc sulphide crystals or the diamond was very much less at the temperature of liquid air than at the ordinary temperature. From the contrast with ordinary metallic conduction in which falling temperature increased the conductivity up to super-conductivity, Lenz concluded that the so-called photo-electric current was not caused solely by illumination, but that thermal effects also occurred. The present authors have examined the photo-electric current per unit of light-intensity of various wave-lengths falling on a crystal of sodium chloride at (*a*) 20° and (*b*) −180°. Over the range 410—490μμ, the current is larger at −180° than at 20°, but over the ranges 340—410μμ and 410—600μμ it is smaller. Lenz takes little account of the wave-length of the light used, so that whilst his observations are doubtless correct, they by no means justify his generalisation. Photo-electric currents were also observed with zinc sulphide and diamond at −180°. The work is discussed theoretically and a mechanism in harmony with the results is put forward.

R. A. M.

Photo-resistance Effect for Metals at Low Temperatures. R. S. BARTLETT (*Physical Rev.*, 1925, [ii], **26**, 247—255).—Thin films of metals were prepared by means of electrode splashing, and after ageing were exposed to ultra-violet radiation at the temperature of liquid air. The resistances of gold and silver were unchanged, that of platinum decreased to a very small extent, and those of bismuth, palladium, and copper decreased by 16, 14, and 1·6 parts in a million, respectively. The effect increased with time and the original value was slowly regained in the dark. Tellurium, which was sensitive at the ordinary temperature, showed a 70% greater effect at −185°. For bismuth, the temperature coefficient of resistance decreased from 0·0014 at 0° to approximately zero at −185°. The results are in accord with the predictions of Waterman's equilibrium theory of resistance (*ibid.*, 1923, **22**, 259).

R. A. M.

Magneton Numbers of Iron in Some Complex Salts. L. A. WELO (*Nature*, 1925, **116**, 359—360).—Preliminary data indicate that the magneton numbers for ferrous iron can have the values 0 and 10 as well as 26, 26·5, 27, and 27·5 (cf. Jackson, this vol., ii, 732, and following abstract), and that the values for ferric iron are 0 and 10 as well as 29. The magnetic moment of iron is thus extremely variable, and is not uniquely defined by a statement of its valency. The iron in iron carbonyl is diamagnetic. Thus the electron system of the iron atom may have at least seven main configurations.

A. A. E.

[**Magneton Numbers of Iron in Some Complex Salts.**] L. C. JACKSON (*Nature*, 1925, **116**, 360; cf. preceding abstract).—Paramagnetic substances do not obey Curie's law, $KT = C$, but the more general law $K(T+\Delta)=C$; hence Welo's magneton numbers need correction. Further, Welo's method of calculating the Bohr magneton numbers is not permissible. A. A. E.

Magnetisation Numbers of the Rare Earth Elements. S. MEYER (*Physikal. Z.*, 1925, **26**, 478—479).—The magnetisation numbers previously reported (this vol., ii, 173) in some cases require correction, owing to the discovery of impurities in the specimens examined. The corrected values of $k\times10^6$ are about 9·3 for ytterbium and about 4·2 for europium, instead of 8·8 and 5·6, respectively. F. G. T.

Simple Characteristic Relationships among the Ferromagnetics. J. R. ASHWORTH (*Nature*, 1925, **116**, 397).—The ratio of the critical temperature (θ°Abs.) to the maximum intensity of magnetisation (I_0) for iron, cobalt, nickel, and magnetite is, respectively, 0·58, 0·95, 1·19, and 1·83, or $2\times\frac{8}{27}$, $3\times\frac{8}{27}$, $4\times\frac{8}{27}$, and $6\times\frac{8}{27}$. Heusler's alloy fits this scale, the ratio θ/I_0 being 1·50 or $5\times\frac{8}{27}$. The numbers 2 to 6 are exactly integral within the accuracy with which θ and I_0 are known. The ratio of I_0 for iron to I_0 for nickel, and that of the values for cobalt and magnetite, are both 3·3, the respective ratios of the critical temperatures being 1·60 and 1·67. A. A. E.

Theory of Ferromagnetism. L. W. MCKEEHAN (*Physical Rev.*, 1925, [ii], **26**, 274—279; cf. ii, 945).—In ferromagnetic materials magnetisation involves (*a*) intra-atomic quantised changes and (*b*) intra-atomic stresses and strains. The interdependence of (*a*) and (*b*) is described as atomic magnetostriction. Hysteresis loss and magnetic hardness are then due to the energy required to produce successively the local deformations associated with changes in the magnetisation of single atoms or small groups of atoms. The high initial permeability and low hysteresis loss in "permalloy" result from locally compensatory atomic magnetostrictions of the nickel and iron atoms in small groups. Differing atomic magnetostrictions account for the differences in the magnetic behaviours of iron, nickel, and cobalt. Mechanical properties account for other differences by altering the energy expended when atomic magnetostriction occurs. R. A. M.

Artificial and Natural Ferromagnetic Ferric Oxide. R. B. SOSMAN and E. POSNJAK (*J. Washington Acad. Sci.*, 1925, **15**, 329—342).—Natural ferromagnetic ferric oxide has the same *X*-ray pattern and nearly the same magnetic susceptibility as magnetite and artificial ferric oxide. It gives a hysteresis curve differing from those of the other two oxides. Other minor differences are recorded. Ferric oxide loses its ferromagnetic property reversibly at a little above 500° and irreversibly at 650°, or lower if heated for some time. Lepidocrocite and goethite, Fe_2O_3,H_2O, yield ferromagnetic and paramagnetic ferric oxides, respectively, on dehydration. S. K. T.

Paramagnetism of "Odd Molecules." N. W. TAYLOR and G. N. LEWIS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 456—457).—Magneto-chemical theory predicts that substances with an odd number of electrons will exhibit paramagnetism. In support of this prediction, preliminary experiments with solutions of chlorine dioxide in carbon tetrachloride, α-naphthyldiphenylmethyl in benzene, sodium in liquid ammonia, and thallium in mercury indicate the existence of paramagnetic substances in solution. J. S. C.

Paramagnetic Salts. (MME.) E. COTTON-FEYTIS (*Ann. Chim.*, 1925, [x], **4**, 9—78).—A more detailed, collected account of previously published work (cf. A., 1911, ii, 367, 1058; 1913, ii, 381). S. K. T.

Optical Properties of Mixed Crystals. M. W. PORTER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 78—98).—The optical properties of mixed crystals of the pairs ammonium magnesium sulphate–ammonium magnesium chromate, and ammonium magnesium chromate–rubidium magnesium chromate have been examined. No proportionality was found between the refractive indices and the composition of the mixed crystals of the former pair, possibly owing to inhomogeneity of the crystals. For mixed crystals of the latter pair, the variation of the principal refractive index for vibrations along the symmetry axis is directly proportional to the composition, expressed as volume or molecular percentage. The other two principal indices are also continuous functions of the composition, but the variation is not linear, the curve for the β-axis being concave, and that for the γ-axis convex, to the composition axis. F. G. T.

Effect of Tension upon Magnetisation and Magnetic Hysteresis in "Permalloy." O. E. BUCKLEY and L. W. MCKEEHAN (*Physical Rev.*, 1925, [ii], **26**, 261—273).—The effect of tension on magnetisation and hysteresis was determined in wires of five nickel–iron alloys (permalloys) containing (*a*), 45, (*b*), 65, (*c*), 78·5, (*d*), 81, and (*e*), 84% of nickel. Alloy (*d*) is nearly indifferent to tension; (*a*), (*b*), and (*c*) are more easily magnetised and have less hysteresis under tension; the reverse is true for (*e*). In (*c*), an abnormally low saturation is observed and the low hysteresis is regarded as due to slight inhomogeneity. The crystals are shown by the *X*-ray method to exhibit random orientation. Alloy (*e*) contracts like nickel; (*a*), (*b*), and (*c*) expand like iron. Thus the magnetostriction change of sign is confirmed (Honda and Kido, *Sci. Rep. Tôhoku Imp. Univ.*; 1920, **9**, 221). The demagnetisation factor for a wire of length 600 times the diameter varies from a maximum of $1{\cdot}6\times10^{-4}$ to a low value (cf. Benedicks, *Ann. Physik*, 1901, [iv], **6**, 726). R. A. M.

Orientation of Crystals in Metal Test-pieces Subjected to Small Strains Followed by Heat Treatment. C. F. ELAM (*Phil. Mag.*, 1925, [vi], **50**, 517—520).—Examination of the orientations of the crystal axes of sixty-four crystals of aluminium, iron, and an aluminium–zinc alloy containing 18% of zinc, produced by a

process of straining followed by heat treatment, show that the variety of orientation is great. For aluminium, most of the crystals favour the (110), but not the (100) axis, and several of the iron and alloy crystals are oriented in the latter direction. Possibly the rate of growth is more rapid in some directions than in others, so that the majority of the largest crystals produced may favour one orientation. There appears, however, to be no relation between crystals in the same test-piece, and the direction of straining has little influence on the orientation of the crystals. A. E. M.

Orientation of Crystals Produced by Heating Strained Iron. C. F. ELAM (*J. Iron and Steel Inst.*, Sept. 1925, advance copy, 2 pp.).—The crystal axes relative to the direction of straining have been determined by *X*-ray analyses and the results show that the orientation is very varied. Two out of ten crystals showed cubic etching pits, and in both of these the surface of the strip was parallel to a cubic (100) plane in the crystal. Crystals of other orientations only showed pitting on prolonged etching; it should therefore be possible to pick out those crystals in which a (100) plane lies in or near the plane of section. [Cf. *B.*, 1925, 806.] M. E. N.

Tensile Properties of Single Iron Crystals and the Influence of Crystal Size upon the Tensile Properties of Iron. C. A. EDWARDS and L. B. PFEIL (*J. Iron and Steel Inst.*, Sept. 1925, advance copy, 32 pp.).—The values for the tensile strength and the limit of proportionality given by single iron crystals were generally very low. Smaller single crystals gave more variable results for tensile strength than larger ones. Elongations were very variable, generally increasing with the tensile strength. Some of the types of fracture encountered in the work are described. Tensile tests made on iron of varying crystal sizes revealed a discontinuity in properties with change in crystal size. [Cf. *B.*, 1925, 806.] M. E. N.

Electrical Conductivity of Some Dilute Amalgams. E. J. WILLIAMS (*Phil. Mag.*, 1925, [vi], **50**, 589—599).—Values obtained for the resistivity of mercury over the temperature range 0—300° are represented by the formula

$$\rho_t=\rho_0(1+0{\cdot}8879\times10^{-3}t+0{\cdot}975\times10^{-6}t^2+0{\cdot}20\times10^{-9}t^3),$$

which gives a value at 100° in accordance with that of Jaeger and Steinwehr (*Ann. Physik*, 1914, [iv], **43**, 1165). For cadmium amalgams containing less than 2% of cadmium, the conductivity is a quadratic function of the concentration. For indium amalgams it is approximately a linear function of the concentration. At 14°, the rates of variation of the relative increase of conductivity with concentration at infinite dilution are 7·2, 50·7, and 7·8 for indium, magnesium, and cadmium amalgams, respectively. The effects of these metals atom for atom on the conductivity of pure mercury are sensibly the same, a result in agreement with that of Skaupy. The change of relative conductivity with the temperature is small. A. E. M.

Change of Resistance of Platinum and Iron Wires in a High Vacuum Due to Absorbed Gas. H. KLEINE (*Z. Physik*, 1925, **33**, 391—407).—In the preliminary experiments with iron, the resistance decreased as the pressure decreased and increased again on admitting air. In the main experiment with platinum, it was necessary to heat the platinum in a high vacuum and get rid of gas from the walls of the vessel. When the platinum was kept glowing for 20 hrs., the fall in resistance amounted to 12%.

E. B. L.

Influence of the Gas Content on the Photo-electric Behaviour and Electrical Conductivity of Platinum. K. HERRMANN (*Ann. Physik*, 1925, [iv], **77**, 503—536).—Methods are described for the measurement of the photo-electric effect and electrical conductivity of platinum foil under conditions such that the occluded gas could be removed by repeated electrical heatings of 10 sec. duration at 50 sec. intervals, or replaced by any desired gas. As the gas content is reduced by heating in a vacuum, the photo-electric effect diminishes. For effective outgassing the temperature of the foil must be near the m. p. After 1500 such heatings, the photo-electric effect was reduced to about one-seventh, and, by subsequent exposure for 3½ days to a pressure less than 10^{-6} mm., to about one-twentieth its original value. At the same time, the resistance of the foil increased. Both these results are in agreement with the view that these properties are due to the free electron content of the foil, the number of such electrons decreasing with diminishing gas-content. The admission of oxygen to the outgassed foil, followed by repeated heatings at 1700°, and further evacuation, resulted in an additional fall of the photo-electric effect to a constant value.

Hydrogen was then admitted at 30 mm. pressure, and the foil reheated 800 times at 1700°, a sharp rise of photo-electric effect occurring. The oxygen treatment caused a rise in the electrical resistance. This was attributed to a dual cause, the formation of pores through the heat treatment, which facilitated the escape of occluded gas, and the oxidation of occluded hydrogen by the oxygen, followed by the removal of the less easily occluded water vapour. Microscopical examination of the foil after heating supported the above suggestion. The rise of photo-electric effect on the admission of hydrogen was accompanied by a marked fall in resistance, both effects being attributable to the increase of free electrons in the foil as a result of occlusion of hydrogen.

The experiments of Velo were repeated, and it was shown that complete outgassing of the foil could not have been attained by his method, and that his interpretation of his results is thus invalid. The photo-electric effect measured by Velo is not a purely metallic effect, but is due mainly to the presence of dissolved gas, the removal of which reduces the photo-electric current.

The minimum in the photo-electric sensitiveness observed between 300° and 400° is now shown to be due to mercury vapour adsorbed on the foil.

F. G. T.

Electrical Resistance of Thin Films of Organic Liquids on Paper. S. S. BHATNAGAR, M. PRASAD, N. G. MITRA, and D. L. SHRIVASTAVA (*Z. physikal. Chem.*, 1925, **117**, 88—96; cf. Reinold and Rücker, *Phil. Trans.*, 1893, **A**, **184**, 505).—Measurements were made of the resistances of thin films and of the specific resistances of thick films of methyl acetate, propyl, *iso*propyl, butyl, and *iso*butyl alcohols, and of mixtures of acetone with acetic and propionic acids, respectively. The resistances of thin films of other substances investigated were too high to be measured conveniently. The resistances of thin films are roughly inversely proportional to their thicknesses. The observed resistances of thin films were greater than those calculated from the data for thick films.

L. F. G.

Physical Properties of Aniline and its Aqueous Solutions. M. P. APPLEBEY and P. G. DAVIES (*J. Chem. Soc.*, 1925, **127**, 1836—1840).—Pure aniline has f. p. −5·98°, b. p. 184° (approx.), d_{20}^{20} 1·02315, n_D^{20} 1·58685. These values are compared with those of Timmermans (A., 1910, i, 533), Knowles (A., 1920, i, 834), Schwers (*J. Chim. physique*, 1911, **9**, 15), and Tyrer (T., 1912, **101**, 84). The lower values obtained by other workers for the f. p. are ascribed to the presence of traces of moisture. Freezing-point curves are given for aniline–water solutions (eutectic at 2·575% water), and evidence is given for the association of water in aniline solution and of aniline in aqueous solution. Water has little effect on the density, that of a saturated solution of water in aniline at 20° being 1·02393. Measurements of the refractive indices of aqueous solutions of aniline show that this property is a linear function of the percentage composition. The viscosity of aniline decreases with time, that of a freshly distilled sample being 1% higher than that of a week-old sample. L. L. B.

Pseudo-symmetry of Racemic Potassium Chlorosulphoacetate. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 423—425).—Detailed crystallographic data for racemic potassium chlorosulphoacetate, $CHCl(SO_3K)CO_2K$, are given. The symmetry is apparently rhombic-bipyramidal with a close approximation to tetragonal, the parameters being 0·9973 : 1 : 2·7650, but examination by polarised light shows that it is really a twin produced by almost perpendicular crossing of monoclinic lamellæ, suggesting that the salt is not a true racemate, but a pseudo-racemic inter-growth of equal proportions of the *d* and *l* antipodes.

J. W. B.

Approximate Calculation of Atomic Frequencies of the Inert Gases. J. NARBUTT (*Physikal. Z.*, 1925, **26**, 470—471).—Theoretical. In calculating the ratio of the atomic frequencies of an element in the solid and liquid states more terms must be considered than are included in Ratnowsky's equation (*Verh. Phys. Ges.*, 1914, **16**, 1033) when, as in the case of the inert gases, the absolute m. p. of the element is not very considerably

greater than the product $4{\cdot}77\times10^{-11}\nu$. The above ratio, for monatomic elements, is usually not constant, and shows marked variations even in adjacent groups of the periodic table. The values of the ratio are about $\frac{4}{3}$ for the alkali metals, and about $\frac{7}{4}$ for the inert gases. F. G. T.

Buffer Method in High-temperature Calorimetry. W. A. Roth (*Z. Elektrochem.*, 1925, **31**, 456).—In determining the specific heats of solids at high temperatures, the calorimeter is charged with a stable salt or mixture of salts melting at a suitable temperature, which is partly melted when the test-piece is dropped in. The temperature of the calorimeter cannot rise above the m. p. of the salt. Hence liquids such as paraffin can be used in the calorimeter; also the allowance for heat-exchange with the atmosphere can be calculated more accurately. W. A. C.

Atomic Heat Capacities of Iron and Nickel at Low Temperatures. W. H. Rodebush and J. C. Michalek (*J. Amer. Chem. Soc.*, 1925, **47**, 2117—2121).—The specific heats of iron and nickel at liquid-air temperatures were determined with the apparatus previously described (A., 1923, ii, 532). The results for nickel differ only slightly from those for iron; the latter agree almost exactly with the figures of Griffiths and Griffiths (A., 1913, ii, 753), but not with those of Günther (*Ann. Physik*, 1917, [iv], **51**, 828). The calculated entropies at 25° are 6·87 units for iron and 7·24 for nickel. At higher temperatures, the atomic heat curves deviate from the theoretical Debye curve (A., 1918, ii, 149; 1924, ii, 666), possibly due to crystal structure. S. K. T.

Thermal Data on Organic Compounds. II. Heat Capacities of Five Organic Compounds. Entropies and Free Energies of some Homologous Series of Aliphatic Compounds. G. S. Parks and K. K. Kelley (*J. Amer. Chem. Soc.*, 1925, **47**, 2089—2097).—The specific heats over the approximate temperature range 70° to 290° Abs., m. p., and latent heats of fusion per gram (λ) of the following compounds have been determined by the method previously described (this vol., ii, 491): *iso*propyl alcohol (λ=21·08), acetone (λ=23·42), ethylene glycol (λ=44·76), acetic acid (λ=46·68), and palmitic acid. The entropies and free energies are calculated and it is suggested that, in organic compounds, these quantities are related to the constitution. In an homologous series of liquids there is an average entropy increase of 9 ± 1 units for each additional CH_2 group, though in the fatty acid series the free energies remain approximately constant. In each case formic acid is an exception. In the series ethylene glycol, glycerol, etc., each additional CH·OH group causes an entropy increase of 7 units for the solid state. In the change: $\cdot CH_2\cdot OH_{(liq.)} \longrightarrow \cdot CO_2H_{(solid)}$ there is an entropy decrease of 6·4 units. Substitution of H by OH in a liquid involves a free energy decrease of about 35,500 cal. The free energy of *n*-propyl alcohol is predicted to be −44,200 cal. S. K. T.

Metastability of the Elements and Chemical Compounds as a Consequence of Enantiotropy or Monotropy. E. COHEN and A. L. T. MOESVELD (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 347—354; cf. A., 1924, ii, 234, 382, 383, 449, 450, 521, 603).—A criticism of the determinations of the specific heats of white and grey tin by Wigand (A., 1914, ii, 99), Brönsted (A., 1915, ii, 221), and Lange (this vol., ii, 96). It is pointed out that in no case was the physical purity determined, and that probably the materials used were mixtures of two modifications. S. I. L.

Thermal Expansion of Alkali Halides at Low Temperatures. II. F. A. HENGLEIN (*Z. physikal. Chem.*, 1925, **117**, 285—292; cf. this vol., ii, 375).—The densities of the fluorides of lithium, sodium, and potassium, and of the chlorides, bromides, and iodides of lithium and rubidium were determined at 0°, −79°, and −184°; from these measurements the coefficients of expansion between 0° and −79° and between −79° and −184° were calculated. As the lithium and rubidium salts were not quite pure, Baxter's data for the densities at 0° were used in conjunction with the above coefficients of expansion (which were not appreciably affected by the impurities) to calculate the true densities of these salts (except lithium fluoride) at −79° and −184°. L. F. G.

Thermal Expansion of Fused Salts. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **147**, 135—141).—The values of the product αT, where α is the coefficient of expansion in the neighbourhood of the m. p. and T the m. p. on the absolute scale, have been calculated for a number of fused salts from existing data. For an ideal substance this product has the value 0·077 and for "ordinary" substances the value 0·230. The calculated values of αT range from 0·103 (silver nitrate) to 0·934 (aluminium chloride).

J. S. C.

Critical Constants and Vapour Pressures of Hydrogen Cyanide. G. BREDIG and L. TEICHMANN (*Z. Elektrochem.*, 1925, **31**, 449—453).—Determinations of critical data by the usual methods on carefully purified materials give the following results: T_c=183·5°±0·1°, P_c=53·2±0·5 atm., d_c=0·195. Vapour pressures have been determined from −15° to 180°; they are given by the formula $\log p=-\lambda_0/4{\cdot}571T\pm1{\cdot}75\log T-\epsilon T/4{\cdot}571+C$ satisfactorily if λ_0=7790, ϵ=0·021675, and C=2·789. From the data at hand, the molecular latent heat of evaporation is calculated to be 6·76 kg.-cal. at 25·6° (b. p.) and 7·22 kg.-cal. at −13·4° (m. p.). The calculated gaseous specific heats agree with the experimental values of Partington and Carroll (this vol., ii, 373). The degree of association of the liquid varies according to the method of calculation from 2·0 to 2·4. W. A. C.

Simple Formula for Determining the Critical Temperature from the Coefficient of Expansion of the Liquid Phase, and the Cause of its Non-applicability for many Molten Salts. J. J. VAN LAAR (*Z. anorg. Chem.*, 1925, **146**, 263—280).—From the straight-line law connecting the mean density of a liquid and its

saturated vapour with the temperature, a formula for determining the critical temperature from the coefficient of expansion of the liquid phase is deduced. This fails with the alkali halides because the straight line law fails. This failure is shown to be related to the very considerable volume contraction in the liquid phase in comparison with the sum of the atomic volumes. Other methods of arriving at the critical temperature are suggested. These require the value of D_0, *i.e.*, the density of the liquid extrapolated to $T=0$. These values are calculated for the alkali halides from Jaeger's results, and their bearing on the abnormal behaviour of these substances is discussed. The theory is to be developed further in later papers. A. B. M.

Theory of State of Matter. I. Internal Pressure, Vapour Pressure, and Critical Data. F. Schuster (*Z. anorg. Chem.*, 1925, **146**, 299—304).—An expression for the internal pressure in terms of the critical pressure and temperature is deduced: $B=41.04T_cT.\log(p_c/p)/V(T_c-T)$. The internal pressures are calculated for a large number of compounds. In general, associated compounds possess higher internal pressures than non-associated, but there are exceptions to this rule. A distinction between the two classes of substances, however, is shown clearly in the temperature coefficient of the internal pressure. For non-associated liquids the temperature coefficient amounts to 2 to 3 atm.; for the others it is much higher, thus for ethyl alcohol it is 5·9 and for water 8 to 10. A. B. M.

Vapour Pressures of Organic Crystals by an Effusion Method. T. H. Swan and E. Mack (*J. Amer. Chem. Soc.*, 1925, **47**, 2112—2116).—The following vapour pressures of the crystalline solids over the range 10° to 30° were obtained by a modified Knudsen method (*Ann. Physik*, 1910, [iv], **32**, 809): naphthalene, $\log p$(mm.) $=-29{,}820/T-200{\cdot}682\log T+595{\cdot}642$; *p*-chloroaniline, $\log p=-22{,}332/T-138{\cdot}475\log T+416{\cdot}007$; *p*-chloronitrobenzene, $\log p=-4339{\cdot}2/T+12{\cdot}918$; *p*-bromonitrobenzene, $\log p=35{,}611/T+305{\cdot}935\log T-879{\cdot}254$. The calculated molar heats of evaporation at 20° are 19600, 21600, 19900, and 21200 (at 30°) cal., respectively. S. K. T.

Statistical Definition of Entropy of an Ideal Gas. E. Schrödinger (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 434—441).—Theoretical. Various definitions of entropy and Planck's recent work (this vol., ii, 495) are discussed. It is shown that by making Planck's assumption that the interchange of energy types is negligible, a form of gas statistics results which is similar to that evolved by Einstein (this vol., ii, 495). F. G. S.

Statistical Definition of Entropy. M. Planck (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 442—451; cf. preceding abstract).—Mathematical. An extension of previous work (this vol., ii, 495) on the energy content and the free energy of gases. F. G. S.

Entropy of Supercooled Liquids at the Absolute Zero. L. PAULING and R. C. TOLMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2148—2156).—Theoretical. It is shown that the entropy of a glass exceeds that of the corresponding crystal by a term $R \log a$, where a is a small number, mathematically defined, which increases with the complexity of the molecule. Different crystalline forms of a substance have the same entropy at the absolute zero, irrespective of the number of atoms in the crystal unit (cf. Eastman, A., 1924, ii, 143). S. K. T.

Capillary and Photo-electric Properties of Mercury. J. G. POPESCO (*Ann. Physique*, 1925, [x], **3**, 402—464).—The surface tension of mercury has been found to be 436·3 dynes/cm. when the drop of mercury is formed and kept in a vacuum. Exposure of the drop formed in a vacuum to various common gases leads to a diminution of the surface tension. When the surface is formed in a gas, the surface tension is greater than when the surface is formed in a vacuum, but decreases within twenty-four hours to the same lower value. These effects have been investigated with different gases and at different temperatures and pressures. They are ascribed partly to adsorption and partly to a change in the orientation of the surface molecules of the mercury (cf. Langmuir, A., 1917, ii, 525; Frenkel, *ibid.*, 191). The initial velocity of photo-electrons from mercury is similarly modified when the drop formed in a vacuum is exposed to a gas. There is a close parallelism between surface tension effects and photo-electric phenomena. A. S. R.

Scattering of Light by Liquid Boundaries and its Relation to Surface Tension. II. C. V. RAMAN and L. A. RAMDAS (*Proc. Roy. Soc.*, 1925, **A**, **109**, 150—157).—Strong evidence of the molecular origin of the surface scattering of incident light at a liquid boundary and of its relation to the surface tension of the liquid has been obtained by a comparative study of some 64 organic liquids. Surface scattering is observed most conveniently with liquids such as the lighter paraffins, ether, and the alcohols, which show a small internal scattering. In liquids of approximately equal internal scattering powers, the surface opalescence varies inversely with the surface tension. Transparent liquids show an effect 30—50 times more intense than that of mercury. The intensity and state of polarisation of the scattered light depend on the angle of incidence of the primary beam and on the direction of observation. When the light is incident from above, the surface opalescence is seen most conspicuously from below. The scattered light has a maximum intensity and a sudden complete polarisation, with the electric vector parallel to the liquid surface, when viewed from below from a direction inclined to the vertical at the critical angle of the liquid. When the light is incident from above, the light scattered upwards exhibits a polarisation, partial for small angles of incidence, but complete, for practically all angles of observation, when the incidence is at the polarising angle. F. G. T.

Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. Triazine and Benzene Derivatives. P. PASCAL (*Bull. Soc. chim.*, 1925, [iv], **37**, 836—840).—Binary mixtures of triphenylbenzene, triphenyltriazine, methyl 1 : 3-diphenyl-5-methyltriazine, ethyl 1 : 3 : 5-benzenetricarboxylate, and ethyl 1 : 3 : 5-triazinetricarboxylate have been studied. The m. p. curves are said to indicate that the interatomic bonds in the benzene and triazine nuclei are identical. Complete isomorphism is still found to exist when the nature of the substituted radical is slightly altered (*e.g.*, diphenylmethyltriazine and triphenylbenzene); but if the difference between the substituted radicals becomes too great, isomorphism gives place to isodimorphism, as with the mixture triphenyltriazine and ethyl triazinetricarboxylate. L. L. B.

Calculation of Points in the Ethyl Alcohol–Water Distillation Curve. E. ÖMAN and A. GUNNELIUS (*Tekn. Tidsk.*, 1925, **55**, 33; *Ind. Eng. Chem.*, 1925, **17**, 964).—If the composition of a water–alcohol mixture is known, the composition of any vapour obtained by its distillation may be calculated as follows. The b. p. of the mixture is obtained by reference to a table (given in the original), and the partial pressure of water vapour above the mixture at the b. p. is calculated from the known molar percentage of water in the liquid and the vapour pressure of water at this temperature. From this, the partial pressure of the alcohol is found by difference and the product of the partial pressure and molecular weight of the vapour of each substance gives the relative proportions of the two in the vapour. The molecular weight of the vapour above an aqueous solution containing 10% of alcohol is 43·15, and above one containing 70% of alcohol 26·05, the variation for each 1% of alcohol being 0·285. A. R. P.

Critical Miscibility and Elevation of B. P. C. DRUCKER and H. WEISSBACH (*Z. physikal. Chem.*, 1925, **117**, 209—241; cf. Timmermans, A., 1907, ii, 229; Drucker and Wagner, A., 1923, ii, 612).—The change in the b. p. of mixtures of carbon disulphide and methyl alcohol on the addition of sodium iodide, carbamide, succinic acid, water, diphenylamine, naphthalene, azobenzene, and acetanilide has been measured. The initial molecular composition of the solvent varied from 36·8 (critical composition) to about 100% methyl alcohol in most cases. The results obtained are not explicable by Nernst's theory (*Z. physikal. Chem.*, 1893, **11**, 1), the deviations from this being especially great in the case of mixtures with high alcohol concentrations. To elucidate this point the following determinations were made. The heats of mixture and the specific heats of a wide range of mixtures of carbon disulphide and methyl alcohol were measured at 20° and 36°. The data of Büchner and Prins for the total vapour pressure of such mixtures were supplemented by additional measurements. The partial vapour pressures of the components were calculated from the total vapour pressures with the aid of data for the composition of the vapour phases, for which a method of determination is described. It is shown that the

inapplicability of Nernst's theory is not due to his neglect of the comparatively small heats of mixture, but to the fact that the composition of the vapour is not independent of the nature and concentration of the solute, as required by the theory. The "salting-out" phenomena which result are quantitatively interpreted by the use of a new equation, derived theoretically. The shifting of the temperatures of critical miscibility is shown to be related to the salting-out effect. L. F. G.

Colloidal Separations in Alloys. J. H. ANDREW and R. HAY (*J. Inst. Metals*, Sept. 1925, advance copy, 3 pp.).—Passage of an alternating current through β-brass at a temperature just below the transformation point causes the gradual appearance of an eutectoidal structure, presumably owing to the neutralisation of the charge on the colloidal particles present after normal cooling. The ageing of "duralumin" after quenching is somewhat accelerated by an alternating current, suggesting that the phase the separation of which is suppressed during cooling is present in a colloidal form. [Cf. *B.*, 1925, 809.] A. R. P.

Tensile Tests of an Aluminium–Zinc Alloy. C. F. ELAM (*Proc. Roy. Soc.*, 1925, **A**, **109**, 143—149).—Tensile tests have been made on large crystals of an alloy containing 18·6% Zn, representing a solid solution near the limit of solubility of zinc in aluminium. *X*-Ray examination indicated a structure of cubic symmetry, similar to pure aluminium, but with a larger lattice, 4·18 Å.[3] The appearance of slip bands on the surface, and a study of the movement of the axis of the test piece relative to the crystal axes indicate the probability of a slip occurring normally on an octahedral (111) plane in the (110) direction as in aluminium. There was a variation of from 16 to 21 tons/in.[2] in the breaking loads for different crystals, but all values for single crystals were higher than for a polycrystalline test-piece. The elongation during test was 10—15%. Compared with aluminium, this alloy has a very much greater hardness, and the amount of slip that can occur before fracture is much reduced. The orientation of the crystal relative to the axis of the test-piece affects the breaking stress and type of fracture. Fracture occurs on planes at approximately 45° to the axis, on the plane of maximum shear. In some cases, however, fracture occurs along the slip plane. F. G. T.

Effect of Composition on the Viscosity of Glass. III. Some Four-component Glasses. S. ENGLISH (*J. Soc. Glass Tech.*, 1925, **11**, 83—98).—In continuation of viscosity determinations between 750° and 1400° with a series of glasses, the successive replacement of lime in the parent glass $1{\cdot}2Na_2O,0{\cdot}8CaO,6SiO_2$ by 0·2, 0·3, 0·4, 0·5, and 0·6 mol. of magnesia, respectively, was found to render the rate of increase of viscosity with falling temperature more uniform, all the glasses having a viscosity lower than that of the lime glass at the upper and lower temperature limits, but approximately the same value between 1100° and 1200°. A series in which

part of the lime of the glass $1{\cdot}1Na_2O,0{\cdot}9CaO,6SiO_2$ was replaced equimolecularly by 0·1, 0·2, and 0·3 mol. of alumina gave glasses which all set more slowly than the parent glass. [Cf. *B.*, 1925, 715.] A. C.

Solubility of Carbamide in Water. L. A. Pinck and M. A. Kelly (*J. Amer. Chem. Soc.*, 1925, **47**, 2170—2173).—The solubility of carbamide in water is redetermined over the range 0° to 70°. The results agree more or less with those of Speyers (A., 1902, ii, 388) up to 10°, but get consistently higher as the temperature increases. S. K. T.

Solubility of Proteins and Proteoses in Aldehydes and Other Organic Solvents. E. A. Cooper and S. D. Nicholas (*Biochem. J.*, 1925, **19**, 533—537).—Benzaldehyde dissolves hydrolytic products of proteins, but not the proteins themselves. Proteoses are only soluble in aldehydes of the aromatic type, but not in the aliphatic and heterocyclic aldehydes. Acetophenone, but not acetone or benzophenone, dissolves proteoses. Previous treatment of proteoses with formaldehyde and nitrous acid destroys their solubility in benzaldehyde. Although proteoses are insoluble in chloral, they are soluble in fused chloral hydrate and butylchloral hydrate. They are insoluble in the alkoxides. Gelatin, albumin, gliadin, and lecithin are also soluble in chloral hydrate, from which they can be precipitated by paraldehyde, but not by alcohol. Lecithin is precipitated from an ethereal solution by anisaldehyde, acetophenone, acetaldehyde, paraldehyde, phenylacetaldehyde, and cinnamaldehyde, but not by benzaldehyde, *m*-tolualdehyde, salicaldehyde, and *n*-heptaldehyde. Acetaldehyde reacts much less readily than formaldehyde with glycine and alanine, whilst acetone has no chemical action on them. Below and above a certain critical range of acetone concentration there is no evidence of any absorption of acetone by the protein. From experiments on the solubility of gelatin and egg-albumin in molten phenols and cresols, the following facts are deduced: The solvent action of the phenols diminishes as the homologous series is progressively ascended. The introduction of a chlorine atom into phenol diminishes the solvent power, but to a less degree than a methyl group. The solvent action is diminished by introduction of the $\cdot CO_2Me$ group and inhibited by that of $\cdot CO_2C_5H_{11}$, CO_2Ph, nitro, and methoxy groups, and by hydrogenation of the benzene nucleus. α-Naphthol and benzyl alcohol have no solvent action on proteoses and gelatin. With amines and their derivatives the following results were obtained. Aniline, *o*-toluidine, *m*-xylidine, methylaniline, chloroaniline, anisidine, and phenylhydrazine dissolve proteoses on warming, but not at the ordinary temperature. Dimethylaniline and ethylaniline, however, dissolve proteoses at the ordinary temperature, but not on warming. Proteoses are slightly soluble in formanilide, but insoluble in benzylamine, dichloroaniline, phenylethylamine, diphenylamine, α-naphthylamine, azobenzene, urethane, pyridine, and camphylamine. S. S. Z.

Absorption of Carbon Dioxide by Salt Solutions under Pressure. W. IPATIEV and A. ANDRJUSCHTSCHENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 851—862; from *Chem. Zentr.*, 1925, i, 2525—2526).—Carbon dioxide is more soluble in a solution of nickel acetate than in water, the difference decreasing with the pressure (5 to 26 atmospheres). No precipitation of nickel carbonate occurs. G. W. R.

Salts of certain Aromatic Carboxylic Acids and their Solubility. F. EPHRAIM and A. PFISTER.—(See i, 1148.)

Distribution of Surface-active Substances between Water and Organic Solvents. R. G. SCHULZ (*Koll.-Chem. Beihefte*, 1925, **21**, 37—54).—In the distribution of a solute at a liquid–liquid boundary the relationships between the surface activity and distribution are similar to those at a liquid–solid boundary. The distribution is said to be determined by the relative surface activities of the solute in the two solvents. E. M. C.

Beryllium Compounds as Adsorption Media. J. KLEEBERG (*Kolloid-Z.*, 1925, **37**, 17—18).—Beryllium hydroxide adsorbs Congo-red and pancreas amylase more strongly and yeast invertase less strongly than does aluminium hydroxide. Dextrose, tributyrin, and acetic acid are not adsorbed, but eosin and methylene-blue are adsorbed slightly. The adsorption is greatly increased when the substance to be adsorbed is added before the beryllium hydroxide is precipitated, and the sedimentation of the precipitate is accelerated. In 14 days, a beryllium hydroxide precipitate completely loses its adsorptive power. E. M. C.

Influence of Salt Content on the Adsorptive Power of an Active Charcoal and a Review of the Chief Properties of the More Important Technical Active Charcoals. H. HERBST (*Koll.-Chem. Beihefte*, 1925, **21**, 1—36).—The true static adsorptive power of active charcoal is reduced on impregnation with water, dry salts, or solutions of salts and alkalis to an extent which is approximately proportional to the amount added and becomes zero for additions of 50—60%. The adsorption velocity falls off more rapidly. A comparison is made of the density and adsorptive powers towards carbon dioxide, sulphur dioxide, and succinic acid solutions for a number of active charcoals of different origins. [Cf. *B.*, 1925, 697.] E. M. C.

Absorptive Power of Cellulose Nitrate for Gases. D. COSTA (*Gazzetta*, 1925, **55**, 540—548; cf. A., 1920, i, 16; 1924, i, 714).—Dry cellulose nitrate containing 12·95% of nitrogen corresponding with the formula $C_{24}H_{48}O_8(OH)_2(O{\cdot}NO_2)_{10}$ was used in the experiments made at 18—24° at atm. pressure. The results indicate that each nitro group fixes 1 mol. of ammonia, forming a true ammonium salt. Denitration and dehydration of the cellulose nitrate complex follow, and each molecule of ammonium nitrate set free takes up 2 mols. of ammonia. After careful washing with boiling

water, the product contains no nitrogen. Both volumetric and gravimetric measurements point to the formation of the compound $C_{24}H_{20}O_{10}(NH_4NO_3)_{10},20NH_3$; titration of the absorption product shows that the free ammonia is not more than two-thirds of the total ammonia absorbed. In order to prove that the absorption of ammonia depends on the nitro groups present, similar experiments were made with a cotton collodion containing 11·31% of nitrogen, corresponding with the formula $C_{24}H_{32}O_{12}(O{\cdot}NO_2)_8$. In this case saturation with ammonia gives the compound

$$C_{24}H_{32}O_{12}(NH_4NO_3)_8,16NH_3.$$

When cellulose nitrate is saturated with hydrogen chloride, all the nitro groups are replaced and the product, soluble in water, reduces Fehling's solution and is optically active. The results obtained in the absorption of sulphur dioxide and carbon dioxide are tabulated; oxygen and hydrogen are not appreciably absorbed. The absorptive powers of cellulose and cellulose nitrate for different gases are compared. W. E. E.

Adsorption [of Alkali from Alcoholic Solutions by Cellulose]. II. S. Liepatov (*Kolloid-Z.*, 1925, **37**, 112—116).—Some of the experiments previously described (this vol., ii, 385) are repeated in 40% and 90% aqueous-alcoholic solutions. The velocity of adsorption by cellulose of sodium hydroxide in 40% alcohol follows the equation $kt=log_e a/(a-\gamma x)$, where γ is a constant. In the stronger solution, the velocity is greater and approximates to that for an aqueous solution. The character of the adsorption curve is unaltered by duration of time. The adsorption of sodium and barium hydroxides from alcoholic solutions is much greater than from pure water and increases with the alcohol content. Adsorption from such solutions is an irreversible chemical process, the presence of the alcohol hindering the hydrolysis. S. K. T.

Adsorption of Acids by Filter-paper. S. G. Mokruschin (*Kolloid-Z.*, 1925, **37**, 144—146).—A theoretical explanation of the constants K in Holmgren's equation (A., 1909, ii, 25), and z in Schmidt's equation (*Kolloid-Z.*, 1913, **13**, 146) is given in which a unimolecular layer of acid on the capillary walls of the filter-paper is assumed in agreement with Langmuir's adsorption theory. Since the constants are independent of the degree of dissociation of the acid, adsorption of the molecules is indicated, and this finds support in the work of Schulov and Lepin [*Ann. d. Lomonosoff. phys.-chem. Ges.* (Moscow), 1919, **1**, 56—65, 66, 67]. The theoretical conclusions are borne out by experiments with hydrochloric, nitric, sulphuric, oxalic, and tartaric acids in 1/4 to 1/1024 molar solutions. N. H. H.

Mechanism of the Adsorption of Sugar by Colloidal Solutions and Precipitates. M. Prasad, D. L. Shrivastava, and R. S. Gupta (*Kolloid-Z.*, 1925, **37**, 101—104).—The adsorption of certain sugars from solution by sulphide sols and precipitates is investigated (cf. A., 1924, i, 942). Except in the case of xylose and

arsenic trisulphide and of lævulose and antimony trisulphide, Freundlich's adsorption equation is not followed. The amount of sugar adsorbed always decreases with diminishing concentration of the adsorbent. Practically no adsorption occurs in presence of powdered substances, such as magnesium oxide, zinc oleate, etc.

S. K. T.

Adsorption. XI. Life Period of Organisms and its Dependence on the Concentration and Volume of the Toxic Medium and on the Concentration of the Organisms. P. N. Pavlov (*Kolloid-Z.*, 1925, **37**, 105—111).—The toxic effect of a medium on the life period, T, of an organism is expressed by the "life period depression" $(T_0-T)/T$, T_0 being the value of T in the natural medium, and not by $1/T$ (cf. Ostwald, A., 1910, ii, 592). Combining this with the adsorption formula, equations are derived connecting the life period with the concentration of the toxic substance, the volume of the medium, and the number of organisms in unit volume. According to the nature of the relations involved the toxic effect is said to be chemical or physical. Experiments carried out with *Gammarus* (at high salt concentrations) and *Artemia salina* in common salt solutions support the chemical explanation of toxicity. At lower salt concentrations (16—19%) the results with *Gammarus* support a physical explanation. Some of the equations deduced are numerically confirmed.

S. K. T.

Adsorption and Surface Energy at the Boundary of Different Phases. B. Ilin (*Physikal. Z.*, 1925, **14**, 497—501).—Szyszkowski's equation (A., 1908, ii, 1018) leads to the relation $Q=b\log_{10}(ac+1)$, in which Q is the heat of adsorption, C the concentration of the capillary-active substance, and a and b are constants. This has been tested by reference to the data of Titoff (A., 1910, ii, 1041) on nitrogen, carbon dioxide, and ammonia, and by Lamb and Coolidge (A., 1920, ii, 471) on carbon disulphide with excellent agreement between observed and calculated values of Q. The theoretical treatment is also supported by the results of Rehbinder (A., 1924, ii, 662) for solutions of valeric acid, butyric acid, and tetrapropylammonium chlorate. R. A. M.

Electrical Theory of Adsorption. B. Ilin (*Z. Physik*, 1925, **33**, 435—469).—On the assumption that adsorption forces are purely electrical a formula is developed connecting the heat of adsorption and adsorptive capacity with the dielectric constant and surface energy of the adsorbent. The electrical moment of the polarisation is found to be about 10^{-19}, and the thickness of the film about 10^{-8} cm. From the formula for the adsorptive capacity the value 2 is obtained for the gas constant, R. A relationship is established between the critical temperature of the adsorbed gas, the van der Waals attraction constant, and the adsorption constant. The effective surface of 1 g. of charcoal is found to be about 10^5 cm.^{2} In the case of charcoal and mica, for gases of about the

same heat of absorption, the amount of adsorption is much the same, from which it is concluded that adsorption is not a specific property. E. B. L.

Derivation of Adsorption Isotherms. A. GORBATSCHEV (*Z. physikal. Chem.*, 1925, **117**, 129—142).—It is assumed that lines of force originate from the surface of an adsorbent, adsorbed molecules being thereby attracted and held. The effective radius of attraction is less than the diameter of a molecule. On this assumption equations are derived which correspond with adsorption isotherms obtained by Langmuir, Freundlich, and co-workers, Reichinstein (A., 1924, ii, 22), Schmidt (A., 1911, ii, 969), Williams (A., 1919, ii, 496), Lockemann and Paucke (A., 1911, ii, 720), and with extended forms of Henry's law (cf. Williams, A., 1919, ii, 392; Abderhalden and Fodor, A., 1921, ii, 21; Fodor and Schönfeld, A., 1922, ii, 688). L. F. G.

Theories of Liesegang Ring Formation. N. R. DHAR and A. C. CHATTERJI (*Kolloid-Z.*, 1925, **37**, 89—97; cf. this vol., ii, 865).—Criticism of previous work is continued. The coagulation of silver chromate sol is brought about by potassium chromate within certain concentration limits; outside these limits a yellow sol is produced. This phenomenon, it is shown, offers a complete explanation of Liesegang ring formation. No rings are formed when the protective colloid has a very small or a very large peptising effect on a sparingly soluble substance, provided, in the latter case, that a peptised sol of the substance is not coagulated by either of the reactants from which it is formed. Rings are only formed when the peptising action is of medium strength. S. K. T.

Precipitates with Stratified Structures. I. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **37**, 78—88).—From a consideration of the dispersion curves for some precipitates with stratified structures it is shown that Liesegang rings result from the periodic variations in the concentrations of the dispersed and dispersing phases caused by the mixing of the appropriate precipitating agents; these are tracks indicating the places of contact of the vessel and the surface skin of the precipitate. The points of contact move downwards as evaporation proceeds. S. K. T.

Structure of Films of Water on Salt Solutions. I. Surface Tension and Adsorption for Aqueous Sodium Chloride Solutions. W. D. HARKINS and H. M. MCLAUGHLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 2083—2089).—The surface tensions of 0·1 to 5*N*-sodium chloride solutions have been measured by the drop method, and by an application of the Gibbs adsorption equation, modified by the introduction of the activity coefficient, the thickness of the water film on the solutions is shown to decrease from 4·00 to 2·30 Å. as the concentration rises. The thickness is of the order of a linear dimension of a water molecule, but some molecules of the type $(H_2O)_2$ may be involved. As the concentration increases

diffusion pressure forces the ions closer and closer to the surface and the surface tension rises. A small departure of the water molecule from perfect symmetry is sufficient to account for the observed variation in the thickness of the water film, but probably other factors are also effective. S. K. T.

Composition of Soap Films. M. E. LAING (*Proc. Roy. Soc.*, 1925, **A**, **109**, 28—34).—The nature of the material which accumulates in soap films has been investigated by determining the concentration changes in a sodium oleate solution as a result of foam formation. The concentration changes were followed by conductivity measurements, and by analysis of the condensed foams and of the residual soap solutions. In every case, the foam is more concentrated than the bulk of the solution. The analytical data show that an acid sodium soap, and not free oleic acid, collects in the interfacial film. From neutral or acid soap solutions, the material adsorbed has the composition 1 mol. sodium oleate + 0·61 mol. oleic acid. Excess of alkali in the solution converts this material into neutral sodium oleate. The absolute amount of substance adsorbed is least from neutral solution, and increases with addition of either oleic acid or alkali. These results are in accord with the suggestion of Bragg that the black spot in soap films is due to the actual contact of the two adsorbed layers, except that it consists of an acid sodium soap, instead of free fatty acid. The presence of this colloidal material is suggested as the cause of the stability of soap films. F. G. T.

Kinetic Theory of Surface Films. I. Surfaces of Solutions. R. K. SCHOFIELD and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, **A**, **109**, 57—77).—When Gibbs' equation, modified by the introduction of the activity in place of the mole fraction of the solute, is applied to the surface tension–concentration curves for aqueous solutions of capillary-active organic substances, evidence is obtained that the adsorbed film is unimolecular in the case of dilute solutions. The analogy between F, the lowering of surface tension, and a three-dimensional gas or osmotic pressure as postulated by Traube has been critically examined and it is shown that whilst existing theories account for the proportionality between F and the mole fraction of the solute for low values of F, the lack of proportionality for large values of F is unexplained. It is possible that the latter anomaly is due to the same causes which render the gas laws inapplicable to compressed gases. Weak solutions, for which F exceeds about 10 dynes/cm., and in which the surface phase is relatively highly condensed, conform to the equation $F(A-B)=xRT$, where A is the area occupied by a g.-mol. as surface excess, B the limiting area of a g.-mol. under high compression, and $1/x$ a measure of the lateral molecular cohesion of the film. This relation has been tested at three interfaces: for a number of the lower fatty acids at a water–air interface, for *n*-butyric acid at a water–benzene interface, and for tertiary butyl and amyl alcohols, sucrose, and pyridine at a water–mercury interface. The above equation, which fits existing data within the limits of experimental error, yields values for the limiting areas of the adsorbed molecules in close agreement with those

anticipated from measurements of molecular dimensions. At water–air and water–benzene interfaces the common value of B, 24—25 Å., found for normal fatty acids, supports Langmuir's orientation hypothesis. The values of x for a series of fatty acids show that at a water–air interface the lateral molecular cohesion increases with the length of the hydrocarbon chain. The *iso*-acids have a slightly larger value of x than the corresponding normal acids, indicating an apparently smaller cohesion between branched chains than between normal chains with the same number of carbon atoms. At a water–benzene interface the value of x for butyric acid is almost unity, indicating that there is little or no cohesion between such molecules at that interface. The similar value of x for sucrose shows that sucrose molecules do not cohere at a water–mercury interface. Strong support is found for the view that the molecules of the capillary-active substances examined are adsorbed from a weak solution in a unimolecular layer, and that the effect they produce on the surface tension is due to their thermal agitation alone. At a given temperature their activity depends solely on the surface concentration, the interfacial area occupied, and on the lateral cohesion. F. G. T.

Capillary Chemical Phenomena. R. Dubrisay (*Bull. Soc. chim.*, 1925, [iv], **37**, 996—1008).—An account of work previously abstracted (A., 1918, ii, 368; 1923, ii, 741; 1924, ii, 154, 731). S. K. T.

Effect of Capillary-active Substances on the Surface Tension of Salt Solutions. Its Relation to Ionic Hydration. W. Seith (*Z. physikal. Chem.*, 1925, **117**, 257—284).—Measurements were made by Stocker's method (A., 1920, ii, 593) to ascertain the effect of different capillary-active substances (methyl, ethyl, *iso*-propyl, *iso*butyl, and *iso*amyl alcohols, and aniline) on the surface tension of pure water and of aqueous solutions of salts (lithium, sodium, potassium, magnesium, and barium chlorides and magnesium sulphate) and carbamide. The lowering of surface tension increases with concentration of salt. When surface tension is plotted against concentration of capillary-active substance, the curves obtained for different concentrations of the same salt cut each other at a point. The concentrations of the capillary-active substances in the surface films are calculated. A method of calculating the hydration of the salt ions from the lowering of surface tension is described. The degrees of hydration thus obtained agree with those calculated from the effect of the salts on the solubilities of non-electrolytes in water (see Armstrong and others, A., 1907, ii, 848). L. F. G.

Surface Tension of Aqueous Phenol Solutions. II. Activity and Surface Tension. A. K. Goard and E. K. Rideal (*J. Chem. Soc.*, 1925, **127**, 1668—1676).—Measurements of the surface tensions of mixtures of water, sodium chloride, and phenol in various proportions have been made by the drop weight method (cf. this vol., ii, 510), and of the partition of phenol between paraffin

oil and water or aqueous sodium chloride solution. From the latter and freezing-point data the activities of phenol in water and aqueous sodium chloride solution have been deduced. Using the differential equation of Gibbs determining the surface adsorption of substances in solution and taking into account the activity of the phenol, the surface adsorption has been calculated. The maximum surface adsorption is found to be independent of the concentration of the sodium chloride and equal to $69{\cdot}2(\pm1)\times10^{-11}$ g.-mol./cm.^{2} Assuming that the surface layer consists of a unimolecular film of phenol molecules, the cross-sectional area and length of the phenol molecule are calculated to be 23·8 and 6·4 Å., respectively. These values are in good agreement with those determined by Adam (A., 1923, ii, 539). The fact that the dissolved sodium chloride exerts a marked effect on the surface tension through this unimolecular film indicates that the surface tension is affected by the presence of molecules below the surface layer, although the opposite has been assumed by Langmuir and some other workers. E. E. W.

Influence of Density and Geometrical Dimensions of a Molecular Stream on the Formation of Deposits. J. Estermann (*Z. Physik*, 1925, **33**, 320—324).—The relation between the critical temperature of condensation of metallic vapours and their concentration has been determined for different surfaces, and the heat of adsorption and the adsorption pressure calculated. The edge of the deposit has a lower temperature of condensation than the centre, owing to the density being lower at the edge. E. B. L.

Angles of Contact and Polarity of Solid Surfaces. N. K. Adam and G. Jessop (*J. Chem. Soc.*, 1925, **127**, 1863—1868).—The equation $W=T_{LV}(1+\cos\theta)$, in which W represents the adhesion of a liquid for a solid surface on which it rests at an angle θ, and $2T_{LV}$ the cohesion of the liquid, has been examined with reference to the polarity of solid surfaces. For solid long-chain aliphatic compounds in contact with water, θ should be low if many polar groups are at the free surface, whilst if the hydrocarbon ends of the chains are all turned outwards, θ should be approximately the same as for paraffin wax. Of the nine solids investigated, paraffin wax and octadecyl iodide (no groups with a strong affinity for water) give practically the same angle at a surface cut from the interior as at the natural surface. Acids and alcohols give varying results for surfaces cut from the interior, according as the cut surface runs parallel or perpendicular to the direction of the crystal flakes. Crystalline flakes (from alcohol or benzene) give a lower angle than the mass solidified after fusion. Alternative explanations for this are suggested. The chief difficulty in measuring the angle of contact (the "dragging" effect or "hysteresis") is attributed to friction of the liquid on the solid. L. L. B.

Action of Silica on Electrolytes. J. Mukherjee (*Nature*, 1925, **116**, 313—314).—Joseph's failure (cf. this vol., ii, 383) to confirm the author's results is ascribed to the use of silica heated at 180°; a suitable method for the preparation of the silica is described.

Three types of adsorption are distinguished: (*a*) primary, resulting from the chemical affinity of the atoms on the surface, (*b*) electrical, and (*c*) adsorption of solutions resulting from the capacity of the substance to adsorb water. A. A. E.

Electric Charge on Sparingly Soluble Substances. L. MICHAELIS and S. DOKAN (*Kolloid-Z.*, 1925, **37**, 67—72).—Two new classes of colloids are described: "obligatory" and "facultative." The former can exist in the medium only in the colloid state (*e.g.*, mastic in water), whilst the latter are sparingly soluble and exist suspended in their saturated solutions (*e.g.*, silver iodide). One of the ions is responsible for the colloid state in the former group, but neither is separately responsible in the latter. The influence of dissolved electrolytes on "facultative" colloids is investigated, especially in the case of barium sulphate. Univalent ions have no perceptible influence on the charge of the colloid, but bivalent ions, excepting such cations as form easily soluble sulphates, exhibit marked effects. Tervalent ions have a still stronger influence (cf. Umetsu, A., 1923, ii, 299). S. K. T.

Contraction, Refractivity, and Absorption of Light in Solutions of Lithium Salts. F. HÜTTIG and M. KELLER (*Z. Elektrochem.*, 1925, **31**, 390—403).—The densities and refractive indices of aqueous solutions of lithium chloride, bromide, and iodide have been measured from saturation down to 0·1*N*, and the coefficients of extinction between λ230 and λ410 down to *N*. The resulting curves show discontinuities at $n=6$ and near $n=30$ and $n=75$, when n is the number of mols. of water per mol. of salt, for all three salts. It is suggested, on the basis of Werner's co-ordination theory, that the lithium ion requires 6 mols. of water for complete envelopment, and that when there are fewer, the partly unprotected ion exerts an attraction on the surrounding halogen ions which causes a corresponding contraction. A second complete envelope will consist of 30 mols. of water, and a third of 76 mols. W. A. C.

Refractive Indices of Perchlorates in Aqueous Solution. A. MAZZUCCHELLI and A. VERCILLO (*Gazzetta*, 1925, **55**, 498—501).—The refractive powers of ammonium and sodium perchlorates and of perchloric acid calculated by Landolt's formula from observations on aqueous solutions are found to be almost independent of the concentration. For perchloric acid, however, the refractive power increases slightly with dilution. The compounds studied are found to obey the law of Le Blanc and Rohland (A., 1896, ii, 345). W. E. E.

Cause of the Colour Change in Cobalt Chloride Solutions. J. GRÓH (*Z. anorg. Chem.*, 1925, **146**, 305—314).—The molecular extinction coefficients for solutions of cobalt chloride in propyl alcohol, ethyl alcohol, methyl alcohol, and water have been measured and plotted against wave-length of light. The effect of addition of lithium chloride to some of the solutions has been observed. The results are in complete accordance with the assumption of an

equilibrium $CoCl_2+2Cl' \rightleftharpoons CoCl_4''$, the blue colour of the solutions being due to the complex ion $CoCl_4''$. A. B. M.

Variation in the Rotatory Power of Tartaric Acid as a Function of p_H. F. Vlès and E. Vellinger (*Bull. Soc. chim.*, 1925, [iv], **37**, 841—845).—The rotatory power of *d*-tartaric acid in *M*/2, *M*/4, and *M*/10 solution has been examined in its dependence on p_H. The curve $\alpha=f(p_H)$ shows a rapid rise of rotatory power between p_H 2 and p_H 5. From p_H 5 up to p_H 13, the rotatory power is practically independent of the acidity of the solution, but above p_H 13 it decreases. Below p_H 2 the value is almost constant. The experimental values agree with the assumption that the rotatory power is the sum of the effects due to the two anions and the undissociated acid molecule. The mechanism of the removal of a hydrogen ion from the tartaric acid molecule, and the consequent change in space arrangement, is briefly discussed. L. L. B.

Viscosity and Surface Tension during Esterification. (Mlle.) G. Cauquil (*Compt. rend.*, 1925, **181**, 114—116).—Measurements have been made of the viscosity and surface tension during esterification of equimolecular mixtures of acetic acid and the following alcohols: *cyclo*hexanol, *o*-methyl*cyclo*hexanol, *o*-ethyl*cyclo*hexanol, *m*-methyl*cyclo*hexanol, *p*-methyl*cyclo*hexanol, 1 : 3-dimethyl*cyclo*hexan-4-ol. Esterification was carried out at 95°, portions of the reaction mixture being cooled to 20° for purposes of measurement. The viscosity and surface tension may be represented by formulæ of the type $\eta_t=\eta_0+Bx$, where x is the percentage of acid esterified. The coefficient B is negative in the case of the viscosity, and positive in that of the surface tension measurements. F. G. T.

Dielectric Constants of Solutions of Electrolytes. H. Ulich (*Z. Elektrochem.*, 1925, **31**, 413—417).—The dielectric constants of solutions of amine halides and tetra-alkylammonium salts in organic solvents show in general, first, a decrease proportional to the concentration, then a minimum, and lastly a steady increase with concentration to values which in some cases exceed those of the pure solvents. The incidence of the minimum is found, applying Walden's rule, at $v=(134\cdot4/\epsilon_0)^3$, where v is the molecular dilution and ϵ_0 the dielectric constant of the solvent. W. A. C.

Osmotic Pressure by the Solubility Method in Concentrated Solutions. M. P. Applebey and P. G. Davies (*J. Chem. Soc.*, 1925, **127**, 1840—1846).—Solutions of sucrose of known concentration are shaken with aniline at 20°, and the solubility of water in the aniline layer determined. From the data of Berkeley and Hartley (A., 1907, ii, 234), the connexion between osmotic pressure and lowering of solubility is obtained. In dilute solutions, this may be calculated by the equation of Nernst, whilst in more concentrated solutions a new combination of the equations of Van Laar and of Berkeley and Burton (*Phil. Mag.*, 1909, **17**, 598) leads to a relation which is in good agreement with experiment up to concentrations of 420 g. per 1000 g. of solution. By finding the

percentage of water in the aniline phase in equilibrium with a solution of unknown osmotic pressure, and reading off from the present results the concentration of the sucrose solution in equilibrium with the same aniline solution, the osmotic pressure of the unknown solution can be equated with that of the sucrose solution.

W. H.-R.

Method for Investigating Diffusion in Gels. R. FRICKE (*Z. Elektrochem.*, 1925, **31**, 430—435).—A microtome is described by means of which gels of elongated shape may be cut transversely into slices down to $\frac{1}{2}$ mm. thickness. W. A. C.

Dialysis of Easily Decomposable Colloidal Systems. A. GUTBIER (*Z. anorg. Chem.*, 1925, **146**, 411—412).—Easily decomposed colloidal solutions are protected from the air during dialysis by covering them, as well as the outer liquid in the dialyser, with a layer of paraffin or other suitable pure oil. A. B. M.

Direct Method of Measuring the Osmotic Pressure of Hæmoglobin. G. S. ADAIR (*Proc. Roy. Soc.*, 1925, **A**, **108**, 627—637).—The difficulties in measuring the osmotic pressure of hæmoglobin, due to alteration of the state of aggregation in the colloidal system, and to chemical change, have been overcome by a method involving the use of an osmometer in which equilibrium is reached rapidly, and by making all measurements at 0°. The osmotic pressures of solutions of various hæmoglobins are tabulated.

L. F. G.

Physico-chemical Study of U.S.P. Agar. E. H. HARVEY (*Amer. J. Pharm.*, 1925, **97**, 447—456; cf. B., 1925, 296).—The heat of combustion of U.S.P. agar (d^{21} 0·7190) is 4870 cal./g. Boiling hydrolyses the agar, lowering the viscosity and destroying the ability to gel. Hot agar sols show no optical activity. Imbibition of water is comparatively rapid at first and becomes gradually slower. The heat of imbibition is 2·7 cal./g. of dry agar. Adsorption of acetic acid is relatively greater from dilute solutions than from more concentrated solutions. Quantitative experiments have been carried out on the rate of adsorption of water vapour, and on the rate of dehydration of agar gels. C. P. S.

Effect of Low Temperatures on Liquid Colloidal Systems. F. BOTTAZZI and G. BERGAMI (*Arch. Sci. biol.*, 1924, **6**, 74—93; from *Chem. Zentr.*, 1925, i, 2539).—At 0°, protein solutions rich in electrolytes are not coagulated, although removal of the electrolytes by dialysis produces a partial coagulation (turbidity). This coagulation is reversible. Differences exist, however, between different proteins. For example, even after removal of electrolytes, octopus blood and, probably, hæmoglobin remain clear at −4°. Neutral electrolytes stabilise dialysed protein in respect of coagulation at low temperatures. Denaturing scarcely takes place even at −25° or by freezing. Native blood-serum and plasma are very stable against the effect of low temperatures. The less stable colloids

are rendered coagulable by removals or additions which modify their reaction in the direction of their isoelectric points.

G. W. R.

Spontaneous Structure-formation in Sols. (New Type of Anisotropic Liquid Media). H. ZOCHER (*Z. anorg. Chem.*, 1925, **147**, 91—109; cf. A., 1922, ii, 102).—When hot aqueous solutions of benzopurpurin and chrysophenin are cooled, sols with an orderly, parallel arrangement of oblong colloid particles are obtained. A similar parallel orientation of particles is observed in old vanadium pentoxide and ferric hydroxide sols. The particles of vanadium pentoxide are rod-shaped with a tendency to form twin-particles, whilst those of ferric hydroxide are disc-shaped. J. S. C.

Photographic Gelatin. S. E. SHEPPARD (*Phot. J.*, 1925, **65**, 380—387).—The very high speed of photographic emulsions is primarily due to the presence of small amounts of foreign substances in the gelatin. The sensitising properties of certain gelatins are due to the presence of traces of organic thiocarbimides and thiocarbamides, viz. allylthiocarbimide and allylthiocarbamide. The sensitiser can be extracted from gelatin deliming liquors by precipitating alumina in the solution, drying the precipitate, and then extracting with alcohol, ether, or light petroleum; also from mustard seeds, and the seeds and hulls of beans, peas, and cereals, and from lucerne. The sensitiser is carried over with the cholesterol. Photographically active gelatins contain 1 part in a million to 1 part in 300,000 of the sensitiser, which is probably present as both thiocarbimide and thiocarbamide. Under fixed conditions the sensitising effect reaches a maximum for a definite amount of sensitiser, further addition resulting in a decrease of sensitivity and an increase in fog. The formation of "sensitivity centres" is due to conversion of the thiocarbimide into thiocarbamide in presence of ammonia, and the reaction of the thiocarbamide with the silver halides to form nuclei of silver sulphide, which is the material of the "sensitivity centres." Silver selenide and silver telluride behave in the same way. The results are in harmony with the author's "orientation" theory of photographic sensitivity. [Cf. *B.*, 1925, 785.] W. C.

Effect of Water on Dried and Pressed Silica Gel. I. S. S. BHATNAGAR, M. PRASAD, and D. D. OHRI (*Kolloid-Z.*, 1925, **37**, 97—101).—The decrepitation of pressed anhydrous silica gels on wetting with water, salt solutions (*e.g.*, sodium chloride and silicate), and organic liquids (*e.g.*, ether, benzene) is accompanied by practically no temperature change, indicating that the phenomenon cannot be due to chemical action or to solution. It must therefore be due to the pressures set up on the walls of the capillaries of the gel caused by adsorption of liquid. A blue opalescence accompanies the adsorption of water by the powdered gel. The effect is quite different from the Pouillet effect since the latter is accompanied by a temperature rise (cf. Bhatnagar and Mathur, *ibid.*, 1922, **33**, 368). S. K. T.

Temperature of Swelling of Starch Granules. W. ARZICHOVSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 349—368; from *Chem. Zentr.*, 1925, i, 2543).—The swelling of starch granules was studied microscopically, using a statistical method. Swelling begins at 55°; at 67·5° it is practically complete. The mean temperature of complete swelling of individual granules is $60{\cdot}97 \pm 0{\cdot}10°$. The distribution about this mean value only follows Gauss' law of error as a first approximation. The frequency curve is asymmetrical, but there is no indication of the occurrence of two kinds of granules.

G. W. R.

Liquefaction of Starch Paste. P. PETIT (*Compt. rend.*, 1925, **181**, 259—260).—Soluble starch is readily obtained by adding to a 2% starch paste (150 g.) 10 c.c. of a solution containing sodium chloride (7 mg.), potassium hydrogen phosphate (5 mg.), and lactic acid (2 mg.). The reaction may be carried out in presence of toluene or ether. The product does not reduce Fehling's solution and has a specific rotation of 195°. Very slight alterations in the amount of lactic acid may retard or stop the reaction. With slow reactions a flocculent deposit is formed, containing silica and alumina. This deposit is not obtained when the operation is conducted in pyrex glass, or in the absence of mechanical agitation. The deposition and clarification can be accelerated by the addition of traces of alkali or lactic acid, or of sodium silicate and lactic acid. R. B.

Action of Alkalis on Konyaku Colloid. S. DOKAN (*Kolloid-Z.*, 1925, **37**, 73—78).—Barium and calcium hydroxides depress the viscosities of Konyaku sols to a much greater extent than the hydroxides of sodium and potassium. The same applies to the action of the chlorides of these metals on slightly alkaline sols; the effect in the case of the alkaline-earth chlorides increases with time. Cataphoresis experiments indicate practically no charge on the colloid in acid and neutral solutions and only a weak negative charge in alkaline solution. These conflicting results are explained on the assumption that the calcium, for example, in the colloid, which cannot be obtained ash-free, reacts with the carbonate in the alkali to form calcium carbonate, which then forms a layer over the colloid particles. In acid solutions, this layer is not formed, so that, indirectly, the observed effects are attributable to hydroxide ions. Measurements of the adsorption of Konyaku by crystalline barium carbonate, prepared *in situ* and added externally, support this explanation. S. K. T.

Kinetics of the Sol–Gel Transformation of Concentrated Ferric Oxide Sols. H. FREUNDLICH and A. ROSENTHAL (*Kolloid-Z.*, 1925, **37**, 129—131).—By reducing the velocity of the sol–gel transformation of concentrated iron oxide sols (cf. Schalek and Szegvary, A., 1923, ii, 423) by the addition of glycine, alanine, and similar substances it has been possible to study the kinetics of the process and to show that it resembles that of coagulation. The glycine etc. do not act as protective colloids in the ordinary sense, but increase the charge on the particles. N. H. H.

Kinetics of the Swelling and Shrinking of Gels. II. S. LIEPATOV (*Kolloid-Z.*, 1925, **37**, 146—150).—The influence of various factors on the velocity of swelling of glue in water has been studied. The velocity is a function of the thickness of the gel; surface and weight play a secondary part. Van Bemmelen's view of the enormous mobility of water in colloids is supported. The swelling can be regarded as the first stage of solution, *i.e.*, peptisation. Temperature and electrolytes have a great influence on the swelling velocity. N. H. H.

Emulsifying Power of Sodium Stearate and Sodium Palmitate. N. A. YAJNIK and B. ILAHI (*Kolloid-Z.*, 1925, **37**, 139—144).—The emulsifying power of sodium stearate and sodium palmitate towards cotton-seed, poppy-seed, mustard, coconut, sesamé, and olive oils has been measured at 80°. The curves connecting oil concentration with the concentration of soap just required for emulsification are of the same type. With increasing oil concentration the soap concentration increases, at first rapidly and then more slowly, until an oil concentration of 20—40% (by volume), depending on the oil, is reached, when a more rapid increase suddenly occurs for which no explanation can be offered. This effect is most marked with cotton-seed and poppy-seed oils. In all cases, the concentration of sodium palmitate required for emulsification is less than that of sodium stearate, in agreement with the fact that soap solutions have a greater emulsifying power, the lower the surface tension. The results show that emulsifying power has an important influence in determining cleansing properties. N. H. H.

Action of Protective Colloids. J. TRAUBE and E. RACKWITZ (*Kolloid-Z.*, 1925, **37**, 131—138).—Traube's concept of "clinging intensity" between a solvent and dissolved substance is extended to colloids and in particular to coagulation and protective action. The magnitude of this quantity is large for lyophile and small for lyophobe colloids. In considering protective action, three clinging intensities come into question, namely, that between the protected substance and water, that between the protecting substance and water, and that between the protected and protecting substances. Since surface-active substances have a smaller clinging intensity towards water than surface-inactive substances, it is to be expected that the former would exert a smaller protective effect on a lyophobe colloid than would the latter. To test this theory the "protection numbers" of gelatin, gum arabic, egg-albumin, dextrin, soap, sodium stearate, saponin, and sodium cholate with reference to the sols of gold, silver, carbon, ferric hydroxide, Prussian-blue, sulphur, and arsenious sulphide have been determined by the Zsigmondy gold number method. With gold, silver, and carbon sols the order of the protection numbers is the same. Surface-inactive colloids such as gelatin are much more effective protectors than surface-active substances such as saponin. Ferric hydroxide sol gives almost the same order of protection numbers. Prussian-blue, sulphur, and

arsenious sulphide, which have small clinging intensities towards water, are on the other hand very differently affected. Here the surface-inactive colloids fall, in general, into the same order as with the gold etc. sols, but the surface-active substances are in many cases as good or better protectors. These observations are generally in accord with the theory.

A new method for the study of protective action is described, which differentiates sharply between surface-active and inactive substances. It depends on the fact that if a gold hydrosol containing a suitable quantity of a surface-inactive substance such as gelatin be shaken with chloroform, the latter forms an emulsion, containing the whole of the gold, under the water layer. If a surface-active colloid such as saponin be used, an emulsion is formed, but no gold is withdrawn from the hydrosol. In the first case, the gelatin, being a good protector for gold, surrounds the gold particles which are carried to the chloroform when the emulsion is formed. In the second case, the saponin, having a low clinging intensity towards gold, surrounds the chloroform drops only, leaving the gold in the hydrosol. N. H. H.

Influence of Added Substances on the Life of Dispersoids. I. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **37**, 151—158).—A general theoretical treatment. Curves are drawn showing the dependence of the life period on the concentration of added substance and some experimental evidence is brought forward in support of them. The treatment is based on the author's views relative to the part played by electrical energy, the existence of free ions, and the nature of adsorptive power, which are: (i) that electrical energy plays no outstanding part in determining the life of dispersoids: it is only one of the many variables which influence this; (ii) that completely free ions do not exist, but that the ions adsorbed by the colloid particles are strongly solvated molecules with greatly weakened linkings between the atoms or atom groups; (iii) that the difference between adsorptive power and chemical affinity is one of intensity only. N. H. H.

Joule Effect in Rubber. L. HOCK (*Z. Elektrochem.*, 1925, **31**, 404—409; cf. Freundlich and Hauser, *B.*, 1925, 514).—Against the view that the heating which takes place when rubber is stretched is due to heat of compression of a liquid phase, it is pointed out that stretched raw rubber retains its extension permanently at 20° and under, which it could scarcely do in presence of a compressed liquid. The heat of extension is ascribed to the enforced orientation of the rubber particles into crystalline fibres, with accompanying disengagement of the heat of crystallisation. It is shown that frozen stretched rubber actually breaks up into fibres under the hammer, whereas if frozen before stretching it breaks up like glass. W. A. C.

Cause of Characteristic Extensibility of Rubber. II. Joule Effect and Formation during Stretching of a Three-dimensional Structure. J. R. KATZ (*Kolloid-Z.*, 1925, **37**, 19—22; cf. *B.*, 1925, 557).—Further observations on the *X*-ray

spectrogram of stretched rubber make it highly probable that the crystalline substance is formed during the stretching and is not present in unstretched rubber. In stretched and twisted rubber the *X*-ray spectrogram corresponds with a spiral arrangement of crystallites as in cotton and other cellulose fibres. The stretching involves the formation of a three-dimensional lattice and not simply the arrangement of molecules in the same direction. The heating of rubber on stretching is regarded as strictly analogous with the liberation of heat on the crystallisation of an amorphous substance. Joule's data are shown to be in harmony with the author's interpretation of the *X*-ray spectrograms. The relationships between extension and tension and between extension and optical anisotropy are also explained. E. M. C.

Kinetic Theory of Compressibility of Solutions and Binary Liquid Mixtures. K. C. Kar (*Physikal. Z.*, 1925, 26, 465—467).—Theoretical. By a statistical method equations are derived giving the connexion between the compressibility of solutions and liquid mixtures and their composition. For solutions, the equation $\beta_x(1+x)^2=\beta_0$ holds, where β_x and β_0 are the compressibilities of the solution and the solvent, respectively, and x is the concentration. For both solutions and liquid mixtures, the compressibility curves have the same form as the corresponding vapour-pressure curves. The calculated values of the compressibilities agree approximately with the experimental values. F. G. T.

Inter-ionic Attraction Theory of Ionised Solutes. III. Testing of the Theory in Alcoholic Solvents. A. A. Noyes and W. P. Baxter (*J. Amer. Chem. Soc.*, 1925, 47, 2122—2129).—The activities of ionised solutes, calculated from the *E.M.F.* of certain cells involving alcoholic solutions of lithium and hydrogen chlorides and sodium ethoxide, are shown to be in agreement with the inter-ionic attraction theory. The results show that the logarithm of the activation is inversely proportional to $\kappa^{3/2}$, where κ is the dielectric constant of the solution, as is required by theory. The numerical coefficients expressing the relationship between activation and its parameters have values 30% to 25% lower than the theoretical values, even at concentrations as low as 0·01*N*, but as the concentration decreases they tend towards the theoretical limiting value. S. K. T.

Inter-ionic Attraction Theory of Ionised Solutes. IV. Influence of Variation of Dielectric Constant on the Limiting Law for Small Concentrations. P. Debye and L. Pauling (*J. Amer. Chem. Soc.*, 1925, 47, 2129—2134).—Consideration of Debye and Hückel's theory indicates that the variations in the dielectric constant of the solution, κ, in the immediate neighbourhood of an ion do not affect the limiting equation for zero concentration. Correct values for the coefficient in this equation are obtained by substituting for κ the value for the pure solvent. The smaller numerical coefficients sometimes found can only be attributed to

variations in κ if it is assumed that the solutions are still too concentrated for the applicability of the limiting equation.

S. K. T.

Activity of Strong Electrolytes. IV. Application of the Debye–Hückel Equation to Alcoholic Solutions. G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, **47**, 2098—2111).—The Debye–Hückel equation for the activities of ions of strong electrolytes is shown to fit the data for the observed *E.M.F.* of the cell $Pt(H_2)|HCl,AgCl|Ag$ in water, alcohol, and 50 mol.% alcohol, up to at least *N*-concentrations. Further confirmation is found in *E.M.F.* measurements on lithium chloride solutions in ethyl and methyl alcohols and in water and also in the solubilities of sodium chloride in aqueous ethyl alcohol. The variation in the activities of the ions of hydrochloric acid in ideally dilute solutions in different solvents indicates the formation of the ion H_3O^+ in water. In dilute alcoholic solutions (negligible hydration) the activity change is more than twice as great for potassium chloride as for hydrogen chloride: this makes it improbable that equal changes in activity for the potassium and chloride ions occur with changing salt concentration in a single solvent. Data and methods are given for calculating the activities of the ions of hydrogen and sodium chlorides in any mixture of alcohol and water.

S. K. T.

Freezing Points of Glycerol and its Aqueous Solutions. L. B. LANE (*Ind. Eng. Chem.*, 1925, **17**, 924).—The f. p. of mixtures of glycerol and water have been determined. The lowest temperature, −46·5°, corresponds with a mixture containing approximately 33% of water. [Cf. *B.*, 1925, 826.]

D. G. H.

Solubility and Freezing-point Curves of Hydrated and Anhydrous Orthophosphoric Acid. W. H. ROSS and R. M. JONES (*J. Amer. Chem. Soc.*, 1925, **47**, 2165—2170).—The solubility and f. p. curves of aqueous phosphoric acid solutions offer no evidence of the existence of a decahydrate (Smith and Menzies, A., 1909, ii, 998). The eutectic points of ice and the hemihydrate (m. p. 29·32°) and of the hemihydrate and anhydrous acid (m. p. 42·35°) correspond with −85·0° and 23·50° and with concentrations of 62·5 and 94·75 g. of anhydrous acid per 100 g. of saturated solution, respectively. The anhydrous acid crystallises 13 times as fast as the hydrated form at 20°

S. K. T.

Freezing-point Curve of Aqueous Sodium Nitrite Solutions. H. HELBERG (*Ann. Chim.*, 1925, [x], **4**, 121—125).—Oswald's determination of the f. p. of sodium nitrite solutions, which fall on an uneven curve, are criticised and repeated. A smooth curve is obtained corresponding with lower freezing temperatures than those found by Oswald. The cryohydric point is −26°, the corresponding nitrite concentration being 38%. The present results give normal figures for the molecular f. p. depression of the solutions (cf. Oswald, A., 1914, ii, 197; Sidgwick and Ewbank, this vol., ii, 38).

S. K. T.

Stability of Additive Compounds between Esters and Acids. J. KENDALL and J. E. BOOGE (*J. Chem. Soc.*, 1925, **127**, 1768—1777).—From the depression of the f. p. of the additive compounds produced by benzene, water, and by one of the constituent compounds, the degrees of dissociation of three ester–acid additive compounds at their m. p. have been derived. For ethyl acetate–trichloroacetic acid (m. p. −26·8°) the dissociation is 12%, for benzyl benzoate–trichloroacetic acid (m. p. 13·6°) 35%, and for methyl succinate–trichloroacetic acid (m. p. 8·3°) 4—6%. The molecular heats of fusion of the three compounds are 5170, 5660, and 9600 cal., respectively. The f. p. depression curves given by water and benzene are almost identical owing to internal pressure differences masking the greater decomposition produced by the water. In dilute benzene solution at temperatures slightly above 0°, the compound ethyl acetate–trichloroacetic acid is still markedly stable, and even the weak complex ethyl acetate–acetic acid is not entirely decomposed. W. H.-R.

Additive Compounds in the Ternary System: Ester–Acid–Water. J. KENDALL and C. V. KING (*J. Chem. Soc.*, 1925, **127**, 1778—1791; cf. preceding abstract).—Measurements of f. p., conductivity, and velocities of hydrolysis have been made for the binary systems acid–water, ester–water, and also for the ternary systems water, ethyl acetate, and hydrochloric, trichloroacetic, chloroacetic, or acetic acids, respectively. Ethyl acetate gives a "pseudo ideal" f. p. depression curve in aqueous solution, indicating that extensive hydration occurs, but the effect of this is marked by internal pressure differences. No appreciable quantity of ester–acid complexes remains undecomposed in aqueous solution. The conductivities of both neutral salts and acids are lowered by the addition of ethyl acetate owing to diminished ionic mobility. The solubility of ethyl acetate in water at 0° varies very greatly when electrolytes are also present. The rate of hydrolysis of ethyl acetate in the presence of hydrochloric acid in equivalent quantity increases more rapidly than the molecular concentration of the acid, but with weaker acids the increase is less rapid, and with acetic acid a maximum rate exists near the saturation point. W. H.-R.

Formation of Martensite in Carbon Steels. K. HONDA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 165—172).—During the cooling of austenite through the A1 point, the atomic configuration of the iron changes from the face-centred γ form to the body-centred α form, and as this form of iron has only a very small power of dissolving carbon the carbon separates from the interspace of the lattice as cementite. If this separation is suppressed by quenching, martensite is produced at temperatures below 300°, but the further change to pearlite does not occur owing to the great viscosity of the metal at these low temperatures. As martensite is harder than austenite or pearlite, maximum hardness of the specimen will be obtained only when the quenching is so conducted that all the austenite has changed to martensite, whilst the further change to pearlite is completely arrested. It is suggested that the hardness

of martensite is due to the bracing action of the carbon atoms distributed in the faces of the elementary lattice cubes of α-iron. [Cf. *B.*, 1925, 722.] A. R. P.

Equilibrium Diagram of the Iron–Carbon–Nickel System. T. KASE (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 173—217).—The iron–nickel binary system consists of a continuous series of solid solutions with a break between 15% and 30% Ni; the A3 point in iron is lowered continuously by the addition of nickel and coincides with the A2 point at about 5% Ni on cooling and 10% Ni on heating. Nickel dissolves 0·55% C at 1300°, but only 0·25% C at 20°, and this solid solution forms a eutectic with carbon which contains 2·22% C and melts at 1318°. The ternary system iron–carbon–nickel contains no ternary eutectic, but a binary eutectic of iron–nickel solid solution and carbon, the carbon content of which decreases as the nickel content increases. The sum of the combined and total carbon in iron–nickel alloys decreases with increasing quantities of nickel to a constant value of 0·3% C with 30% or more Ni, whilst the A1 point of iron is lowered by nickel, eventually disappearing with 10% Ni. [Cf. *B.*, 1925, 724.] A. R. P.

β-Transformations in Copper–Zinc Alloys. J. L. HAUGHTON and W. T. GRIFFITHS (*J. Inst. Metals*, Sept. 1925, advance copy, 9 pp.).—A sudden and marked decrease in the temperature coefficient of the electrical resistance of copper–zinc alloys takes place at the transformation temperature. As this varies from 453° to 470° between 55% and 51 % Cu, the authors consider that this transformation is not eutectoidal (cf. Andrew and Hay, ii, 954). Electrical resistance measurements confirm Genders and Bailey's delineation of the β-phase boundaries (this vol., ii, 297). A. R. P.

α-Phase Boundary in the Copper–Tin System. D. STOCKDALE (*J. Inst. Metals*, Sept. 1925, advance copy, 9 pp.).—The α-phase in the copper–tin system is bounded by the solidus, which is a smooth curve connecting the m. p. of copper to the triple point at 799° (13·3% Sn), by a straight line connecting this point to the triple point at 518° (16·0% Sn) and then by a line parallel to the temperature axis. The β-phase undergoes a polymorphic transformation at 590°. [Cf. *B.*, 1925, 809.] A. R. P.

Equilibrium at High Temperatures in the Iron–Carbon–Silicon Systems. M. L. BECKER (*J. Iron and Steel Inst.*, Sept., 1925, advance copy, 13 pp.).—As the silicon content of iron–carbon–silicon alloys increases up to 4·0%, the solubility of carbon at any constant temperature between 1100° and 940° decreases, whilst the effect of temperature in raising the solubility becomes less marked. Below 940° the solubility drops rapidly to zero, probably in the neighbourhood of 920°. [Cf. *B.*, 1925, 806.] M. E. N.

Iron–Nickel and Iron–Cobalt Equilibrium Diagrams. L. GRENET (*J. Iron and Steel Inst.*, Sept. 1925, advance copy, 9 pp.).—The author postulates the existence of "limited states" between the

α- and γ-phases and shows how a diagram based on this idea may be used to relate the α–γ transformation and the magnetic transformation and also to explain anomalies of dilatation and density at different temperatures. [Cf. *B.*, 1925, 808.] M. E. N.

Constitution of Alloys of Aluminium, Copper, and Zinc. D. HANSON and M. L. V. GAYLER (*J. Inst. Metals*, Sept. 1925, advance copy, 45 pp.).—The five invariant points found by Jareš (*Z. Metallk.*, 1919, **10**, 1) in the aluminium–copper–zinc system are confirmed, but the reaction at 406° is found to be liq.+(CuAl) $\rightleftarrows$ β+($CuZn_4$). In addition, two new invariant points have been found due to reactions taking place in the solid state. These occur at 265° and 270° and are due to the invariant reactions, β+[$CuZn_4$] $\rightleftarrows$ [CuAl]+[Zn] and β+[$CuAl_2$] $\rightleftarrows$ [CuAl]+[Al], respectively. Copper depresses the temperature of the β-transformation in aluminium–zinc alloys until the presence of CuAl causes it to take place at a constant temperature, 245°. [Cf. *B.*, 809.]

A. R. P.

Equilibrium of the System Cryolite–Alumina. G. A. ROUSH and M. MIYAKE (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 99—103).—The eutectic temperature is 935°, corresponding with 18·5% of alumina. The solubility of alumina in cryolite in solid solution extends to about 12% and that of cryolite in alumina to about 77·5%. These results were confirmed by metallographic observations. Pure cryolite melts at 995° (cf. Pascal and Jouniaux, A., 1913, ii, 508). S. K. T.

Equilibria in Molten Salts. (Reactions between Molten Alloys of the Alkalis and Alkaline-earths and their Molten Chlorides.) K. JELLINEK and J. WOLFF (*Z. anorg. Chem.*, 1925, **146**, 329—387).—The equilibria between molten binary mixtures of alkali or alkaline-earth chlorides and molten alloys of the corresponding metals with a third metal have been investigated (cf. A., 1924, ii, 658; this vol., ii, 123, 124). The alloy was formed by electrolysis, using the third metal as cathode and a carbon anode. The temperature being maintained between 900° and 1200°, the mixture was electrolysed until an alloy of suitable concentration was obtained (0·5 to 2·5 hrs. with 6 to 14 amp.). The current was then discontinued, the crucible allowed to cool, and the mass of mixed salts and the alloy analysed. Results which show that the variation of the equilibrium with the temperature is negligible have been obtained for the following equilibria: in lead: $Ba+CaCl_2 \rightleftharpoons BaCl_2+Ca$; in tin: $Ba+2KCl \rightleftharpoons BaCl_2+2K$; $Ba+2NaCl \rightleftharpoons BaCl_2+2Na$; in antimony: $Ba+2KCl \rightleftharpoons BaCl_2+2K$; $Ba+2NaCl \rightleftharpoons BaCl_2+2Na$; $Sr+2NaCl \rightleftharpoons SrCl_2+2Na$; $Ca+2NaCl \rightleftharpoons CaCl_2+2Na$; in bismuth: $Ba+2KCl \rightleftharpoons BaCl_2+2K$; $Ba+2NaCl \rightleftharpoons BaCl_2+2Na$; $Ca+2NaCl \rightleftharpoons CaCl_2+2Na$.

The equilibria are to a large extent independent of the cathode metal employed. Taking the alkali metals as diatomic, the alkali chlorides as double molecules, the alkaline-earth metals as mon-

atomic, and their chlorides as simple molecules, it is shown that the law of mass action and Nernst's partition theorem lead to a value for the equilibrium constant which expresses the results at least to a first approximation. Thus in the equilibrium $Ba+2NaCl \rightleftharpoons BaCl_2+2Na$, the constant is given by (At.-%Na . Mol.-% $BaCl_2$)/(At.-% Ba . Mol.-% NaCl), and the values obtained, with antimony as the cathode metal, are 0·20, 0·13, 0·12, and 0·15. The same equilibrium with bismuth as cathode metal gives values 0·22 and 0·23. The results are compared and shown to be in accord with those of G. McP. Smith on equilibria between amalgams of sodium, potassium, and strontium and aqueous solutions of their chlorides. The effect of association and dissociation of the molten salts as well as of the metals in the alloys is discussed. A more rigid theory of the equilibria is developed (cf. Lorenz, A., 1924, ii, 484), but cannot be fully tested owing to lack of numerical data. The equilibria can be calculated approximately from thermodynamical considerations based on the difference of the heats of formation of the solid chlorides. The normal potentials between the alloys and the molten salts are calculated and the theory of the electrolysis of ternary metallic alloys is discussed. A. B. M.

In-, Uni-, and Multi-variant Equilibria. XXIX. Influence of One or More New Substances on an Equilibrium in which a Phase Reaction may Occur. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 252—261).—A mathematical treatment of various cases which may arise from the addition of new components to a system in equilibrium. S. I. L.

Equilibria in Systems with Phases Separated by a Semi-permeable Membrane. VI and VII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 231—242, 243—251).—VI. The osmotic water attractions of various systems separated by a membrane from a second system are derived mathematically from the changes in the thermodynamic potentials which accompany the passage of small quantities of liquid through the membrane. From a discussion of cases in which one of the systems consists only of solids, it is deduced that all solutions, which can exist in equilibrium with a system of solid substances in which a phase-reaction may occur by the addition or removal of the diffusing substance, have the same osmotic water attraction and are isotonic. Special cases dealt with in preceding papers are discussed in the light of the general treatment.

VII. When two systems are in osmotic equilibrium with respect to d diffusing substances, the osmotic solvent attractions of the two for each such substance are equal. Since the phase law is valid for each system separately, it follows that the number of degrees of freedom is the sum of the freedoms of each, less d, *i.e.*, if n_1, n_2 be the components, and v_1, v_2 the phases for the two systems, respectively, the freedom of the two in osmotic equilibrium is $n_1+n_2-(v_1+v_2)+2-d$; this constitutes the membrane–phase-rule. A number of special cases are considered. S. I. L.

Heats of Solution of Enantiotropic Modifications (of Ammonium Nitrate) at the Transition Point. E. COHEN and H. L. BREDÉE (*Z. physikal. Chem.*, 1925, **117**, 143—155; cf. this vol., ii, 23).—Further determinations have been made of the solubility of ammonium nitrate III and IV between 33° and 48° and 0° and 32°, respectively, and of the specific volumes of solutions saturated with ammonium nitrate III at 50°. The results obtained are not in agreement with those of Mondain-Monval (A., 1923, ii, 635; this vol., ii, 654), and his proof of Le Chatelier's tangent law is therefore invalid. L. F. G.

Heats of Solution and Dilution of Salts. J. WÜST and E. LANGE (*Z. physikal. Chem.*, 1925, **117**, 336).—Amendments to a previous paper (this vol., ii, 791). The correctness of Richards and Rowe's method of calculating heats of dilution is now upheld. L. F. G.

Measurement of Very High Electrolyte Resistances by Kohlrausch's Method. H. ÜLICH (*Z. physikal. Chem.*, 1925, **117**, 156).—An amplification of the statements made in a previous paper (this vol., ii, 671) concerning the method of Lorenz and Klauer. L. F. G.

Conductivity of Acids of Medium Strength in Methyl Alcohol, and their Catalytic Action. H. GOLDSCHMIDT and H. AARFLOT (*Z. physikal. Chem.*, 1925, **117**, 312—333; cf. A., 1924, ii, 825; this vol., ii, 128).—A detailed investigation of the conductivities, degrees of ionisation, affinity constants, and activity constants of trichloroacetic, trichlorobutyric, and picric acids in absolute and in aqueous methyl alcohol solutions. On the assumption that catalytic activity is proportional to hydrogen-ion concentration, theoretical values based on Bjerrum's theory are obtained for the effect of these acids on the velocity of various esterifications in methyl alcohol solutions. These values agree with those actually observed. This, however, is not the case when ethyl alcohol is the solvent. L. F. G.

Conductance by Metallic Colloids and its Electro-technical Applications. H. ANDRÉ (*Compt. rend.*, 1925, **181**, 243—244).—When concentrated sulphuric acid is electrolysed by alternating current between silver electrodes, the resistance of the liquid decreases progressively with the electrolysis, and a colloidal solution of silver, showing Brownian movement, is produced. Similar results are obtained with orthophosphoric acid and also by the use of graphite in place of silver. Used in conjunction with a non-oxidisable metal cathode, the electrode of colloidal silver is a convenient depolarising agent. With a current density of 1—2 amp./cm.^{2} at 40—60°, the following effective potentials are attained: copper, 8 volts; nickel, 16; ferronickel (50%), 18; soft iron, 25; ferrosilicon, 35; silicon, 80 volts. A thermal effect is observed on drying the colloids. The current is established at 300—400°, but ceases on cooling. R. B.

Separation of Rare Earths by the Ionic Migration Method. J. KENDALL and B. L. CLARKE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 393—400).—The technique devised in the attempted separation of isotopes by the ionic migration method has been developed and applied to the separation of mixtures of rare earths. A 2% agar-agar gel containing a given mixture (0·5*N*) is placed in a long glass tube, between similar gels containing a faster cation ($K^{\cdot}$), nearer the cathode and a slower cation ($Cr^{\cdot\cdot}$) nearer the anode. On electrolysis, the more mobile rare earth cation accumulates in the forward portion of the sample. The gel is cut into slices and analysed. Three typical pairs of binary mixtures were studied: yttrium–erbium, neodymium–praseodymium, gadolinium–samarium. In the first pair, a mixture containing 27·5% of yttrium yielded in 14 days extreme samples of 97·1% and 21·2%. In 21 days, with a longer tube, the purest fraction contained 99% of yttrium. In all three mixtures a very considerable degree of separation was effected.

The experiments could be followed by direct-vision absorption spectra, or by conductivity and refractivity measurements. The technique is being applied to hafnium–zirconium and rubidium–potassium mixtures. R. A. M.

Migration of Ions in Solid Electrolytes. M. LE BLANC and M. KRÖGER (*Z. Elektrochem.*, 1925, **31**, 359—360).—Controversial in reply to Tubandt (*ibid.*, 1924, **30**, 253). W. A. C.

Hydrogen and Oxygen Electrode Titrations of Some Dibasic Acids and of Dextrose. H. T. S. BRITTON (*J. Chem. Soc.*, 1925, **127**, 1896—1917).—Approximately 0·025*M*-solutions of oxalic, tartaric, succinic, and malonic acids were titrated electrometrically at 18° with 0·1*N*-sodium hydroxide solution, the p_H values being determined with a hydrogen electrode. New formulæ are derived for the calculation of dissociation constants of dibasic acids from any two points on the titration curve. These are more accurate than the formulæ given by Auerbach and Smolczyk (this vol. ii, 118), and the relation $K_1K_2=h^2$, where h is the hydrogen ion concentration at the mid point of the titration curve, is inconsistent with the author's data. The following dissociation constants are recorded: oxalic acid, $K_1=0{\cdot}17$, $K_2=1{\cdot}34\times10^{-4}$; tartaric acid, $K_1=1{\cdot}27\times10^{-3}$, $K_2=9{\cdot}65\times10^{-5}$; succinic acid, $K_1=9{\cdot}21\times10^{-5}$, $K_2=5{\cdot}30\times10^{-6}$; malonic acid, $K_1=2{\cdot}02\times10^{-3}$, $K_2=4{\cdot}41\times10^{-6}$. A solution of dextrose, similarly titrated with sodium hydroxide, gave for the first dissociation constant $K=[H^{\cdot}][C_6H_{11}O_6']/[C_6H_{12}O_6]=5{\cdot}77\times10^{-13}$. Attempts made to use an oxygen electrode for similar titrations show that the results are complex and not reproducible with different electrodes. W. H.-R.

Thermodynamics of Solutions of Simple Electrolytes. H. S. HARNED (*Z. physikal. Chem.*, 1925, **117**, 1—50; cf. A., 1916, ii, 597; 1920, ii, 664; 1922, ii, 255; 1923, ii, 115).—The thermodynamics of the activity function is discussed. An apparatus for

measuring the *E.M.F.* of cells having streaming alkali-amalgams as liquid junctions is described (cf. Knobel, A., 1923, ii, 116); it was employed with the following systems at 25°: $H_2|NaOH(c_2)|Na_xHg|NaOH(c_1)|H_2$, $H_2|NaOH(c_1),NaCl(c)|Na_xHg|NaOH(c_1)|H_2$, $H_2|KOH(c_1),KCl(c)|K_xHg|KOH(c_1)|H_2$. From the data obtained in this and earlier work, the activity coefficients of sodium hydroxide in sodium chloride solutions, of potassium hydroxide in potassium chloride solutions, and of water in potassium chloride and sodium chloride solutions were calculated. Further calculations give the degree of ionisation of water in sodium chloride and in potassium chloride solutions. With increasing salt concentration, the degree of ionisation of water at first increases rapidly, but soon attains a maximum, after which it decreases (cf. Schreiner, this vol., ii, 96). The individual properties of simple ions in concentrated solutions are discussed in the light of these results and of the theory of Debye and Hückel. L. F. G.

Thermodynamics of Quinhydrone Electrodes. Chemical Constants of Hydrogen. E. Schreiner (*Z. physikal. Chem.*, 1925, **117**, 57—87).—The total and free heat contents of benzoquinone, quinol, quinhydrone, and hydrogen, between 10° and 300° Abs., are calculated from published data for the molecular heats of these substances. The electromotive forces of the cells quinol–quinhydrone|hydrogen and benzoquinone–quinhydrone|hydrogen, using *M*-sulphuric acid as the common electrolyte, were measured at different temperatures. Corrections are made for neutral substance effect. Measurements were made of the solubilities and heats of solution of benzoquinone and quinol and the heats of combustion of benzoquinone, quinol, and quinhydrone. From the above data the affinities and heats of the reactions involved were determined. The heats of reaction calculated from calorimetric data agree, within the limits of error, with those calculated from electrometric data. The quinhydrone electrode is regarded as an unsaturated benzoquinone–quinol electrode and its constants are determined on that basis. Values for the true and the normal chemical constants of hydrogen were obtained agreeing approximately with those put forward by other investigators. L. F. G.

Electrode Vessel for Liquids Heavier and Lighter than the Liquid Junction Potential Eliminator. L. E. Dawson (*J. Amer. Chem. Soc.*, 1925, **47**, 2172—2173).—A form of apparatus is described which facilitates the use of solutions of different densities in potential measurements. S. K. T.

Turgoelectricity. W. Kopaczewski (*Compt. rend.*, 1925, **181**, 244—246).—The addition of water to a number of powders, hydrosols, and hydrogels under defined conditions produces displacements in a capillary electrometer. With emulsoid hydrosols such as inulin, dextrin, fibrin, glycogen, and with fine powders such as animal charcoal, kaolin, flowers of sulphur, there is little or no displacement, whereas the swelling of gels such as mucin, gelatin,

gum arabic, etc., or the process of jellification, *e.g.*, the addition of water to ethyl salicylate, or of acetic acid to aluminium hydroxide, gives rise to pronounced displacements in the electrometer. These movements are regarded as the manifestation of a new kind of electricity, turgoelectricity, produced by the rupture of the external layer of the molecules of water, causing the fall of potential observed. The hydrogel lattice acquires a negative charge, the dispersed liquid becomes positively charged (cf. this vol., ii, 529). R. B.

Passage of an Alternating Current through Sulphuric Acid. R. T. LATTEY (*Phil. Mag.*, 1925, [vi], **50**, 444—453).—The effective resistance and the capacity of a pair of platinum electrodes immersed in a solution of sulphuric acid of maximum conductivity have been measured for alternating currents of periodicity varying from 25 to 500. The resistance is regarded as made up of r, the resistance of the electrolyte, and S, the resistance in the surface layers of the electrodes. The variation of the capacity and of S with periodicity has been investigated for electrodes platinised in different ways and for bright electrodes. The most consistent results were obtained with electrodes coated with pure platinum, electrodes otherwise treated behaving more or less erratically. The relation between capacity C and periodicity p is expressed by $pC=A+pB$, and that between S and p by $pS=D$, where A, B, and D are constants depending on the condition of the electrode surfaces.

A. B. M.

Electrolytic Polarisation. III. The Diffusion Layer. S. GLASSTONE (*J. Chem. Soc.*, 1925, **127**, 1824—1831; cf. this vol., ii, 43, 133).—The rate of fall of back-*E.M.F.* of polarised mercury and lead cathodes in different electrolytes has been examined, and indicates that the thickness of the diffusion layer at an electrode, from which gas is being freely liberated, decreases with rise of current density owing to the stirring effect of the bubbles. With mercury cathodes in sulphuric acid containing alkali sulphates, the back-*E.M.F.* first decreases gradually when the polarising current is stopped, and then shows a sudden decrease after a period of time which diminishes with rise of temperature and of current density, since these factors diminish the thickness of the diffusion layer. Owing to the diffusion of anodic chlorine, abnormal results are obtained in hydrochloric acid unless the electrodes are separated by a porous pot. W. H.-R.

Apparatus for Anodic Processes [Dichromates, Per-Salts, Chloroform]. I. STSCHERBAKOV (*Z. Elektrochem.*, 1925, **31**, 360—362).—When a porous pot is used as diaphragm, there are losses of yield owing to diffusion of cathodically formed alkali into the electrolyte. This is avoided by filling the porous pot with mercury acting as cathode; the catholyte floating on this becomes progressively alkaline and may be run off continuously. The mercury, on the upper surface of which a layer of alkali-amalgam is formed, may also be continuously replenished. Sodium chromate is thus converted into dichromate with a current efficiency

of 92—95% at the ordinary temperature; persulphates are obtained at 7—8 volts with an efficiency of 80—90%. In the chlorination of alcohol in presence of sodium chloride solution, the requisite alkali is supplied to the anolyte by means of a suitably adjusted auxiliary cathode of iron, and chloroform is produced with almost theoretical current efficiencies. W. A. C.

Effect of Infra-red Radiation on the Rate of Combustion of Inflammable Gaseous Mixtures. W. T. David (*Proc. Roy. Soc.*, 1925, **A**, **108**, 617—627).—The effect of infra-red radiation on the rate of combustion of mixtures of air with hydrogen, carbon monoxide, and methane, respectively, was measured. An increased rate of combustion was found in all cases when the superimposed radiation, or the radiation emitted by the burning gases, was of a type which could be absorbed by the combustible gas. [Cf. *B.*, 1925, 793.] L. F. G.

Influence of Curvature on Air Saturation of Water and its Relation to the Air-binding of Filters. J. R. Baylis (*Ind. Eng. Chem.*, 1925, **17**, 974—979).—A concave water surface increases and a convex surface decreases the solubility of air and other gases in water. The rate of solution of air from a very small bubble decreases with the age of the bubble. When two air–water surfaces come violently into contact with each other the minute bubbles so formed dissolve rapidly when the water is in equilibrium with a plane surface but increase in size if the equilibrium is greater than that for the diameter of the bubble. This is the case if the water is more than 100% supersaturated. These facts are considered in relation to the air-binding of sand filters. [Cf. *B.*, 1925, 824.] A. R. P.

Corrosion Effect of Naphtha Solutions of Sulphur and Sulphur Compounds. A. E. Wood, C. Sheely, and A. W. Trusty (*Ind. Eng. Chem.*, 1925, **17**, 798—802).—A study of the action on metals of naphtha solutions of sulphur, mercaptans, hydrogen sulphide, alkyl sulphates, sulphonic acids, and other sulphur compounds shows a general increase in corrosion in presence of water. In some cases, this is due to ionisation, but in other cases, as with free sulphur, apparently to the formation of anodic and cathodic areas. A mercaptan solution yields a mercaptide with most metals which is decomposed on heating, yielding sulphide. [Cf. *B.*, 1925, 745.] C. I.

Hydration of Anhydrite. M. Farnsworth (*Ind. Eng. Chem.*, 1925, **17**, 967—970).—Anhydrite ($CuSO_4$) cannot be hydrated by heating it with water under a pressure of 19 atm. (210°) and no hydration takes place in a sealed tube containing excess of water between 100° and 210°; in fact under these conditions gypsum is converted into the hemihydrate at 107° and into anhydrite at 160°. When, however, anhydrite is ground extremely finely in a colloid mill hydration takes place slowly at the ordinary temperature, particles of 7μ size being completely converted into gypsum in

3 weeks and coarser particles taking correspondingly longer. [Cf. *B.*, 1925, 804.] A. R. P.

Reduction of Ferric Oxide and Iron Ores by Hydrogen. H. KAMURA (*J. Iron and Steel Inst.*, Sept. 1925, advance copy).—The reduction velocity of pure ferric oxide and iron ores by hydrogen at 500°, 600°, and 700° was determined. The higher the temperature of reduction, the less was the volume of hydrogen required; also the velocity of reduction increased with the temperature. At 600°, the velocity of reduction increased rapidly and the volume of hydrogen required decreased to a marked extent; this was probably due to the appearance of the solid phase FeO, which cannot exist below 570°. Thus below 570° the reduction takes place according to the equation $Fe_3O_4+4H_2=3Fe+4H_2O$, whilst above 570° it takes place in two stages: (i) $Fe_3O_4+H_2=3FeO+H_2O$; (ii) $FeO+H_2=Fe+H_2O$. M. E. N.

Kinetics of the Oxidation-Reduction Reaction of Formaldehyde. H. VON EULER and T. LÖVGREN (*Z. anorg. Chem.*, 1925, **147**, 123—134).—Investigation of the kinetics of the reaction whereby formaldehyde is converted into methyl alcohol and formic acid (Cannizzaro reaction) at 50° over the p_H range 11—13, shows that the process is bimolecular and that it occurs between formaldehyde anions. The value of k_a for formaldehyde at 50° is found to be $3{\cdot}3\times10^{-13}$. J. S. C.

Relation of Homogeneous to Catalysed Reactions. Catalytic Decomposition of Hydrogen Iodide on the Surface of Gold. C. N. HINSHELWOOD and C. R. PRICHARD (*J. Chem. Soc.*, 1925, **127**, 1552—1559).—The decomposition of hydrogen iodide on the surface of a heated gold wire is a catalytic reaction of zero order. The temperature coefficients of such reactions are not affected by the changing degree of adsorption of the reactant. Therefore the "heat of activation" calculated from the temperature coefficient may be expected to have, without correction, the direct physical significance which it possesses in the case of homogeneous reactions. The "heats of activation" found for the homogeneous thermal decomposition of nitrous oxide, hydrogen iodide, and ammonia, and the heterogeneous decomposition of nitrous oxide on platinum and gold, of hydrogen iodide on gold, and of ammonium on tungsten are compared and it is shown that the surface reactions have heats of activation only about half as great as those of the bimolecular homogeneous changes. Probably all (and certainly some) surface reactions of this type involve only one molecule. Thus the function of the surfaces in these reactions is to permit the occurrence of a unimolecular process instead of a bimolecular process requiring an energy of activation about twice as great. E. E. W.

Catalytic Decomposition of Hydrogen Peroxide in Acid Chlorine-Chloride Solution. R. S. LIVINGSTON and W. C. BRAY (*J. Amer. Chem. Soc.*, 1925, 47, 2069—2082).—The catalytic influence of mixtures of hydrochloric acid with sodium chloride

and with perchloric acid on the decomposition of hydrogen peroxide solutions at 25° and 40° is investigated. The previous work of Maass and Hiebert (A., 1924, ii, 326) is criticised. The reaction is of the first order with respect to the peroxide, within concentrations 0·22 to 0·02*N* of the latter. The velocity constant is increased 3·60 times for a 10° temperature rise with hydrochloric acid alone between the concentrations 0·244*N* and 0·498*N*. At the steady state, in solutions of ionic strength below unity, the rate of decomposition is given by: $d[H_2O_2]/dt = -(0{\cdot}000101 \pm 0{\cdot}000005)[H_2O_2][H^{\cdot}][Cl']\gamma^2_{HCl}$, γ being the activity coefficient; in more concentrated solutions a negative deviation occurs. Assuming Brönsted's theory (A., 1922, ii, 699), this deviation indicates that the activity coefficient of the neutral "reaction complex" is greater than that of the hydrogen peroxide. In the steady state, with hydrochloric acid concentrations between 4·55*N* and 5·86*N*, the relation $[Cl_2]/[H^{\cdot}]^2[Cl']^2\gamma^4_{HCl} = 1{\cdot}5 \times 10^{-8}$ holds. A method of calculating the time required for the chlorine concentration to reach a given fraction of its steady state is given, based on the calculations of Abel (A., 1921, ii, 35). The suggested mechanism of the reaction is similar to that outlined by Maass and Hiebert. The reaction between hydrogen peroxide and hypochlorous acid has a large reaction rate, of the same order of magnitude as with hypobromous acid. S. K. T.

Reduction of Carbon Monoxide to Methane with Metal Catalysts. F. Fischer, H. Tropsch, and P. Dilthey (*Brennstoff-Chem.*, 1925, **6**, 265—271).—The metals catalysing the reduction of carbon monoxide to methane in order of decreasing efficiency, are ruthenium, iridium, rhodium, nickel, cobalt, osmium, platinum, iron, molybdenum, palladium, and silver. Copper, gold, tungsten, antimony, manganous oxide, and chromic oxide are without influence. Since no carbonyls of osmium, iridium, palladium, or rhodium are known, it cannot be definitely stated that the formation of a metal carbonyl is a stage in the reaction. Similarly, no relation can be traced between the affinity of the metal for hydrogen and its efficiency as a catalyst. No intermediate products likely to be formed, such as formaldehyde etc., could be isolated, but unsaturated hydrocarbons were observed with ruthenium and platinum which cannot be accounted for. Ruthenium is also active in the reduction of carbon dioxide to methane; although poisoned by sulphur compounds, it is reactivated by heating at 600—700° in a current of air. Oxides such as aluminium oxide in conjunction with nickel have a beneficial catalytic influence. B. W. C.

Catalytic Decomposition of Nitroamide. II. Catalysis by Simple Amino-bases. J. N. Brönsted and H. C. Duus (*Z. physikal. Chem.*, 1925, **117**, 299—311; cf. A., 1924, ii, 331).—The basic dissociation constants of aniline, *o*-, *m*-, and *p*-toluidine, and *o*-, *m*-, and *p*-chloroaniline were determined by an electrometric and by a kinetic method, the latter depending on the rate of decomposition of ethyl diazoacetate. The catalytic decomposition of

nitroamide by these bases was found to follow very nearly, but not exactly, the same quantitative law as that previously found for anions of carboxylic acids used in this connexion. L. F. G.

Effect of Diluents on the Initial Stages of Catalytic Action. F. H. CONSTABLE (*Nature*, 1925, **116**, 278—279).—The depressant action on the reaction velocity at a catalytic surface of diluent vapours in the reactants is considered from a quantitative point of view, and the expressions deduced have been verified experimentally, within the limits of experimental error, in the case of the effect of water vapour on the initial stages of the dehydrogenation of ethyl alcohol by copper. A. A. E.

Interaction of Carbon Dioxide and Hydrogen on the Surface of Tungsten. C. N. HINSHELWOOD and C. R. PRICHARD (*J. Chem. Soc.*, 1925, **127**, 1546—1552).—The kinetics of the interaction of hydrogen and carbon dioxide on the surface of a heated tungsten filament have been investigated between 953° and 1303°. Above a certain pressure the surface becomes saturated with the gases, the rate of reaction becoming independent of the initial pressure. The adsorption of the one gas is almost independent of the pressure of the other, and the rate of reaction is proportional to $\sigma_{H_2} . \sigma_{CO_2}$, where σ_{H_2} and σ_{CO_2} are the fractions of certain active portions of the surface which are covered with adsorbed hydrogen and carbon dioxide, respectively. The portions of the surface which adsorb and render active the one gas are different from those parts which adsorb the other gas. Interaction is supposed to take place when the two gases are adsorbed on adjacent centres of appropriate kinds. The value of the apparent heat of activation calculated by means of the Arrhenius formula is 30,000 cal. E. E. W.

Catalytic Oxidation of Hydrogen Cyanide. R. HARA and H. SINOZAKI (*Tech. Repts. Tôhoku*, 1925, **5**, 71—113).—The oxidation of mixtures of hydrogen cyanide and air in presence of fine platinum gauze according to the equation $2HCN+5O=2NO+2CO+H_2O$ appears to occur at the first point of contact with the catalyst. The reaction starts abruptly at 450°, independently of the velocity of flow. High yields (80%) of nitric oxide are obtained between about 600° and 800°, this range widening with increasing velocity of flow. At higher temperatures, combustion to nitrogen occurs before the gases reach the catalyst, and the yield is then greatly influenced by the rate of flow; the reaction $2NO+2CO=N_2+2CO_2$ also occurs. Maximum yields are obtained with a rapidly flowing inlet gas containing 8% of hydrogen cyanide; with just above 15% of the latter explosions occur and at higher concentrations (30%) cyanuric acid and cyamelide are formed. The intermediate stage of the oxidation is probably the immediate formation of cyanic acid, which either polymerises or decomposes into water, carbon monoxide, and nitric oxide, according to the conditions. The mass action constants, K_p, for the oxidation are comparable in magnitude with those for ammonia oxidation. Contrary to Wehrheim's observation, hydrogen cyanide decomposes slowly in acid potassium permanganate solution. S. K. T.

Electrolysis of Equimolar Mixtures. R. SAXON (*Chem. News*, 1925, **131**, 129—131).—When solutions containing metallic sulphates in equimolecular proportions are electrolysed the hydroxide of the more electronegative metal is deposited around the cathode when the two metals are widely separated in the electrochemical table, *e.g.*, copper and zinc, whereas a mixture of hydroxides is deposited when the metals are near one another in the table, *e.g.*, cobalt and nickel, the hydroxide of the less electropositive element tending to concentrate in the first fractions.

A. R. P.

Electrolytic Separation of Alkali and Alkaline-earth Metals. R. SAXON (*Chem. Trade J.*, 1925, **77**, 236).—With an anode of Meldrum's acid-resisting metal and a porous cathode compartment containing mercury, electrolysis of a paste of sodium hydroxide and water yields an amalgam containing 3·4% of sodium. The mercury is preferably covered with a little petroleum. Lithium, rubidium, barium, and calcium have been obtained by a similar method, using for the last a mixture of the chloride, nitrate, and iodide.

S. I. L.

Quantum Laws in Photochemistry. E. WARBURG (*Naturwiss.*, 1924, **47**, 1058—1063).—A summary of the investigations carried out to test Einstein's law of photochemical equivalence. Provided that certain assumptions are made as to the nature of the specific photochemical reaction and the secondary reactions, the law has been proved to apply when the quantum absorbed is greater than the energy of dissociation, but in certain cases the molecule may dissipate part of the energy absorbed by collision with other molecules and the law is not fulfilled. When the quantum absorbed is smaller than the energy of dissociation, the reaction is probably the result of collisions between excited molecules, but here again the dissipation of energy absorbed prevents more than a fraction of the excited molecules from reacting. The photodecomposition of ozone in presence of chlorine is an example of a sensitised photochemical reaction which obeys Einstein's law.

E. B. L.

Photochemical Formation of Hydrogen Chloride. G. KORNFELD and H. MÜLLER (*Z. physikal. Chem.*, 1925, **117**, 242—256).—Experimental evidence is given that the rate of photochemical formation of hydrogen chloride is proportional to the intensity of the activating light; this is not in agreement with Baly and Barker (T., 1921, **119**, 653). With the most sensitive mixture that could be employed it was found that $1{\cdot}10\times10^5$ molecules of hydrogen chloride were formed per quantum of absorbed energy.

L. F. G.

Condensation Nuclei Produced by the Illumination of Air–Halogen Mixtures. I. JONES (*Proc. Physical Soc.*, 1925, **37**, 287—296).—When dust-free air, saturated with iodine or bromine vapour, or mixed with small amounts of chlorine, is illuminated and subjected at atmospheric pressure to a pressure fall of

about 20 cm., dense clouds are formed. With iodine or bromine, illumination for 1 sec., and with chlorine for 2 secs. is necessary to produce clouds of maximum density. By keeping gas mixtures, activated by illumination, in darkness before expansion, it was shown that all the nuclei persist for 5 secs., and that some are still present after 30 secs. in darkness. By experiments on the production of clouds under various conditions, it was shown that in addition to illumination, the presence of a trace of moisture and of some oxidisable impurity on the walls of the apparatus is necessary for the production of nuclei. Oxygen is unnecessary. The conditions for the formation of nuclei in air–halogen mixtures resemble in several respects those for the occurrence of an induction period in the photochemical combination of hydrogen and chlorine, and it is suggested that the induction period is due to the consumption of the available light energy in the formation of nuclei before the activation of the chlorine–hydrogen mixture occurs.

F. G. T.

Combination of Bromine with Unsaturated Hydrocarbons under the Influence of Light. J. PLOTNIKOV (*Bull. Acad. Sci. St. Pétersbourg*, 1916, 1083—1114, 1563—1594; from *Chem. Zentr.*, 1925, i, 2535).—The author derives equations, on the assumption of Beer's law and the proportionality between light absorption and the amount of decomposition, for the velocity of reaction in the case of a photosensitive compound, a sensitive compound and a non-sensitive compound, and two sensitive compounds, respectively, for receptacles of different shape, with transparent or reflecting walls. Formulæ are given for photochemical balanced actions and for the reaction between bromine and α-phenylcinnamonitrile.

G. W. R.

Photochemical Potential Changes. K. SCHAUM and W. SCHLEUSSNER (*Z. wiss. Phot.*, 1925, **23**, 319—324).—The criteria for the recognition of a true Becquerel effect, and in particular the influence of other reactions and of the presence of a foreign substance, are discussed. Investigation of vanadium salts of different valencies showed that pure solutions of a single salt generally give a bad adjustment, and uncertain and scarcely reproducible effects. Mixtures of two salts of different valencies, or the addition of foreign substances capable of reacting, often give very clear results. The reaction between ferric ions and iodine provides an example of a case where the reversible photochemical reaction predominates over the Becquerel effect.

W. C.

Silver in Photography. LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 294—302).—The author summarises the published work on the forms and colours of silver produced by electrolysis and by reduction of silver salts, colloidal silver, dichroic fog, and the silver of the "print-out" image. The adsorption of thiosulphate by silver with particular reference to persulphate reduction is considered.

W. C.

[Photographic] Ripening Process. V. LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 286—293; cf. *B.*, 1925, 150, 477).—The influence of excess of bromide used in preparing emulsions on the rate of ripening, the grain size, and fog formation is considered. The influence of potassium bromide is generally less marked than that of the equivalent amount of ammonium bromide, although with some emulsions the potassium salt and with others the ammonium salt is preferred. The difference is probably due to inclusion of the salts in the silver bromide lattice, precipitated under different conditions. Observations are also made on the effect of rate of stirring, rate of mixing, etc. on the properties of an emulsion. [Cf. *B.*, 1925, 829.] W. C.

Solarisation of the Photographic Plate. J. M. EDER (*Z. physikal. Chem.*, 1925, **117**, 293—298).—Experimental evidence is adduced to show the incorrectness of Arens' view that the direct photochemical blackening of a silver bromide–gelatin plate impregnated with sodium nitrite is so intense that solarisation is masked (see this vol., ii, 313). Arens' consequential inferences are therefore not valid. L. F. G.

Potassium Chloroiminodisulphonate. F. RASCHIG (*Z. anorg. Chem.*, 1925, **147**, 1—4).—Potassium chloroiminodisulphonate, $NCl(SO_3K)_2$, is obtained as colourless, anhydrous crystals when a hot solution of sodium hypochlorite and potassium iminodisulphonate, $NH(SO_3K)_2$, is allowed to cool slowly to the ordinary temperature. The substance is unstable and decomposes into nitrogen trichloride and potassium nitrilotrisulphonate, $N(SO_3K)_3$. J. S. C.

Systematic Doctrine of Affinity. XXXI. Thiohydrates. W. BILTZ and E. KEUNECKE (*Z. anorg. Chem.*, 1925, **147**, 171—187). —The existence of the following *thiohydrates* is demonstrated: $BeBr_2,2H_2S$; $BeI_2,2H_2S$; $AlCl_3,H_2S$; $AlBr_3,H_2S$; $AlI_3,2H_2S$; $AlI_3,4H_2S$; $TiCl_4,H_2S$; $TiCl_4,2H_2S$; $TiBr_4,H_2S$; $TiBr_4,2H_2S$; $SnCl_4,2H_2S$; $SnCl_4,4H_2S$. The formation and stability of thiohydrates are discussed. J. S. C.

Action of Hydrogen Sulphide on Mercuric Salts. H. PÉLABON (*Bull. Soc. chim.*, 1925, [iv], **37**, 854—856).—The action of hydrogen sulphide at the ordinary temperature on a solution of mercuric chloride containing hydrochloric acid causes an immediate precipitation of the white chlorosulphide, with liberation of hydrogen chloride. If this, together with the acid initially in the mixture, brings the concentration of acid up to that demanded by the formula $HCl,6H_2O$, the precipitate remains white, however long the gas is passed. If this concentration limit is not reached, the precipitate blackens, partly or completely, owing to the formation of mercuric sulphide (cf. Jolibois and Bouvier, A., 1920, ii, 494). L. L. B.

Aluminium Sulphide. W. BILTZ (*Z. anorg. Chem.*, 1925, **146**, 289—290; cf. A., 1911, ii, 804).—Colourless crystals obtained

when a preparation of aluminium sulphide was sublimed in a vacuum and described as aluminium sulphide itself are now shown to be silicon disulphide. A. B. M.

Combustion of Carbon. II. F. G. KEENEN, L. W. PRINE, and W. C. EBAUGH (*Ind. Eng. Chem.*, 1925, **17**, 804—805).—The gases resulting from the combustion of the carbons of an electric arc in oxygen contain increasing proportions of carbon monoxide with increase of temperature, indicating that at high temperatures this gas is the primary product of the combustion. [Cf. *B.*, 1925, 744.] C. I.

Thermal Decomposition of Carbonyl Chloride. A. STOCK and W. WUSTROW (*Z. anorg. Chem.*, 1925, **147**, 245—255).—Carbonyl chloride not only decomposes into carbon monoxide and chlorine, but also to a slight extent into carbon dioxide and carbon tetrachloride. The rate of the latter decomposition, which is very small in the temperature region 400—500°, is accelerated in presence of certain catalysts (silica, blood charcoal, etc.). Although the thermodynamical treatment of the problem predicts that the major portion of the carbonyl chloride should be decomposed in this way, only about 1% of carbon tetrachloride is observed even after several hours. J. S. C.

Formation of Mullite from Cyanite, Andalusite, and Sillimanite. J. W. GREIG (*J. Amer. Ceram. Soc.*, 1925, **8**, 465—484).—When heated, cyanite, andalusite, and sillimanite are decomposed into mullite and silica, or into mullite and a silicious liquid, the silica being probably cristobalite. No definite point of temperature is observed at which the minerals decompose sharply, or below which they remain unaffected for indefinitely long periods. Cyanite requires the lowest, and sillimanite the highest temperature. Decomposition is accompanied by an expansion in all three cases; with cyanite it is very pronounced. In the case of cyanite and andalusite, the alteration commences on the surfaces of the grains and advances inward, whereas with sillimanite it appears to take place throughout the grain. The rate of decomposition increases rapidly with a rise in temperature in all three minerals. The mullite crystals newly formed from andalusite and sillimanite are oriented parallel to the original crystals, whereas with cyanite this orientation is determined by the surfaces from which the mullite grows. An absorption of heat is observed when cyanite and andalusite decompose. F. S.

Phenomena in the Electric Arc Process of Nitrogen Fixation. S. KARRER (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 25—32).—The author discusses the factors which may possibly affect the efficiency of the arc method of nitrogen fixation, more particularly with regard to those phenomena, other than purely thermal, which occur in the arc core. The following points are dealt with: dissociation of oxygen and nitrogen molecules into neutral atoms; ionisation within the arc; excitation; radiation; energy transfer. N. H. H.

Attempt to Prepare Nitro-nitrogen Trichloride. III. Failure to Obtain a Compound containing only Nitrogen and Chlorine from Oxides of Nitrogen. W. A. NOYES (*J. Amer. Chem. Soc.*, 1925, **47**, 2159—2164).—An account of unsuccessful experiments carried out to prepare a new compound containing only nitrogen and chlorine. (Cf. A., 1921, ii, 42.)

S. K. T.

New Oxide of Nitrogen, Nitroso-nitrogen Trioxide, and its Bearing on the Oxidation of Nitric Oxide. R. L. HASCHE (*J. Amer. Chem. Soc.*, 1925, **47**, 2143—2148).—*Nitrosonitrogen trioxide*, $(N_3O_4)_x$, is prepared as a green solid by bubbling nitric oxide through liquid oxygen or by the action of air on solid nitric oxide kept at the temperature of liquid air. It decomposes just above the b. p. of oxygen to the blue oxide, N_2O_3 (Helbig, A., 1903, ii, 361); Raschig's formula for this compound (A., 1911, ii, 346) could not be substantiated. Assuming, because of its instability and its instantaneous formation, that the green oxide is a peroxide of polymerised nitric oxide, its formation may be explained as follows:

$$\cdot O\cdot O\cdot + 2(NO\cdot NO\cdot N{:}O) \longrightarrow O{:}N\cdot NO\cdot NO\cdot O\cdot O\cdot NO\cdot NO\cdot N{:}O.$$

The phenomena observed in the oxidation of nitric oxide may be explained by the assumption of similar intermediate compounds, *viz.* at higher temperatures, $O{:}N\cdot NO\cdot O\cdot O\cdot NO\cdot N{:}O$, formed by the oxidation of $(NO)_2$, and, in the gaseous state, $O{:}N\cdot O\cdot O\cdot N{:}O$, formed by the oxidation of NO.

S. K. T.

Amphoteric Hydroxides, their Alkaline Solutions and Alkali Salts. III. Alkali Antimonates from Aqueous, Alkaline Solutions. G. JANDER and L. BRANDT (*Z. anorg. Chem.*, 1925, **147**, 5—15).—The hydrated crystalline precipitates of sodium and lithium antimonates obtained by oxidising alkaline solutions of antimony trisulphide with hydrogen peroxide, are not of fixed composition, the alkali content varying with the alkalinity of the mother-liquor and the temperature of precipitation. Potassium antimonate obtained by the oxidation of alkaline solutions of antimony trioxide with hydrogen peroxide is difficult to obtain in a crystalline form. The value of the ratio $[K_2O]:[Sb_2O_5]$ usually approximates fairly closely to unity.

J. S. C.

Bismuth Dihydride. E. J. WEEKS and J. G. F. DRUCE (*J. Chem. Soc.*, 1925, **127**, 1799—1800).—Bismuth dihydride, Bi_2H_2, is obtained as a grey, flocculent precipitate by the addition of bismuth chloride to a mixture of zinc and concentrated hydrochloric acid. It deposits metallic bismuth when heated, and is rapidly oxidised by fused potassium nitrate.

S. I. L.

Action of Ozone on Aqueous Colloidal Solutions of Inorganic Substances. E. H. RIESENFELD and W. HAASE (*Z. anorg. Chem.*, 1925, **147**, 188—195).—Silver sols are converted into solutions of silver hydroxide. Mercurous oxide is precipitated from mercury sols. Gold sols are only partly dissolved, the red

colour changing to blue. Whereas lead oxide sols are easily oxidised, cuprous oxide sols are quite stable. Arsenic and antimony trisulphide sols are decomposed with formation of sulphur, sulphuric acid, and the corresponding pentoxides. Silver, mercury, and copper sulphide sols are converted into solutions of the corresponding sulphates. J. S. C.

Formation of Ozone in Incandescent Capillaries. E. H. RIESENFELD (*Z. Elektrochem.*, 1925, **31**, 435—440).—When pure dry oxygen is passed rapidly through quartz capillaries heated at 1000—1500° Abs., ozone is found in the issuing gas to the amount of several millionths of an atmosphere partial pressure. Presence of moisture reduces the yield; nitrogen (1%) does not affect it. There is more than 1000 times as much ozone as would be expected by calculation from Nernst's theorem. It is suggested that particles from the quartz adsorption layer, in which the equilibrium leans towards ozone, are carried over by the rapid current in the quartz capillary, thus giving rise to a false equilibrium. W. A. C.

Decomposition of Sulphur Monochloride by Water. E. NOACK (*Z. anorg. Chem.*, 1925, **146**, 239—262).—The course and the end products of the reaction between sulphur monochloride and water have been shown to agree qualitatively and quantitatively with those of the reaction between sulphur dioxide and hydrogen sulphide in the presence of water. A slight difference in the amount of sulphuric acid produced, even when rigid precautions are taken to exclude air, is probably due to the oxidising action of a small quantity of a higher chloride produced by dissociation of the monochloride. In one experiment sufficient of the latter was dissolved in water to give 0·2 g.-at. of sulphur per litre, an atmosphere of carbon dioxide being maintained, and the following end-products were obtained (expressed as percentage of total sulphur): sulphur as sulphuric acid, 3·2%, as polythionic acids, 35·7%, as sulphurous acid, 0·7%, and elementary sulphur, 60·4%. The results support the assumption that the first stages of the reaction can be represented by the schemes: $S_2Cl_2+H_2O \longrightarrow S_2(OH)_2+2HCl$; $S_2(OH)_2 \rightleftharpoons H_2S+SO_2$. The existence of hydrogen sulphide and sulphur dioxide as intermediate products is demonstrated, and the change of their concentration with time shown to confirm the assumption made. Attempts to prepare the assumed intermediate compound $H_2S_2O_2$, however, by the action of hydrogen sulphide on sulphur dioxide in the absence of water, *e.g.*, in alcoholic solution, or by passing hydrogen sulphide into liquid sulphur dioxide, failed. The reaction under such conditions proceeds thus: $2H_2S+SO_2 \longrightarrow 2H_2O+3S$. The reaction between a thiosulphate and hydrogen sulphide is shown to admit of a simple interpretation on the assumption of the formation of $H_2S_2O_2$ as an intermediate product. A. B. M.

Amidopersulphuric Acid [Hydroxylamine*iso*monosulphonic Acid]. F. SOMMER, O. F. SCHULZ, and M. NASSAU (*Z. anorg. Chem.*, 1925, **147**, 142—155; cf. A., 1914, ii, 458).—Amidopersulphuric acid, $NH_2O{\cdot}SO_2{\cdot}OH$, prepared by the interaction of

chlorosulphonic acid and hydroxylamine sulphate, may be obtained pure as colourless prisms by dissolving in cold dry methyl alcohol and precipitating with dry chloroform. Alcohols react to form compounds of the type $RO{\cdot}SO_2{\cdot}OH,NH_2OH$. Aldehydes and ketones in alkaline solution react to form salts of oxime acids, *e.g.*, $CR_1R_2{:}NO{\cdot}SO_2{\cdot}OK$. On boiling with alkali, the acid is decomposed according to the equation $3NH_2O{\cdot}SO_2{\cdot}OH+6KOH=3K_2SO_4+6H_2O+NH_3+N_2$. The salts are very unstable and liable to explode. Many of the reactions of the acid suggest that it possesses the alternative structural formula $HN{:}O{:}SO(OH)_2$. On boiling aqueous solutions of the acid with a considerable excess of ammonia yields of hydrazine of the order of 50% are obtained. Amino compounds yield the corresponding hydrazine derivatives. Alkaline solutions of ethylenediamine react to form *α-hydrazino-β-aminoethane* (*dioxalate*, needles, m. p. 204°; *dipicrate*, yellow crystals, m. p. 166° [decomp.]; *dihydrochloride*, colourless crystals, sintering at 165—166°, and decomposing at 200—205°); *α-Benzylidenehydrazino-β-aminoethane oxalate*, needles, m. p. 150—152° (decomp.), and *α-o-hydroxybenzylidenehydrazino-β-aminoethane oxalate* were also prepared. J. S. C.

Bivalent Chromium. W. Traube, E. Burmeister, and R. Stahn (*Z. anorg. Chem.*, 1925, **147**, 50—67; cf. A., 1916, ii, 625).—Concentrated solutions of pure chromous chloride are obtained by the prolonged electrolytic reduction of aqueous solutions of green chromic chloride, using lead plates as electrodes and employing a current density of 0·175 amp./dm.^{2} Electrolysis of chromous chloride solutions using an iron cathode results in the formation of a cathodic deposit of metallic chromium mixed with chromium oxides. The autoxidation of chromous salts in acid solution with evolution of hydrogen is considerably accelerated in presence of catalysts such as palladium chloride. Precipitation of solutions of chromous salts by alkali yields a mixture of hydrated chromous oxide and chromium sesquioxide in varying proportions.

Chromous formate exists also as a violet salt. The following double salts have been prepared: *chromous pyridine formate*, $[Cr(C_5H_5N)](CO_2H)_2$, *chromous pyridine chloride*, $[Cr(C_5H_5N)_2]Cl_2,2H_2O$, *chromous formate ammonium chloride*, $Cr(CO_2H)_2,NH_4Cl$, *chromous ammonium fluoride*, $CrF_2,NH_4F,2H_2O$, *chromous potassium fluoride*, CrF_2,KF. J. S. C.

Complex Uranyl Carbonates. J. A. Hedvall (*Z. anorg. Chem.*, 1925, **146**, 225—229).—A large number of metallic ions give a precipitate with solutions of the alkali uranyl carbonates, but analytical results, the visible evolution of carbon dioxide, and the gradual colour change due to hydrolysis show that most of these products even shortly after precipitation cannot be regarded as definite compounds. Least hydrolysis occurs when the potassium uranyl carbonate in not too dilute a solution is precipitated in the cold by addition of excess of the metallic salt solution; the pre-

cipitate is rapidly washed with water and allowed to dry in the air. *Silver uranyl carbonate*, $Ag_4UO_2(CO_3)_3$, forms yellow flocks which turn to a crystalline powder. It darkens in colour even when kept in the dark, owing to the uranium radiation. The dry salt begins to evolve its carbon dioxide at 165°. *Barium uranyl carbonate*, $Ba_2UO_2(CO_3)_3,6H_2O$, yellow, microscopic plates, loses water slowly at the ordinary temperature, more quickly at 50°, changing in colour from bright yellow to lemon-yellow. Above 350°, considerable quantities of carbon dioxide are given off and the colour becomes orange-yellow. A. B. M.

Chlorine Hexoxide. M. Bodenstein, P. Harteck, and E. Padelt (*Z. anorg. Chem.*, 1925, **147**, 233—244).—Analysis and measurements of f. p. depression in carbon tetrachloride solution show that the dark-red oil obtained by exposure to light of chlorine dioxide is chlorine hexoxide, Cl_2O_6. The substance has a very low vapour pressure, 1 mm. at 20°, d^{20} 1·65, and m. p. −1°. When in an impure condition it is readily explosive, but at the ordinary temperature in the pure state it is much more stable. Contact with organic substances, however, brings about violent decomposition. At high temperatures, chlorine hexoxide decomposes into chlorine and oxygen. The substance reacts with water as a mixed anhydride, forming chloric and perchloric acids. Chlorine hexoxide is also formed on illumination of a mixture of ozone and chlorine, rays in the red portion of the spectrum being active and not those in the blue. J. S. C.

Mechanism of Reduction of Iron Oxides in a Current of Gas. II. K. Hofmann (*Z. angew. Chem.*, 1925, **38**, 715—721).—Samples of ferric and ferrosoferric oxide powder were reduced by heating them in a current of hydrogen, the degree of reduction being taken as the percentage of the total oxygen reduced. The reduction of ferric oxide is practically complete at 550° and 1000°, but between these temperatures the degree of reduction shows minima due to adhesion of the solid particles and to the process of β–γ transformation. It is most complete when the diameter of the oxide particles is 0·02—0·05 mm. Similar minima occur in the reduction of ferrosoferric oxide, which, however, is less easily reduced than ferric oxide. Adhesion phenomena can be eliminated by admixture of basic oxides, *e.g.*, magnesia. In other cases, reduction is hindered by the diminished diffusive power of the water produced through the shell of metallic iron formed round the oxide particles. The reduction of ferric oxide in a current of hydrogen does not progress in the anticipated stages, and the oxide Fe_3O_4 is not produced, although in a static system the case is otherwise. The mechanism of reduction cannot be explained from the equilibrium diagram, but account should rather be taken of surface phenomena, *e.g.*, adhesion, sintering. Further light may be expected from a study of the spatial configuration of the iron oxides and of the rearrangements of the oxygen atoms during the reduction process. W. T. K. B.

Ageing of Ferrous Carbonate and Ferrous Hydroxide. Ageing of Natural Mineral Waters. O. BAUDISCH and L. A. WELO (*J. Biol. Chem.*, 1925, **64**, 753—770, 771—779).—Ferrous hydroxide and ferrous carbonate, precipitated and stored in the absence of air, although apparently stable even to boiling, gradually lose their power of reducing nitrates to nitrites or of catalysing the oxidation of organic compounds such as uracil and lactic acid, although on exposure to air they still absorb oxygen. It is suggested that the ageing process consists in a gradual passage from the amorphous to the crystalline state.

The loss of therapeutic efficacy, undergone by certain mineral waters through keeping, has been correlated with a precipitation and consequent inactivation of ferrous salts analogous to the ageing process described above; it was found that the ageing of the mineral waters was accelerated by exposure to light.

C. R. H.

Cobaltammines with more than Six Molecules of Ammonia. F. EPHRAIM (*Z. anorg. Chem.*, 1925, **147**, 24—41).—Hexamminecobaltic chloride, bromide, and iodide, chloropentamminecobaltic iodide, aquopentamminecobaltic chloride, bromide, and iodide, *cis*-dinitritotetramminecobaltic bromide and iodide, *trans*-dinitritotetramminecobaltic bromide, and potassium tetranitritodiamminocobaltate can take up ammonia at temperatures in the region of −20° to form more complex compounds. The number of molecules of ammonia added per mol. of salt varies between 2 and 10. On raising the temperature, ammonia is evolved and less complex compounds result. Generally speaking, these complexes are completely decomposed to the original cobaltammine when the ordinary temperature is reached.

J. S. C.

Fractional Precipitation. I. Dependence on Solubility Products, Dissociation Constants, Constitution of the Precipitate, etc. O. RUFF and B. HIRSCH (*Z. anorg. Chem.*, 1925, **146**, 388—410).—The possibility of separating a mixture of metals in solution by fractional precipitation as hydroxides, carbonates, or sulphides has been studied. The method is exemplified by the separation of iron and nickel by sodium hydroxide, which depends on the reaction $FeCl_3+3Ni(OH)_2 \rightleftharpoons Fe(OH)_3+3NiCl_2$. If one equivalent of ferric chloride is added to two equivalents of nickelous hydroxide, the reaction proceeds completely in the direction from left to right. The same occurs if one equivalent of ferric chloride is added to 0·5 equivalent of nickelous hydroxide. In the first case, all the iron is precipitated; in the second, all the nickel passes into solution. Thus the two metals can be completely separated. The result is confirmed by the actual separation of a mixture of iron and nickel salts by the gradual addition of sodium hydroxide, the precipitate being separated in stages and analysed. Experiments have been carried out with a large number of metallic salt mixtures and with hydroxyl, carbonate, and sulphide as precipitating ions. The mixtures that can be successfully separated are tabulated. The theory of the process is briefly outlined, and

it is shown that in cases where the solubility products are known the results are in accordance with the theory provided that no mixed crystals or adsorption phenomena occur and no other compounds are formed. These exceptions, however, are infrequent.

A. B. M.

Concentration of Praseodymium Material and the Preparation and Properties of Metallic Praseodymium. J. WIERDA and H. C. KREMERS (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 65—74, advance copy).—High-grade praseodymium material with a probable purity of 99·7% has been prepared from cerium earth residues. The impurities known to be present in the final product were 0·02% of neodymium and less than 0·01% of lanthanum. In the course of the investigation the following methods of separation were tried: fractional crystallisation of the double magnesium nitrates, the double manganese nitrates, and the double ammonium nitrates; fractional decomposition of the nitrates by heat; fractional precipitation with ammonia in the presence of ammonium salts; fractional precipitation by magnesium oxide. As a result, the authors recommend a procedure which involves fractional crystallisation of the double magnesium or, at certain stages, manganese nitrates, cerium being removed at an intermediate point. The average magnetic susceptibility of the product was $13{\cdot}28\times10^{-6}$.

Preparation of the metal was effected by electrolysis of the fused chloride, using a low current density. The metal is silvery white, corrodes rapidly in air, is slightly attacked by hot water, and vigorously attacked by mineral acids and free halogens. The kindling temperature is 290°. The metal is not pyrophoric. The Brinell hardness (500 kg. weight) is 25, d^{25} 6·60. Alloys with most common metals are readily formed.

N. H. H.

Preparation of Mixed Iodides and Sulphides. T. KARANTASSIS (*Bull. Soc. chim.*, 1925, [iv], **37**, 854).—The compound $PI_3,3S_8$ may be obtained by dissolving phosphorus tri-iodide and a slight excess of sulphur in carbon disulphide. On cooling and evaporating in a slow stream of dry carbon dioxide, reddish-brown prismatic crystals are obtained, which change rapidly in air. An attempt to prepare the substance $PI_5,5S_8$, gave, on proceeding as above and evaporating at −10° or −15°, deep red crystals, which on analysis proved to be $PI_3,3S_8$. The mother-liquor contained free iodine.

L. L. B.

Preparation of Nitric Oxide from Sodium Nitrite. W. A. NOYES (*J. Amer. Chem. Soc.*, 1925, **47**, 2170).—Nearly pure nitric oxide is rapidly generated by dropping concentrated sulphuric acid on to sodium nitrite covered with two or three times its weight of water: $3HNO_2=HNO_3+2NO+H_2O$. By washing the gas with concentrated sulphuric acid or water the trace of nitrogen dioxide present is removed.

S. K. T.

Nitrogen Tetrasulphide and Nitrogen Tetraselenide. H. B. VAN VALKENBURGH and J. C. BAILAR, jun. (*J. Amer. Chem. Soc.*, 1925, **47**, 2134—2137).—Good yields of nitrogen tetrasulphide

are obtained by passing dry ammonia at the rate of 1 litre/min. through 150 c.c. of ether containing 5 c.c. of sulphur monochloride. On keeping, orange crystals separate, ether extraction of which yields the tetrasulphide. Hydrolysis of the latter with a large excess of boiling water yields a neutral solution in which 21·3% of the sulphur is present as pentathionic acid, 40·6% as sulphurous acid, 38·1% as free sulphur, and all the nitrogen as ammonia. Prolonged passage of ammonia through an ethereal solution of sulphur monochloride yields, after evaporation, a viscous *liquid* of offensive odour which does not lose ammonia on heating. A similar compound was obtained with selenium. Liquid ammonia gives a black solid when mixed with sulphur monochloride. Nitrogen tetraselenide is prepared as above, using, however, more dilute solutions of selenium monochloride in carbon disulphide. The molecular weight, determined by a cryoscopic method, corresponds with the formula N_4Se_4. S. K. T.

Preparation of Phosphorus Trichloride and Tribromide from Red Phosphorus. V. Rekschinski (*Trans. Inst. Pure Chem. Reagents Moscow*, 1924, [3], 46—49).—Dry red phosphorus is treated with dry chlorine or bromine in an atmosphere of carbon dioxide, the formation of higher halides being prevented by suitably regulating the temperature and admission of halogen. The procedure is described in detail; the yields are more than 60% for the chloride and 80% for the bromide. G. A. R. K.

Preparation of Arsenic Di-iodide. T. Karantassis (*Bull. Soc. chim.*, 1925, [iv], **37**, 853).—One part of finely powdered arsenic and 2 parts of iodine are introduced into a retort-shaped tube. After repeated evacuation and filling with pure, dry hydrogen, the tube is sealed and the mixture heated to the b. p. for 2 hrs. On careful distillation, pure arsenic di-iodide is obtained. The undistilled product melts at 117—120°, the distilled compound at 130°, the change in m. p. proving the solubility of arsenic in the crude product. In an atmosphere of hydrogen or carbon dioxide, the compound boils at 375—380°. L. L. B.

Factors Affecting the Physical Condition of Bismuth Carbonate. A. J. Jones (*Pharm. J.*, 1925, **115**, 143—144).—Bismuth carbonate, prepared by adding bismuth nitrate solution to sodium carbonate solution, varies in density as follows: at constant concentration of sodium carbonate, precipitation at 45° yields the lightest powders, increase or decrease of temperature increasing the density. When the basic solution consists of a mixture of sodium carbonate and hydrogen carbonate, increase in the ratio carbonate/hydrogen carbonate seems to increase the density of the precipitate. There seems to be one particular set of values of all variables yielding bismuth carbonate of least density, increase or decrease of any of the values leading to a denser form. B. F.

Application to Chromium of a General Method for Synthesis of Fluorides and Silicates. A. Dubois (*Compt. rend.*, 1925, **181**, 336—337; cf. A., 1892, 1161).—Small quantities of the

precipitated oxide or fluoride of chromium are added to molten potassium hydrogen fluoride. The mixture is heated to redness and silica is then added. When the mass is cooled and treated with water, silica in the form of tridymite (d 2·32) and the double fluoride of chromium and potassium (CrF_3,3KF) can be isolated. The double salt consists of well-formed green crystals which are quite white when powdered. The material dissolves readily in hydrochloric and nitric acids; d^0 2·93. Analytical details are given. R. A. M.

Lithium Arc Spectrum for Polarimetric Use. P. C. Austin (*J. Chem. Soc.*, 1925, **127**, 1752—1753).—A method of producing a lithium spectrum by introducing lithium carbonate into the arc produced between carbon, copper, or silver electrodes is described. The value of the lithium lines in polarimetry is pointed out. E. E. W.

Spiral Springs of Quartz. H. D. H. Drane (*Nature*, 1925, **116**, 315).—A method is described for the production of spiral springs of silica fibres having a diameter of about 10^{-3} cm. (cf. this vol., ii, 818). A. A. E.

Flow Calorimeter for Specific Heats of Gases. N. S. Osborne, H. F. Stimson, and T. S. Sligh, jun. (*U.S. Bur. Standards*, 1925, **20**, [503], 119—151).—The paper describes the design, construction, and operation of a calorimeter for the measurement of C_p at pressures below 100 atm. and temperatures below 150°. The application of the instrument to superheated ammonia vapour has already been described. [Cf. *B.*, 1925, 497.] N. H. H.

Calorimetric Bomb with Platinum Lining. C. Moureu and P. Landrieu (*Bull. Soc. chim.*, 1925, [iv], **37**, 986—996).—Details are given of the calorimetric bomb built to replace that of Berthelot (cf. this vol., ii, 427). S. K. T.

Theory and Construction of Lever Manometers. O. Frank (*Z. Biol.*, 1925, **83**, 1—15).—The theory and construction of lever manometers is discussed and an equation obtained from the roots of which the system is calculable. If the volume elasticity coefficient is made equal to infinity, a system results having two degrees of freedom and possessing the essential properties of a lever manometer. The chief data are calculable to within 1%. P. W. C.

Sensitive Glass Manometer for Gases which Attack Mercury. A. Klemenc (*J. Amer. Chem. Soc.*, 1925, **47**, 2173—2175).—The manometer consists of an inverted funnel-shaped capillary tube with a very thin glass diaphragm over the end, which is nearly filled with a light paraffin oil and sealed into a thick-walled vessel. The latter, which is sealed up at the temperature at which the vapour-pressure measurement is to be made, contains a sample of the substance being investigated sealed up in a bulb and also a piece of iron, so arranged that the latter can be made to break the bulb by the application of a magnet. The top end of the capillary

tube is connected to a differential mercury manometer, the reservoir of which is raised during an experiment so as to keep the level of the oil in the capillary constant. The pressure is then read in the usual way. S. K. T.

Apparatus for the Extraction of Solids. R. STRUENSEE (*Chem.-Ztg.*, 1925, **49**, 647).—A modified form of the Soxhlet apparatus has a small glass cup with a bottom plate of sintered glass instead of the usual asbestos or paper thimble. The apparatus is useful for the extraction of sulphur from gas purification residues, using carbon disulphide or tetrachloride. A. R. P.

Device for Estimating Corrosion. W. R. FETZER (*Ind. Eng. Chem.*, 1925, **17**, 788).—A device for making comparative corrosion tests of metals in which the samples, consisting of small pieces of sheet metal, are partly immersed in the corrosive liquid in bent glass tubes and rocked uniformly. [Cf. *B.*, 1925, 765.] C. I.

Electrolytic Gas Explosions. W. NORMANN (*Chem.-Ztg.*, 1925, **49**, 757).—A discussion of the Fresenius safety-tube and other safety-devices. R. A. M.

Glass Filter Apparatus. P. H. PRAUSNITZ (*Analyst*, 1925, **50**, 440—444).—Glass filter apparatus is made by a process of grinding and sieving suitable glasses, and fusing particles of equal size to form filter discs with pores of approximately equal diameter. These discs may be fused together with the same type of glass in various pieces of apparatus, many of which are described. D. G. H.

Prevention of Bumping when Boiling Liquids. J. W. REBBECK (*Canadian Chem. Met.*, 1925, **9**, 177—178).—Small glass tubes closed at one end and having a small opening with sharp edges at the other are laid on the bottom of the container. S. I. L.

Mineralogical Chemistry.

Distribution of the Chemical Elements in the Earth's Crust. W. VERNADSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1916, [6], 1323—1342; from *Chem. Zentr.*, 1925, i, 2545).—Most of the bismuth minerals occur in the weathering zone of the earth's crust and are thus exposed to atmospheric influences. It is characteristic of the less numerous primary bismuth minerals that they generally occur in the presence of larger amounts of copper, cobalt, nickel, gold, lead, silver, or tin. The most important of the primary minerals have been deposited by steam. The natural concentration of bismuth is very slow and incomplete. G. W. R.

Occurrence of Hydrogen Sulphide in Limestone and Dolomite. W. NENADKEVITSCH (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1037—1040; from *Chem. Zentr.*, 1925, i, 2545).—Many limestones and dolomites yield hydrogen sulphide when pulverised. From 0·006% to 0·012% of hydrogen sulphide has been found to be present. G. W. R.

Hydrogen Sulphide in Limestone and Dolomite. W. VERNADSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1379—1388; from *Chem. Zentr.*, 1925, i, 2545; cf. preceding abstract).—The amount of hydrogen sulphide in different limestones and dolomites approximates closely to an average figure of 0·01%. This is regarded as not fortuitous, but it is not known whether it represents an equilibrium or a stable condition. Gypsum or natural gas may be the source of hydrogen sulphide. If the former be the case, the limestones and dolomites in question must have originated by the metamorphosis of clays or marls rich in gypsum. G. W. R.

Leverrierite as a Schist-forming Mineral. C. S. CORBETT (*Amer. J. Sci.*, 1925, [v], **10**, 247—268).—A number of schists from localities in the United States, especially those associated with quartzite, show a defect of potash by analysis, and some of them are found by a microchemical test to be free from potash. The micaceous schist-forming mineral in these cases is considered to consist wholly or partly of leverrierite. *X*-Ray powder photographs, compared with those of pure specimens of leverrierite, also gave clear indications of its presence. W. A. C.

Crystalline Modifications of $NaAlSiO_4$. N. L. BOWEN and J. W. GREIG (*Amer. J. Sci.*, 1925, [v], **10**, 204—212).—Whereas the hexagonal form, nephelite, is stable up to 1248°, the highly-twinned, possibly triclinic, form known as carnegieite or sodium anorthite undergoes a transition from a birefringent to an isotropic form at temperatures between 650° and 690°, varying with the specimen. The inversion, as followed under the microscope, is sharp in both directions. Another inversion at 226·5° is indicated by the heat-curves and also by a change of birefringency, which is sharp on heating but gradual on cooling. W. A. C.

Amphibolites from Austria. A. MARCHET (*Tsch. Min. Mitt.*, 1924, **36**, 170—211; 1925, **36**, 229—320).—Detailed petrographical descriptions with 25 chemical analyses are given of amphibolites, granulites, eclogites, and other rocks from the Waldviertel in Lower Austria. L. J. S.

Rhine Water. F. HABER and J. JÄNICKE (*Z. anorg. Chem.*, 1925, **147**, 156—170).—Twenty-three samples of Rhine water showed the presence of gold in amounts up to $10·3\times10^{-9}$ g./litre. The silver content varied between the limits 0—65×10^{-9} g./litre. J. S. C.

Measurement of the Altitude of the Layer of Ozone in the Atmosphere. J. CABANNES and J. DUFAY (*Compt. rend.*, 1925, **181**, 302—304).—Optical measurements lead to the conclusion that the altitude of the layer of ozone is of the order of 50 km.

J. S. C.

Analytical Chemistry.

Quartz Apparatus with Filtering Bottoms. G. F. HÜTTIG and H. KÜKENTHAL (*Chem.-Ztg.*, 1925, **49**, 716).—Silica crucibles with porous filtering bottoms of transparent or translucent, sintered quartz particles have been prepared in a manner similar to the porcelain crucibles previously described (Hüttig and Nette, this vol., ii, 431). The crucibles have the same resistance to attack by chemicals as the ordinary silica crucible, do not flake on heating or cooling, and are superior to ordinary Gooch crucibles.

A. R. P.

Oxycalorimeter. F. G. BENEDICT and E. L. FOX (*Ind. Eng. Chem.*, 1925, **17**, 912—918).—The principle involved is the accurate measurement of the contraction in volume produced when the substance under examination is burnt in a known volume of nearly pure oxygen, provision being made for the rapid absorption of the carbon dioxide produced. The calorific value is then found by application of a factor representing the calorific value of oxygen. The most accurate apparatus suitable for fuels is described in detail, whilst a simpler form may be used for substances with a greater error in sampling, such as foods and excreta. D. G. H.

Simplified Method of Micro-combustion; the Micro-Dennstedt Method. C. FUNK and S. KON (*J. Chem. Soc.*, 1925, **127**, 1754—1755).—The apparatus consists of a "pyrex" glass tube of the Pregl pattern fitted with an inner tube reaching about one-third the length of the outer and a diffusion stopper providing a double supply of oxygen. The combustion tube contains a platinum contact star and three boats filled respectively with molecular silver, lead peroxide, and red lead. The substance to be burnt is placed in a small boat in the inner tube and the combustion is carried out as described by Dennstedt, the temperature of the absorbents being maintained at 320°. In the determination of nitrogen by Pregl's method, high results are obtained unless the layer of reduced copper is placed at the end of the tube, as in the Dubsky process. A. R. P.

Preparation of Standard Solutions. F. PREGL (*Z. anal. Chem.*, 1925, **67**, 23—27).—A 12-litre cylinder is calibrated as nearly as possible by weighing and then filled with water to the 10-litre mark. A slight excess over the theoretical amount of substance the standard solution of which is required is added and, after

mixing, 40 c.c. are titrated with an approximately standard solution. The extra amount of water required to bring the desired solution to standard is calculated, but only 90% of this is added. Titration is repeated as before, and again 90% of the necessary water is added. A third titration is made against a weighed quantity of the standard substance, using the burette that is to be employed when working with the solution that is being prepared, and from the result of this the correct amount of water to be added to the solution to bring it exactly to standard strength is calculated and added. Finally, the solution is again titrated against a weighed amount of standard. In this manner, errors in the calibration of the measuring instruments are nullified. To prepare sodium hydroxide solution free from carbonate the hydroxide is dissolved in its own weight of water and the solution is kept at nearly 100° for several hours, then cooled slowly over-night. The clear liquor can be siphoned off and diluted as required; the residue contains all the sodium carbonate. A. R. P.

Differential Electro-titration. D. C. Cox (*J. Amer. Chem. Soc.*, 1925, **47**, 2138—2143).—The solution to be titrated (0·1 to 0·05*N*) is divided into two equal parts. Platinum wires are immersed in each and connected to a millivoltmeter. The two solutions, which are connected with a strip of filter paper, are now simultaneously titrated, one burette being always kept 0·2 c.c. ahead of the other. As the end-point is passed, the voltmeter readings suddenly pass from zero through a sharp maximum (end-point) and then rapidly decrease to nearly zero. Curves are not necessary for finding the maximum. Two maxima are obtained with soluble carbonates, one almost corresponding with the phenolphthalein, and the other with the methyl-orange, end-points. S. K. T.

Spectrophotometric Determination of Hydrogen-ion Concentrations and of the Apparent Dissociation Constants of Indicators. IV. Sodium α-Naphthol-2-sulphonate Indophenol. W. C. Holmes and E. F. Snyder (*J. Amer. Chem. Soc.*, 1925, **47**, 2232—2236).—The ratio R_2, the relative intensity of the two absorption bands at 520$\mu\mu$ and 600$\mu\mu$ (cf. Holmes, A., 1924, ii, 346), at various p_H values is determined for sodium α-naphthol-2-sulphonate indophenol. The indicator is relatively unstable in aqueous solution, but is stable in absolute alcohol. The dissociation of the dye follows the normal course of a monobasic acid, the apparent dissociation constant in 5% aqueous alcoholic solution being 8·63. In the spectrophotometric determination of hydrogen-ion concentration, the measurements must be made immediately after the preparation of the solutions. Data for the use of the indicator in the drop-ratio method (cf. Gillespie, A., 1920, ii, 282) are as follows: drop ratio, 1 : 9, 2 : 8, 3 : 7, 4 : 6, 5 : 5, 6 : 4, 7 : 3, 8 : 2, 9 : 1, p_H values, 7·68, 8·03, 8·26, 8·45, 8·63, 8·81, 9·00, 9·23, and 9·58, respectively. J. W. B.

Micro-determination of Hydroxyl Groups. B. Flaschenträger (*Z. physiol. Chem.*, 1925, **146**, 219—226).—By means of

a special apparatus and particular care in the preparation of the reagents, the method of Tschugaev and Zerewitinov (A., 1907, ii, 509) for the determination of hydroxyl groups, by measurement of the methane evolved on treatment with magnesium methyl iodide, has been adapted for use with 3—10 mg. of material. The best solvent in most cases is pyridine. C. R. H.

Determination of Chlorine in Benzaldehyde. J. D. Bukschnewski (*Z. angew. Chem.*, 1925, **38**, 723—724).—The sample (2 g.) is burnt in oxygen under pressure in a bomb calorimeter, which is then cooled with water. In releasing the pressure the gases are passed through 0·01*N*-silver nitrate, to which are added the washings from the calorimeter. Nitrous acid is removed by adding nitric acid and ferric alum and evaporating the whole to about half bulk. When cold, the unchanged silver nitrate is determined by titration with 0·02*N*-ammonium thiocyanate. The error is ±0·0018%. W. T. K. B.

Determination of Chlorine in Benzaldehyde and Cinnamaldehyde. T. H. Faust and T. Spängler (*Chem.-Ztg.*, 1925, **49**, 724—725).—Small quantities (*e.g.*, 0·02%) of chlorine in benzaldehyde and cinnamaldehyde are rapidly and accurately determined by gradually adding 25 g. of the sample, from a dropping funnel, to a mixture of 5 c.c. of fuming nitric acid and 25 c.c. of concentrated sulphuric acid. The resulting hydrogen chloride and sulphur dioxide are passed into a solution of silver nitrate. Heat is applied to complete the reaction, the silver nitrate solution is acidified with nitric acid, and the silver chloride determined gravimetrically. W. T. K. B.

Titration of Iodides with Iodate. I. M. Kolthoff (*Pharm. Weekblad*, 1925, **62**, 878—882).—Lang's method of titration in presence of cyanide is rendered even more delicate by using carbon tetrachloride in place of starch as an indicator. Mere traces of combined iodine in presence of large excess of bromides or chlorides can be determined, 0·1 mg. being titrated by means of a microburette and an *M*/60,000 solution of potassium iodate with an error not exceeding 1% in presence of 1 g. of potassium bromide. S. I. L.

Microchemical Determination of Sulphur. I. Determination of Sulphur in Easily Soluble Sulphides. W. Geilmann (*Z. anorg. Chem.*, 1925, **146**, 324—328).—Sulphur in easily soluble sulphides can be determined microchemically by titration with 0·05*N*-iodine and thiosulphate with an accuracy equal to that of the macrochemical determination. One to 2 c.c. of 2*N*-hydrochloric acid and 3—5 c.c. of the iodine solution are introduced into a stoppered Erlenmeyer flask. The sulphide solution is added from a pipette, or a solid sulphide weighed on the micro-balance and added from the weighing bottle as quickly as possible and the flask at once re-stoppered. The contents are shaken and after 10 mins. titrated back with thiosulphate. A blank experiment is carried out under the same conditions. Loss of iodine by evapor-

ation must be prevented, and the concentration of acid in the solution must be kept as low as possible. A. B. M.

Action of Some Oxidising Agents on Sulphite. II. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1925, **47**, 2156—2159; cf. this vol., ii, 712).—Sulphites may be determined accurately by titration with iodate solution, with free bromine, or with bromate, permanganate, or dichromate solutions containing half their equivalent of iodide. In the case of bromate, one-sixth of an equivalent of iodide suffices. It is recommended that titrations in which the action of air or escape of gas is to be guarded against should be carried out in a vacuum flask, which is described. S. K. T.

Action of Sodium Carbonate on Phosphates. A. COLANI (*Bull. Soc. chim.*, 1925, [iv], **37**, 937—940).—An investigation of the accuracy of the method frequently adopted in qualitative analysis for the separation of metals of the iron group in presence of phosphates. The action of sodium carbonate on phosphates of iron, chromium, manganese, barium, calcium, strontium, and magnesium was studied by adding to a solution of sodium phosphate four-thirds of the quantity of metallic salt necessary to form the tribasic phosphate, redissolving the precipitate in acid, precipitating with ammonium chloride and ammonia, and heating this precipitate with sodium carbonate. The phosphates of manganese and calcium are scarcely attacked by sodium carbonate, whilst those of chromium, strontium, and magnesium lose about half their phosphorus by this treatment. The method is completely successful only in the case of iron and barium. The addition of a little sodium hydroxide to the sodium carbonate gives identical results. L. L. B.

Determination of Small Quantities of Carbon Dioxide. S. NISHI (*Act. Schol. Med. Univ. Imp. Kyōtō*, 1925, **7**, 263—270). —In Warburg's method of determination of carbon dioxide (A., 1909, ii, 830) an error is introduced and the end-point of the titration rendered uncertain by the slow decomposition of barium carbonate. An apparatus has been devised whereby the barium carbonate is removed by filtration before titration. By this means the experimental error is reduced to less than 1% in determining 1·0 to 2·5 mg. of carbon dioxide. L. F. H.

Determination of Small Amounts of Carbon Dioxide. S. NISHI (*J. Biochem.*, 1925, **4**, 473—480; cf. preceding abstract).—To avoid the error involved in Warburg's method (*loc. cit.*) and the cumbersome filtration described in the preceding abstract, the carbon dioxide is absorbed in sodium hydroxide and the solution is titrated using thymolphthalein as indicator. Both systematic and casual errors are reported as being obtained by this method. L. F. H.

Separation of the Alkalis in Silicate Analysis. O. CANTONI (*Z. anal. Chem.*, 1925, **67**, 33—34).—In the method of Berzelius for decomposing silicates by hydrofluoric and sulphuric acids time

may be saved and a preliminary separation of the iron, alumina, and alkaline earths effected by evaporation of the sulphuric acid completely to dryness followed by ignition of the crucible to a dull red heat. The cold mass, when extracted with water, leaves a residue free from alkalis and the solution may be treated immediately with barium chloride to remove sulphuric acid and convert the alkalis into chlorides. The analysis is finished as usual. A. R. P.

Critical Studies on Methods of Analysis. XVI. Zinc. L. A. CONGDON, A. B. GUSS, and F. A. WINTER (*Chem. News*, 1925, **131**, 65—68, 81—84, 97—100, 113—117).—Comparative analyses of pure zinc nitrate were made by various modifications of the phosphate, sulphide, sulphate, oxide, and volumetric ferrocyanide methods and by several other less known methods. Practically all the results were within 0·2% of the theoretical. In using the phosphate method, the precipitate must be washed with dilute ammonium nitrate solution and not with hot water, which has a slight solvent action on the precipitate. For the determination of zinc in solutions containing alkali or magnesium salts, precipitation of the zinc with thiocyanate and pyridine followed by ignition to oxide gives satisfactory results. A. R. P.

Gravimetric Determination of Zinc by Means of Cyanamide. W. MARCKWALD and H. GEBHARDT (*Z. anorg. Chem.*, 1925, **147**, 42—49).—To a neutral solution of zinc salt 1—2 g. of ammonium acetate are added for each 0·1 g. of zinc. Dilute ammonia is added until the precipitate formed redissolves and the solution is faintly alkaline. Excess of ammonia must be avoided. A considerable excess of cyanamide is now added and the precipitate of zinc cyanamide allowed to settle on the steam-bath, filtered, washed with very dilute ammonia, and finally ignited and weighed as zinc oxide. In presence of nickel, for each 0·1 g. of metal 0·5—1 g. of ammonium thiocyanate or acetate is added and then an excess of cyanamide solution. Dilute ammonia is added dropwise until the solution just turns red litmus paper blue. The solution should have a green and not a blue colour. The zinc cyanamide precipitate is converted into oxide and weighed as such. Zinc can be determined in presence of magnesium by precipitation as cyanamide in presence of ammonium chloride and ammonia.

Cadmium may be precipitated as cyanamide in presence of ammonium chloride and ammonia. The washed precipitate is dissolved in dilute hydrochloric acid and the solution evaporated to dryness. The residue is then evaporated to fuming with sulphuric acid and weighed as sulphate.

The cyanamide solution is prepared by treating a mixture of calcium cyanamide with twice its weight of water with carbon dioxide at 40—70° until no more gas is absorbed. The filtered solution is treated with air to precipitate calcium hydrogen carbonate and again filtered. If a solution of cyanamide free from any traces of impurity is desired, the solution is evaporated in a vacuum

with a little acetic acid. The residue is extracted with ether and pure cyanamide obtained after evaporating the ethereal solution to dryness. In presence of a little acetic acid, cyanamide solutions undergo very small changes in concentration on long keeping.

J. S. C.

Determination of Very Small Quantities of Lead in Animal Tissues and the Ageing of Very Dilute Solutions of Lead Nitrate. H. BERNHARDT (*Z. anal. Chem.*, 1925, **67**, 97—105).—After destruction of the organic matter by any suitable process, the solution is treated with ammonium citrate and saturated with hydrogen sulphide. The precipitate is collected and dissolved in nitric acid and the solution is electrolysed at 2·8—3·2 volts for 1·5—2 hrs., using a rotating platinum gauze anode on which the lead is deposited as peroxide. The deposit is dissolved in 5% potassium iodide solution containing acetic acid, and ammonium acetate is added until the lead iodide dissolves. The liberated iodine is titrated with 0·001*N*-thiosulphate. Very dilute solutions of lead nitrate appear to undergo hydrolysis on keeping, the lead content segregating towards the bottom or top layers according as to whether the water used was boiled or not. In addition, there appears to be a considerable action on the glass involving the formation of a silicate of lead.

A. R. P.

Detection of Copper. G. SPACU (*Z. anal. Chem.*, 1925, **67**, 31—32).—The neutral solution is treated with a little ammonium thiocyanate and then with two drops of a 2% alcoholic tolidine solution. A flocculent precipitate of $CuC_{14}H_{16}N_2(CNS)_2$ having a Prussian-blue colour indicates the presence of copper. A similar precipitate is obtained by the use of potassium iodide and alcoholic benzidine. The tolidine compound is readily soluble in alcohol, whilst the benzidine compound is only slightly soluble.

A. R. P.

Standardisation of Titanous Chloride Solutions, and Potentiometric Titration of Copper. E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1925, **146**, 281—288).—Methods of standardising titanous chloride solutions, using the potentiometric method, have been investigated. The author recommends a standard copper sulphate solution for the purpose. The titration proceeds more smoothly, the potential reaching its equilibrium value more rapidly, than with potassium dichromate or ferric alum. The copper solution must be free from iron. Its strength is accurately determined by electrolytic deposition. The titration by titanous chloride is carried out in the presence of 4—8% hydrochloric acid with complete exclusion of air. Several determinations can be carried out with one and the same solution by re-oxidising after reduction with a few drops of concentrated bromate or dichromate solution. The method can be applied to the determination of copper in the presence of mercury, lead, cadmium, zinc, and arsenic.

A. B. M.

Separation of Copper and Mercury. G. Spacu (*Z. anal. Chem.*, 1925, **67**, 27—31).—The hot dilute solution of the chlorides of copper and mercury is treated with pyridine until it becomes blue, then with eight to ten times the weight of the combined metals in ammonium thiocyanate. After cooling, the green flocculent copper pyridine thiocyanate (cf. Spacu, A., 1923, ii, 40) is collected, washed with water containing pyridine and ammonium thiocyanate, and ignited very slowly to copper oxide for weighing. Mercury is recovered from the filtrate by acidifying with hydrochloric acid and passing a stream of hydrogen sulphide. A. R. P.

Direct Determination of Tervalent Iron in Silicates Insoluble in Acids. Use of the Method in Determining the Ratio of Ferric to Ferrous Iron after Decomposition of the Mineral with Sulphuric and Hydrofluoric Acids. O. Hackl (*Z. anal. Chem.*, 1925, **66**, 401—430).—Ferric iron may be determined directly in silicates by dissolving the minerals in the minimum quantity of sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, and, after cooling, pouring the solution into a saturated solution of boric acid sufficient to combine with all the hydrofluoric acid; the liquid is then titrated with 0·1*N*-titanous chloride solution using potassium thiocyanate as indicator. The results agree closely with those obtained by the indirect method (determination of total and ferrous iron and calculation of the ferric iron by difference), but are always 2 mg. too high due to slight oxidation during decomposition of the mineral. The process is useful in determining the ratio of ferric to ferrous iron in substances containing organic matter which would interfere in the permanganate titration. [Cf. *B.*, 1925, 711.] A. R. P.

Application of Liquid Amalgams to Volumetric Analysis. I. Determination of Molybdenum, Titanium, and Iron. T. Nakazono (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 109—117). —See A., 1921, ii, 596.

Electro-analytical Precipitation of Antimony. A. Schleicher and L. Toussaint (*Chem.-Ztg.*, 1925, **49**, 645—646).—Complete precipitation of antimony in an adherent and dense form may be obtained from a chloride solution to which tartaric acid and hydrazine sulphate have been added if the temperature is maintained at 60° and the voltage at 0·6 volt throughout the electrolysis, and a small amount of ammonium persulphate is added towards the end of the analysis. [Cf. *B.*, 1925, 740.] A. R. P.

Potentiometric Titration of Bismuth in Presence of Other Metals. E. Zintl and A. Rauch (*Z. anorg. Chem.*, 1925, **146**, 291—298).—The method previously described for the potentiometric titration of bismuth with titanous chloride (this vol., ii, 442) can be used for the determination of bismuth in the presence of other metals. Ferric iron is first reduced to ferrous, then the bismuth is precipitated. The solution is made slightly acid with hydrochloric acid (in acetic acid solution the method fails) and is

titrated hot. The beginning and the end of the reduction of the bismuth salt are shown by a well-marked fall in potential. The presence of a small quantity of an iron salt simplifies the titration of bismuth, obviating the necessity of first boiling out the air from the solution. Bismuth can be determined also in presence of lead (in a solution acidified by hydrochloric or acetic acid), tin (only in acetic acid solution), cadmium (in dilute hydrochloric acid solution), and arsenic (as arsenic acid in hydrochloric acid solution), but not in the presence of antimony. A. B. M.

Precipitation of Bismuth Sulphide from Acid Medium. S. RAMACHANDRAN (*Chem. News*, 1925, **131**, 135).—Precipitation of bismuth sulphide from hydrochloric acid solutions by hydrogen sulphide begins to take place when the proportion of concentrated acid to water is 1 : 3 and is complete when the ratio is 1 : 5. Conversely, precipitated bismuth sulphide is completely soluble at 30° in 1 : 3 hydrochloric acid. A. R. P.

Potentiometric Titration of Gold. E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1925, **147**, 256—261).—Solutions of gold, free from nitric acid, after first being boiled in an atmosphere of carbon dioxide for 10 mins. to expel dissolved air, followed by addition of a drop of bromate solution, are titrated potentiometrically with titanous chloride. The first fall of potential corresponds with the complete reduction of bromate and the commencement of the $Au^{\cdots} \longrightarrow Au$ reduction. The solutions should contain 4—10% of hydrochloric acid. In this way, gold can be determined in presence of mercury, tin, lead, and copper. In the case of copper, both metals may be determined in one operation. In presence of iron, a considerable amount of phosphoric acid should be added.
J. S. C.

Separation of Palladium from Platinum. F. KRAUSS and H. DENEKE (*Z. anal. Chem.*, 1925, **67**, 86—96).—A review of the methods of separating palladium from platinum by precipitation with α-nitroso-β-naphthol, acetylene, α-dimethylglyoxime, and mercuric cyanide shows that all these methods yield bulky precipitates which retain small quantities of platinum when the proportion of palladium present is high. The following method is recommended: the chloride solution is evaporated to dryness with a slight excess of ammonium chloride, the residue is dissolved in water, and the solution saturated with ammonium chloride. The precipitated ammonium chloroplatinate is collected, washed with saturated ammonium chloride solution, and dissolved in hot water. The platinum in this solution and the palladium in the filtrate are each precipitated by boiling with sodium formate.
A. R. P.

"Höchst Test" for the Determination of Anthracene. F. H. RHODES, M. L. NICHOLS, and C. W. MORSE (*Ind. Eng. Chem.*, 1925, **17**, 839—842).—The Höchst test (*Z. anal. Chem.*, 1877, **16**,

61) has been critically investigated. Loss may arise if an excess of chromic acid is present (as happens with rich samples of crude anthracene) because anthraquinone itself is oxidised by the hot chromic–acetic acid mixture. Very little loss takes place in the precipitation of the acetic acid solution by dilution, the separation being almost quantitative, and no loss by sulphonation occurs in the purification by solution in fuming sulphuric acid. In drying the anthraquinone a slight loss by volatilisation may occur. Filtering loss is prevented by using hardened filter paper in a Gooch crucible and is eliminated in the second filtration by using an asbestos mat, from which the anthraquinone is directly sublimed, preferably in a special oven at 350°. At that temperature sublimation is complete in ½ hr. Revised directions are given. [Cf. *B.*, 1925, 838,] W. A. S.

Determination of Methyl and Ethyl Alcohol. J. WIMMER (*Z. angew. Chem.*, 1925, **38**, 721—723).—Methyl and ethyl alcohol in aqueous solutions, the former also in the presence of acetone or formaldehyde, are determined by esterifying with a large excess of formic acid, with a small quantity of sulphuric acid as catalyst, and removing the ester as fast as formed by fractional distillation. The ester is distilled into sodium hydroxide, whereby it is quantitatively saponified, the last traces of ester being swept out of the apparatus with nitrogen, and the unchanged alkali is titrated. When formaldehyde is present, the sodium hydroxide should be cooled with ice. W. T. K. B.

Colour Reaction of *tert.*-Amyl Alcohol. L. EKKERT (*Pharm. Zentr.*, 1925, **66**, 599).—A strong alcoholic solution (0·5 c.c.) of *tert.*-amyl alcohol is mixed with 5 c.c. of concentrated sulphuric acid and strong tartaric acid solution is added. A rose-red colour appears first in the surface of contact and then throughout the supernatant layer. Guaiacol, resorcinol, or potassium guaiacolsulphonate can replace the tartaric acid, but the last named gives the most rapid reaction. A definite coloration is obtained with 3 mg. of *tert.*-amyl alcohol. R. B.

Comparison of the Polarimeter and Copper Reduction Values of Dextrose Solutions. H. L. WHITE (*Amer. J. Physiol.*, 1924, **68**, 116).—In the presence of 0·1*M*-phosphate solution, neither the copper value nor the polarimeter value of dextrose solution is changed in the presence of insulin and liver extract. Consistently lower figures are, however, obtained with the polarimeter than by copper reduction. A. A. E.

Influence of Nitrogenous Substances on Dextrose Determinations. L. ROSENTHALER (*Pharm. Zentr.*, 1925, **66**, 517—520). Determinations of dextrose by six well-known methods, involving reduction of copper solutions or of iodine, have been made in presence of small quantities of added ammonium chloride, asparagine, glycine, carbamide, uric acid, peptone, or urine, and the influence of the added substances is shown in tabular form.

Urine causes large errors in all cases and uric acid in most. The Rupp–Lehmann and Willstätter–Auerbach methods are in general least affected. G. M. B.

Analysis of Acetic Anhydride. W. S. CALCOTT, F. L. ENGLISH, and O. C. WILBUR (*Ind. Eng. Chem.*, 1925, **17**, 942—944).—Orton's method of determining small amounts of acetic anhydride in glacial acetic acid (T., 1911, **99**, 1181) has been adapted to the determination of acetic anhydride by acetylation of 2 : 4-dichloroaniline in glacial acetic acid. The 2 : 4-dichloroacetanilide is separated from the excess of dichloroaniline by extraction and washing with 10% hydrochloric acid and is hydrolysed by refluxing with 19% hydrochloric acid, and the resulting 2 : 4-dichloroaniline titrated with 0·1*N*-sodium nitrite solution. The dichloroacetanilide does not interfere, however, if the temperature is kept below 26° and the titration completed within 1 hr. of the time of dilution of the acetylated mass. [Cf. *B.*, 1925, 826.] D. G. H.

Colour Reaction for Lactic Acid. L. EKKERT (*Pharm. Zentr.*, 1925, **66**, 552—553).—If a dilute solution of lactic acid is poured on to a 1% solution of pyrocatechol in concentrated sulphuric acid, a blood-red coloration is produced at the surface of contact of the liquids. Alternatively, the dilute lactic acid solution, mixed with sulphuric acid, may be poured on to a 1% aqueous or alcoholic solution of pyrocatechol. The coloration is visible with 0·02% solutions of lactic acid. Resorcinol, quinol, and α-naphthol yield with lactic acid only greenish-yellow colorations. W. T. K. B.

Detection of Small Quantities of Lactic Acid in Fruit [Tomato] Juice as Calcium Lactate. A. BORNTRÄGER (*Z. anal. Chem.*, 1925, **66**, 430—460).—The detection of lactic acid in fruit juices containing citric, malic, and succinic acids is based on the solubility of calcium lactate in 75% alcohol and the insolubility of the calcium salts of the other acids in this solvent. After dilution of the alcoholic extract with water so that the alcohol content is about 93 vol.-%, addition of an equal volume of ether precipitates the calcium lactate as a syrup which crystallises in small bunches of needles after keeping for some hours. The fruit juice is treated with calcium chloride and milk of lime until slightly alkaline, evaporated to a syrupy consistency, and extracted with 95% alcohol, the extract being evaporated to dryness and the residue extracted with 93 vol.-% alcohol; the clear filtrate is then treated with ether as above. An alternative method consists in shaking the acidified juice with several small portions of ether, evaporating the ether extracts to dryness, and continuing the process as in the first method after neutralisation with calcium hydroxide. [Cf. *B.*, 1925, 734.] A. R. P.

Oxidimetric Determination of Tartaric Acid and Other Organic Substances. K. TÄUFEL and C. WAGNER (*Z. anal. Chem.*, 1925, **67**, 16—20).—Tartaric acid, sucrose, β-naphthol,

salicylic acid, and phthalic acid may be determined by heating the substance with twice the theoretical quantity of potassium dichromate and a large excess of 85% sulphuric acid for 15 mins. on the water-bath. After cooling and diluting the solution the excess of dichromate is determined iodometrically. A. R. P.

Precipitation of Oxalic Acid with Basic Bismuth Nitrate in Qualitative Analysis. A. KESCHAN (*Z. anal. Chem.*, 1925, **67**, 81—86).—Oxalic acid may be removed from the solution before precipitation of the group III metals by boiling the liquid with nitric acid until the bulk of the hydrochloric acid is expelled, adding basic bismuth nitrate and boiling for some time. Iron must be reduced to the ferrous condition and a little phosphoric acid added if chromium is present. The procedure is the same as that used for the separation of phosphoric acid (cf. Keshan, this vol., ii, 328). A. R. P.

Tests for Ethyl Phthalate. H. LEFFMANN and M. TRUMPER (*Amer. J. Pharm.*, 1925, **97**, 507—510).—The conditions suitable for the detection of small quantities of ethyl phthalate in alcohols by condensation with phenol or resorcinol are discussed. S. I. L.

Detection of Ethyl Phthalate. S. LEVINSON (*Ind. Eng. Chem.*, 1925, **17**, 929).—Ethyl phthalate, phthalic acid, or its salts may be detected by adding dry boric acid to the nearly evaporated sample and resorcinol to the dry residue. After further heating the mass is dissolved in water, and on rendering alkaline with sodium hydroxide a fluorescence indicates a positive reaction. [Cf. *B.*, 1925, 821.] D. G. H.

Detection of Ethyl Phthalate in Essential Oils. H. THOMS (*Apoth.-Ztg.*, 1925, **40**, 196; from *Chem. Zentr.*, 1925, i, 2475).—An adulteration of 10% of ethyl phthalate may be detected in certain essential oils as follows. The oil is evaporated to dryness on a water-bath with ethyl alcohol and sodium hydroxide solution. If a resinous residue is obtained, this is extracted with water and the aqueous extract evaporated to dryness. The residue is treated with cold sulphuric acid and resorcinol and heated at 80—85°. Some of this mixture is then added to ammonia solution. Freedom from ethyl phthalate is shown by the absence of any greenish-yellow fluorescence after 15 mins. Certain phenols such as eugenol interfere with the test since they also yield fluorescent condensation products with resorcinol. G. W. R.

Winkler's Bromine Method of Determining the Iodine Value of Fats. K. SCHEFFLER (*Pharm. Zentr.*, 1925, **66**, 533—538).—Winkler's bromine method of determining the iodine value of fats and oils gives equally good results as the Hübl iodine method in a much shorter time if the work is carried out in a flask or bottle of brown glass and the iodine value does not exceed 120. The results with fats having a higher value than

this do not agree very well with those obtained by the iodine method. The determination is carried out by shaking a solution of the fat in carbon tetrachloride with potassium bromide and bromate and a little hydrochloric acid; after 15 to 20 mins. for fats having an iodine value below 100, or 40 to 60 mins. for fats with a higher value, an excess of standard arsenite solution is added and the excess is determined by titration with potassium bromate. [Cf. *B.*, 1925, 728.] A. R. P.

Preparation of Bromine–Acetic Acid Solution for Determination of Iodine–Bromine Number [of Fats and Oils]. L. W. WINKLER (*Pharm. Zentr.*, 1925, **66**, 581—583; cf. *ibid.*, 571).—Commercial glacial acetic acid is distilled, rejecting the first and last fractions; the distillate is adjusted by addition of water to 96—97% strength, 0·3% by volume of bromine added, and the product distilled after one day. Further bromine is added, the solution standardised against castor oil, and adjusted to 0·1*N*. S. I. L.

Determination of Formaldehyde. G. ROMEO (*Annali Chim. Appl.*, 1925, **15**, 300—304).—With potassium hydrogen sulphite, especially in presence of the normal sulphite, formaldehyde reacts readily with formation of the neutral sulphonate, $OH{\cdot}CH_2{\cdot}SO_3K$. The excess of the hydrogen sulphite may be determined by titration with standard alkali hydroxide free from carbonate. [Cf. *B.*, Oct. 30th.] T. H. P.

Determination of Camphor in Plants, and Industrial and Pharmaceutical Products. G. GORI (*Annali Chim. Appl.*, 1925, **15**, 283—300).—Giglioli's method for the determination of camphor in plants, based on extraction of the distillate with ether and removal of the essential oil by means of filter-cloth and filter-paper, is tedious and results in considerable loss of camphor. Better results are obtained by using carbon tetrachloride in place of ether, and by eliminating the oil of camphor by oxidation with permanganate. Details of the procedure are given for plants, celluloid, spirit of camphor, camphorated oil, etc. [Cf., *B.*, Oct. 30th.] T. H. P.

Iodometric Determination of Cyanogen Compounds. R. LANG (*Z. anal. Chem.*, 1925, **67**, 1—15).—Cyanide or thiocyanate may be determined in a solution by addition of bromine and phosphoric or acetic acid followed by removal of the excess of bromine with ferrous ammonium sulphate or hydrazine sulphate, addition of potassium iodide, and titration of the liberated iodine with thiosulphate (cf. Schulek, A., 1923, ii, 591). When both cyanide and thiocyanate are present together the sum is obtained by the above process; in a second portion the cyanide is destroyed by the addition of formaldehyde and sodium or ammonium hydroxides and the thiocyanate is determined as above. In the presence of mercury salts, sufficient formaldehyde must be added to reduce the mercury to metal and sufficient bromine to effect its solution. If the solution contains also ferrocyanide, zinc sulphate is added before carrying out the foregoing operations and the ferrocyanide is determined

in a third portion by oxidation with permanganate in hydrochloric acid solution followed by destruction of the excess of permanganate with a little sodium nitrite and carbamide and titration of the iodine liberated by the ferricyanide on addition of potassium iodide. Details are given of the procedures employed in determining the above acids and the halogen acids in admixture.

A. R. P.

Determination of Cyanides and the Use of Benzene as an Indicator in Iodometry. N. KANÔ (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 101—107).—In the iodometric determination of cyanides a mixture of equal volumes of dilute solutions of boric acid and borax may be used for acidifying the solution before titration or by adding a solution of carbonic acid obtained by mixing the stoicheiometrical quantities of sodium hydrogen carbonate solution and dilute hydrochloric acid; in either case benzene is a better indicator than starch, as it has no action on the cyanogen iodide formed in the titration. More exact observations of the end point in the iodometric determination of chromates may also be made if the starch indicator is replaced by benzene. Ferricyanides may be determined iodometrically by the addition of potassium iodide followed by zinc sulphate to remove the ferrocyanide ions and subsequent titration of the iodine with thiosulphate, using benzene as indicator. A. R. P.

Determination of Allantoin in Presence of Uric Acid, Creatinine, and Amino-acids. E. LANGFELDT and J. HOLMSEN (*Biochem. J.*, 1925, **19**, 715—716).—In the determination of allantoin by precipitation with mercuric acetate, figures are obtained for the amount of allantoin in aqueous solution not more than 10% below the real amount. In presence of amino-acids in small quantities, and of creatinine and uric acid in quantities such as are present in normal urine, figures for allantoin obtained by the above method are higher and approximate to the real amount of allantoin. This is most probably due to the precipitation of other nitrogenous constituents. When amino-acids are present in larger amounts (0·2%), the figures for allantoin are too high. S. S. Z.

Reactions of Some Opium Alkaloids. L. DAVID (*Pharm. Ztg.*, 1925, **70**, 969—972).—The substance is dissolved in glacial acetic acid to which has been added a little "magnol" powder (commercial basic magnesium hypochlorite) and the solution carefully poured on to the surface of concentrated sulphuric acid. The various colour changes observed for thirteen opium alkaloids are tabulated, the colours being described by comparison with those of synthetic dyes of specified commercial origin.

G. M. B.

Identification of Secale Cornutum Preparations. [Detection of Ergotinine]. W. P. H. VAN DEN DRIESSEN MAREEUW (*Pharm. Weekblad*, 1925, **62**, 789—793).—The various methods of

identifying ergotinine by means of colour reactions are recapitulated. A more delicate test is the addition of an ethereal solution to 50% nitric acid, an intense blue ring developing at the surface of separation, and remaining for two days. The ether plays a part in the reaction, since only a faint yellow-brown colour appears if light petroleum be used. The reaction is attributed to the presence of nitrous acid. S. I. L.

Determination of Morphine by Conductometric Titration with Silicotungstic Acid. F.-E. RAURICH SAS (*Anal. Fís. Quím.*, 1925, **23**, 277—289).—Morphine in tincture of opium may be titrated with silicotungstic acid by a conductometric method. Narcotine and codeine may be similarly determined. Mixtures of these alkaloids give curves showing points of inflexion corresponding with successive precipitation of the alkaloids. G. W. R.

Physico-chemical Studies on Proteins. II. Alkali Binding. Comparison of the Electrometric Titration of Proteins and of Phosphoric Acid with Sodium and Calcium Hydroxides. W. F. HOFFMAN and R. A. GORTNER (*J. Physical Chem.*, 1925, **29**, 769—781).—The electrometric titration of phosphoric acid by sodium and by calcium hydroxides (cf. Wendt and Clarke, A., 1924, ii, 417) shows that dicalcium phosphate and tricalcium phosphate are formed at the same hydrogen-ion concentration as is disodium phosphate, in spite of the much smaller tertiary ionisation constant of phosphoric acid. It is supposed that dicalcium phosphate consists of 2 mols. of phosphoric acid, one of which has all its hydrogen atoms replaced by calcium, whilst the other has its secondary and tertiary hydrogen atoms free. The presence of a secondary hydrogen atom in dicalcium phosphate is also indicated by its reaction with sodium hydroxide at p_H 7·5. If the tertiary hydrogen atoms only of phosphoric acid were present, no combination would have occurred below p_H 12·0. The stability of tricalcium phosphate in relatively acid solutions and its bearing on physiological and biochemical problems are discussed.

Sodium and calcium hydroxides behave similarly towards the proteins, casein, durumin, teozein, and fibrin, which have been titrated electrometrically with these alkalis over the p_H range 4·7 to 11·0 and titrated back with hydrochloric acid. The titration curves of casein and fibrin show binding of alkali at p_H 5·5 and that of durumin at p_H 11·0, and are similar to the titration curves of weak acids. F. G. S.

Quantitative Colour Test for the Grignard Reagent. H. GILMAN and F. SCHULZE (*J. Amer. Chem. Soc.*, 1925, **47**, 2002—2005).—The solution to be tested (0·5—1 c.c.) is treated with an equal volume of a 1% solution of Michler's ketone in dry benzene. Water (1 c.c.) is then added slowly with agitation, and finally several drops of a 0·2% solution of iodine in glacial acetic acid. The presence of Grignard reagent is indicated by the development

of a characteristic greenish-blue colour. Positive results were obtained for 25 Grignard reagents examined. Calcium and barium phenyl iodides, and sodium ethyl and sodium *p*-tolyl, also gave colorations. No coloration was given by compounds in which the magnesium atom was attached to any element other than carbon. Zinc ethyl iodide, zinc diethyl, mercury diethyl, mercury di-*p*-tolyl, mercuric *p*-tolyl iodide, and lead tetraethyl also gave negative results, as well as normal and basic halides of magnesium. Magnesium ethyl bromide gave a positive test in 0·037*M* solution, whilst magnesium phenyl bromide gave a strong coloration in 0·02*M* solution. Metallic magnesium may give rise to a blue or purple colour on the addition of acetic acid in the test, and should be removed by prior filtration. F. G. W.

New Principle for Testing Organotherapeutic Powders. JAVILLIER, H. ALLAIRE, and [MLLE.] M. GROC (*J. Pharm. Chim.*, 1925, [viii], **1**, 513—525).—Dried materials from horse, pig, ox, calf, and sheep contain total lipoids: nervous tissue, 40—80% or more; suprarenal gland, liver, pancreas, and testicle, 25—40%; and lung, heart, kidney, muscle, spleen, thyroid, and ovary, less than 25%; total phosphorus: thymus, nervous tissue, pancreas, suprarenal gland, and testicle, 1·3—2% or more; spleen, kidney, liver, and lung, 1—1·3%; and heart, ovary, muscle, and thyroid, less than 1%; lipoid phosphorus: nervous tissue, pituitary, and suprarenal glands, 0·6—1·4%; testicle, liver, pancreas, lung, heart, kidney, and ovary, 0·35—0·6%; and placenta, spleen, thymus, thyroid, breast, and muscle, less than 0·35%; nucleic phosphorus: thymus gland, more than 1%; pancreas, spleen, placenta, lung, and testicle, 0·3—0·6%; prostate, liver, kidney, and ovary, 0·1—0·3%; and nervous tissue, heart, and muscle, less than 0·1%. Tables are also given of the percentage of total phosphorus which is lipoid: nervous tissue, 60—90%; pituitary, testicle, kidney, liver, heart, lung, suprarenal gland, and ovary, 35—55%; and pancreas, muscle, and spleen, 10—25%; the percentage of total phosphorus which is nucleic: calf thymus, 60%; pituitary, pancreas, spleen, thyroid, gastric mucous membrane, breast, placenta, ovary, lung, and prostate, 20—40%; testicle, liver, and kidney, 10—20%; nervous and muscular tissue, less than 10%. The figures differ so much from organ to organ as to be indexes to their respective organs, and this method may therefore be used for the characterisation and testing of organotherapeutic powders. B. F.

General, Physical, and Inorganic Chemistry.

Structure in the Secondary Hydrogen Spectrum. III. O. W. RICHARDSON (*Proc. Roy. Soc.*, 1925, **A**, **109**, 239—266; cf. this vol., ii, 909).—In a previous paper (cf. this vol., ii, 11), it has been shown that many of the lines of the secondary hydrogen spectrum which are weakened in electron discharges can be arranged in series. Regularities have now been found among the lines not selectively affected by the discharge; 132 additional lines have been classified. Up to the present, 20 combinations have been found, leading to 40 sets of term numbers, of which 22 are of half-quantum type. The changes of intensity in the spectrum produced by varying the temperature (from liquid air to the ordinary temperatures) are discussed, and it is held that they cannot decide between the translational and rotational origin of the lines, a point which is still under discussion. S. B.

Spark Spectrum of Lithium. S. WERNER (*Nature*, 1925, **116**, 574).—With an apparatus including a very intense source of light, and so arranged that fluorite windows are not introduced in the path of light, the classification of the spectrum denoted by Schüler as the doublet system of the Li II spectrum has been extended, and the conclusions already reached (this vol., ii, 165) have been confirmed. A. A. E.

Structure of the Red Lithium Line 6708 Å. J. B. GREEN (*J. Opt. Soc. Amer.*, 1925, **11**, 213—216).—Light from the negative electrode of a vacuum arc was focussed on the slit of a spectrometer and a Lummer plate placed between the collimator and prism. The Lummer pattern was found to be that of a simple doublet for low vapour densities. Changes in appearance with increased vapour density are ascribed to self-reversal. With increased current, a wide quadruplet pattern is formed which is attributed to Stark effects due to interatomic fields. E. B. L.

Series Spectra of Two-valency-electron Atoms of Boron (B II) and Carbon (C III). I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **26**, 310—318).—Thirteen lines additional to the *pp'* group of B II have been identified, and the identification has been completed of all the known boron lines of appreciable intensity; the classification into series of all the lines due to B II and B III is also completed. Term values assigned to the series lines for B II are tabulated. For C III, eight lines additional to the *pp'* group are recorded, and term values assigned. The progression of frequency separations and of screening constants for regular doublets from lithium to oxygen for 1 to 6 valency electrons is also tabulated. A. A. E.

Spectra of Silicon and Aluminium. W. C. MCQUARRIE (*Phil. Mag.*, 1925, [vi], **50**, 819—821).—The spectra of the under-water spark and arc between electrodes of an alloy of 23% silicon

and 77% aluminium have been observed. In addition to the known aluminium absorption lines, the under-water spark showed those of the silicon multiplet 2507—2529 and the first member of the silicon sharp series 2882. Attempts to photograph the silicon multiplet 1977—1988 gave only a continuous spectrum over that region. The under-water arc gave no silicon absorptions, but twelve aluminium absorptions in addition to those observed in the spark. A. B. M.

Arc Spectrum of Phosphorus. N. K. SUR (*Nature*, 1925, **116**, 542).—Series relations arising from Saltmarsh's observations (A., 1924, ii, 436) are pointed out. A. A. E.

***K*β Lines in the *X*-Ray Emission Spectra of Phosphorus and Potassium.** O. LUNDQUIST (*Z. Physik*, 1925, **33**, 901—915).—The *K*β line of phosphorus is dependent on the state of chemical combination of the element and also on the material of which the anticathode is composed. The chemical combination of the potassium does not affect the wave-length of its *K*β line. E. B. L.

Spectrum of Potassium at Low Voltages. F. H. NEWMAN (*Phil. Mag.*, 1925, [vi], **50**, 796—803; cf. this vol., ii, 723).—The radiation emitted by potassium vapour when bombarded by electrons depends on the energy of the electrons. Potassium vapour in a suitable discharge tube was bombarded by electrons which had been accelerated through a measured potential difference, and the radiation produced with gradually increasing *P.D.* was examined spectroscopically. The first doublet of the principal series appeared at 1·9 volts, and then other lines in the order corresponding with the energy levels calculated from the applied voltage. A. B. M.

Structure of the Nickel Spectrum. II. K. BECHERT (*Ann. Physik*, 1925, [iv], **77**, 537—559; cf. this vol., ii, 913).—The previous analysis is extended so that, in all, the intensities and combinations of 568 lines are tabulated. Two quintuplet and three triplet systems are described, the combinations being, respectively, $\varphi_1\delta_1$, $\varphi_1\gamma_1$, g_1f_1, d_1g_1, and f_2g_1. Several intercombinations of the singlet–triplet, singlet–quintuplet, and triplet–quintuplet types are recognised. Many of the latter type occur with lines of the high-temperature class, the quintuplet term φ_1 combining with d_1, d_2, $\bar{f}_1$, $\bar{f}_{1a}$, $\bar{f}_2$, and g_1. Of the singlet–quintuplet type, which usually is weak, the most easily excited is the $\bar{D}_1\delta_1$ combination. A comparison of the suggested energy levels of the iron, nickel, and cobalt atoms emphasises the spectroscopic regularities shown by this triad. Heisenberg's selection rule applies successfully to the intercombinations in the nickel spectrum. F. G. T.

Analysis of the Arc Spectrum of Copper. A. G. SHENSTONE (*Nature*, 1925, **116**, 467).—The copper spectrum is even more complex than was previously supposed. About 125 lines are accounted for by the new terms, which can be divided into two

sets, (*a*) all positive and combining with one or both of the known abnormally high *d*-terms, (*b*) negative, each combining with three or more of the first positive set. An explanation of the abnormally large inverted *d*-terms, due to Turner, is given. A. A. E.

Experimental Determination of the Relative Intensities of Some of the Molybdenum and Copper *K* Lines and the Tungsten *L* Lines. S. K. Allison and A. H. Armstrong (*Proc. Nat. Acad. Sci.*, 1925, **11**, 563—566).—By means of an ionisation method, the relative intensities of the strong *L* lines of tungsten, the *K* lines of molybdenum, some of the *K* lines of copper, and the weaker *L* lines of tungsten have been evaluated. The numbers are considered in relation to the extension to *X*-ray spectra by Sommerfeld and by Coster and Goudsmit of Burger and Dorgelo's rules (*Z. Physik*, 1924, **23**, 258) for relative intensities in the optical region. J. S. C.

Arc Spectrum of Palladium, its Zeeman Effect, and Spectral Type. C. S. Beals (*Proc. Roy. Soc.*, 1925, **A**, **109**, 369—384).—New observations have been made on the Zeeman effects in the palladium spectrum. Most of the Zeeman resolutions show marked dissymetries. The results have been used in analysing the spectrum, and it has been found that the arc lines consist of singlets, triplets, and intercombinations between singlet and triplet terms. The discovery of odd multiplicities in this spectrum suggests a rearrangement of the eighth group of the periodic table into three sub-groups corresponding with the three vertical columns. S. B.

Fine Structure, Absorption, and Zeeman Effect of the 2536 Mercury Line. R. W. Wood (*Phil. Mag.*, 1925, [vi], **50**, 761—774).—The fine structure of the 2536 mercury line has been studied by using two crossed Lummer-Gehrke plates of quartz. A magnetic field was used to press the discharge in the mercury arc against the wall of the lamp and so prevent reversal of the components of the line. The technique of the method is fully described. The line has five components of very nearly equal intensity, the separations being 0·014, 0·010, 0·011, and 0·011 Å., respectively. The apparent structure of seven elements observed by Nagaoka is shown to be due to absorption by the column of unexcited vapour in the type of lamp he used. The absorption of the light by mercury vapour is abnormally increased by the presence of nitrogen. Some qualitative observations on the Zeeman effect of the 2536 line were made. The interference dots were widened by the application of a sufficiently strong magnetic field, but only in one case were they split into distinct components. A. B. M.

Optical Excitation of the Mercury Spectrum, with Controlled Orbital Transfers of Electrons. R. W. Wood (*Phil. Mag.*, 1925, [vi], **50**, 774—796; cf. this vol., ii, 3).—The spectrum emitted by mercury vapour when excited by the radiation from a mercury arc has been studied with the view of testing Bohr's theory of the absorption and emission of light by metallic vapours.

A water-cooled quartz–mercury arc of the vertical type with tungsten anode was mounted close to a vertical quartz tube containing mercury vapour in a vacuum at the ordinary temperature. A magnetic field was used to deflect the discharge in the arc against the wall of the tube and so prevent reversal of the lines by absorption (cf. preceding abstract). The light emitted by the vapour was examined by a quartz spectrograph. By the use of suitable filters between the tubes, the vapour can be illuminated with two or more monochromatic mercury radiations. The lines emitted by the excited vapour are shown to conform with the possible orbital transfers of electrons on Bohr's theory. The effect of introducing nitrogen and other gases into the resonance tube is remarkable, certain frequencies being strongly enhanced and others decreased in intensity. Yet others appear which cannot be accounted for by the orbital transfers previously considered, but are due apparently to intermediate excitation of the nitrogen. A. B. M.

Screening-doublets of the Bowen-Millikan Ultra-violet Spectra. A. UNSÖLD (*Z. Physik*, 1925, **33**, 843—848).—A formula is obtained relating separation between the doublets and the effective charge of the core of the atom which is in satisfactory agreement with experiment. E. B. L.

Multiple Electron Transitions and Primed Spectral Terms. A. E. RUARK (*J. Opt. Soc. Amer.*, 1925, **11**, 199—211).—Low-voltage arcs were produced in heated silica tubes containing metallic magnesium and cadmium. The stronger lines of Mg^+ appeared at the expected potential above the ionisation potential of the metal. A single electron impinging on an atom can, therefore, ionise the atom and simultaneously raise another electron to a higher orbit. Photographs of the space between the grid and anode showed the lines Mg *pp'* (2776—2783 Å.), which are produced by the jump of two electrons as the result of a single impact. In cadmium, the similar group appears at its quantum voltage, but is too faint to be detected unless the current density is increased beyond the point which excludes the possibility of excitation by successive impacts. A number of new lines of cadmium were found, belonging to the singlet and triplet subordinate series. The cadmium lines were found to appear at the voltage to be expected. E. B. L.

Intensities of Zeeman Components of Multiplets. W. C. VAN GEEL (*Z. Physik*, 1925, **33**, 836—842).—Höhl's theory of the intensities was found to be in satisfactory agreement with experimental results for manganese (octuplets) and chromium (septuplets and quintuplets). E. B. L.

Diamagnetism and the Anomalous Zeeman Effect. P. TARTAKOVSKI (*Z. Physik*, 1925, **34**, 216—226).—Anomalous Zeeman effect is presumed to be caused by anomalous precession of the electron orbits and, as diamagnetism is a phenomenon the explanation of which involves precession of the orbits, a relationship may be expected to exist between the magnetic properties and the

anomalous Zeeman effect. A formula is obtained and applied to the cases of helium, lithium, sodium, potassium, and cæsium.

E. B. L.

Electrically Exploded Wires. S. SMITH (*Astrophys. J.*, 1925, **61**, 186—203).—By the use of a rotating mirror spectrograph, the order of appearance of lines in the spectra of exploded wires of various elements can be recorded photographically. Data are tabulated for lines between 3000 and 5000 Å. in the spectra of lead, tin, aluminium, copper, cadmium, and magnesium. Values representing the relative resistances of the vapours of copper, silver, gold, nickel, tungsten, zinc, aluminium, lead, tin, lithium, and iron are also given. In the case of certain elements, small areas of the surface of the vapour produced by the explosion were very opaque for wave-lengths in the region studied; the phenomenon is possibly due to anomalous dispersion. A. A. E.

Persistence of the Radiation excited in Mercury Vapour. L. J. HAYNER (*Physical Rev.*, 1925, [ii], **26**, 364—375).—The decay of radiation excited in a quartz cell containing mercury vapour at 40—100° by an intermittent mercury arc is shown by a photographic method to be exponential, and independent of the vapour pressure within the limits investigated. No persistence is observed if the cell does not contain liquid mercury, or if the cell is sealed off; thus the presence of fresh distilling mercury appears necessary, as well as the absence of air or water vapour which might be introduced during sealing. A. A. E.

Ionisation of Hydrogen Chloride by Electron Impacts. E. F. BARKER and O. S. DUFFENDACK (*Physical Rev.*, 1925, [ii], **26**, 339—345).—Earlier determinations of the ionisation potential of hydrogen chloride as 14 volts are confirmed by plotting current–voltage curves obtained with a two-electrode hot-cathode discharge tube, whether the gas was stationary or flowing. In the latter case, no hydrogen lines or bands whatever appeared with accelerating potentials up to 120 volts, and it is therefore considered that ionisation takes place without dissociation, as was postulated by Mackay. In the former case, faint hydrogen lines and bands are attributed to dissociation products arising from the thermal action of the filament. The fact that no critical potentials have been detected below that of ionisation indicates that when a hydrogen chloride ion is neutralised the electron is probably bound in a single operation. Exposure of the tungsten filament to hydrogen chloride increased its conductivity; Langmuir suggests that the chloride WCl_6 is formed and subsequently decomposed. A. A. E.

Critical Potentials in Secondary Electron Emission from Iron, Nickel, and Molybdenum. R. L. PETRY (*Physical Rev.*, 1925, [ii], **26**, 346—359).—Precision experiments were carried out in order to determine whether the number of secondary electrons emitted per primary electron changes gradually as the velocity of the primaries is increased, or whether at certain critical velocities

this number changes abruptly. All three metals after heat treatment gave similar results, the curves representing the ratio of the secondary emission to the primary current exhibiting maxima at 348, 455, and 356 volts for iron, nickel, and molybdenum, respectively. The ratio varied only slightly with the primary current, and neutralisation of the earth's magnetic field was also without influence. Up to 40 volts, good agreement was obtained between the critical potentials (about 60 in all) located by slight changes of slope of the curves, and soft X-ray levels determined by Thomas, suggesting that a common phenomenon is involved in the origin of the two effects. With high voltages, however, different phenomena have apparently been studied in the two investigations, photo-electric emission due to X-radiation being here masked by larger effects. A. A. E.

Electron Affinity of the Halogens. E. B. LUDLAM (*Trans. Faraday Soc.*, October 1925, advance proof).—Methods of determining the electron affinity of the halogens are considered. It is still doubtful whether the band of shorter wave-length observed in the spectra of the halogens originates in the atom and can be used for calculating the electron affinity. A. B. M.

Chemical Statics of Electronic Phenomena. L. ROLLA and G. PICCARDI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 29—31).—A thin metallic wire heated in a flame tends to emit electrons, and if the flame contains atoms A which give ions A^+ and electrons, these ions, on approaching or impinging on the metal, will be transformed into neutral atoms by the electrons of the metal. The electrons will remain free in the flame and, if collected and led back to the incandescent wire through a conductor, will give rise to a continuous electronic current, the intensity of which will be $15{\cdot}84\times10^{-20}$ amp. for each electron passing per second. The number of electrons per second is equal to the number of ions per second given by the reaction $A \rightleftarrows A^+ + \ominus$ and, since the concentration $[A]$ is readily calculable from the weight of substance volatilised in unit time and from Avogadro's number, the dissociation coefficient and the equilibrium constant of the reaction may be determined at once.

Preliminary experiments show that fine wire gauze is a suitable generator of electrons, and a piece of foil, placed above the gauze, a suitable collector. T. H. P.

Chemical Statics of Electronic Phenomena. Mass-action Law applied to Electronic Equilibrium. L. ROLLA and G. PICCARDI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 128—132).—The applicability of the law of mass-action to the thermal ionisation of salts according to the expression $A=A^+ + \ominus$, has been investigated. A bead of the salt to be examined is introduced into the flame, and the current through the flame, at a known potential-difference, is measured by a galvanometer. The concentration of the salt is varied by varying the number and size of the beads and the nature of the salt of any single metal. By this means

the law in question is shown to hold over a wide range of concentration for the thermal decomposition of salts of lithium, sodium, and barium. If x is the percentage dissociation of the salt and C the concentration of its vapour, x^2C is constant. The ionisation potential of a salt is obtained from the equation $\log K_2 - \log K_1 = U(1/T_1 - 1/T_2)/R$, the equilibrium constant being measured at two different temperatures. Experiments on lithium, sodium, potassium, rubidium, calcium, barium, thallium, copper, boron, and phosphorus show that, at the flame temperature used, only those elements with decomposition-potentials less than 8 volts are appreciably ionised. Since all elements of acid radicals exceed this limit, the observed current is entirely due to the ionisation products of the metallic atoms, which agrees with Arrhenius' observation that the conductivity of the flame is independent of the nature of the acid radical of the vaporised salt (A., 1891, i, 515).

W. E. E.

Refraction and Electron Constraint in Ions and Molecules. C. P. Smyth (*Phil. Mag.*, 1925, [vi], **50**, 715; cf. this vol., ii, 843).—Attention is directed to the work of Fajans and Knorr (*Chem.-Ztg.*, 1924, **48**, 403) on the same subject as the author's recent paper.

A. B. M.

Electronic Conduction in Crystals. H. Lenz (*Physikal. Z.*, 1925, **26**, 642—643; cf. *ibid.*, 1925, **26**, 36; this vol., ii, 920).—A reply to a criticism by Gudden and Pohl (this vol., ii, 943).

M. S. B.

Attachment of Electrons to Gas Molecules. V. A. Bailey (*Phil. Mag.*, 1925, [vi], **50**, 825—843).—A method is described for measuring the rate at which ions are formed when a stream of electrons moves through a gas. The electrons, generated by the incidence of ultra-violet light on a zinc plate, and the ions formed by collision with gas molecules move under a uniform potential gradient through equal apertures in three parallel metal plates, and finally impinge on a fourth plate. The stream of electrons and ions diverges between the plates, only part of it passing through the next aperture. The currents received by the plates, and therefore the ratio of the number of electrons and ions passing any particular aperture to the number impinging on that plate, are determined for varying gas pressures and potential gradients. From these it is shown possible to calculate k, the factor by which the mean energy of agitation of the electrons exceeds that of the molecules, and h, the factor giving the fraction of the number of collisions between electrons and molecules which produce ions. The apparatus is tested by using hydrogen, for which values of k are known. Results are given for dry air at pressures p of 8, 11·3, 16, and 22·6 mm. and gradients Z of 5, 7·07, 10, and 20 volts/cm. For values of Z/p, 0·5, 1, and 2, those of h are $3{\cdot}3\times10^{-6}$, 2×10^{-6}, and $0{\cdot}7\times10^{-6}$, respectively.

A. B. M.

Absorption Coefficient for Slow Electrons in Vapours of Mercury, Cadmium, and Zinc. R. B. BRODE (*Proc. Roy. Soc.*, 1925, **A**, **109**, 397—405).—The absorption coefficient, or the effective area of a molecule within which an electron is deflected, has been measured for electrons of from 0·4 volt to 50 volts velocity, in the vapours of these metals. With a few minor deviations the curves approximate to hyperbolas of the same size. No indications of long free paths at low velocities were found. S. B.

Negative Ion Emission from Oxide-coated Filaments. H. A. BARTON (*Physical Rev.*, 1925, [ii], **26**, 360—363).—Platinum, coated with barium oxide or strontium oxide, emits when heated negative ions (having a value for e/m of about 33) as well as electrons, but no positive ions. The ions are oxygen molecules which are probably detached from the filament in the already ionised condition. A. A. E.

Passage of Slow Canal Rays through Hydrogen. A. J. DEMPSTER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 552—554).—Experiments are described which show that protons with a velocity of $4{\cdot}16\times10^7$ cm./sec., corresponding with a fall through 900 volts, will pass through a great many hydrogen molecules without being neutralised. J. S. C.

Isotope Effect in Band Spectra. IV. Silicon Nitride. R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **26**, 319—338; cf. this vol., ii, 833).—The band spectrum between 3800 and 5300 Å., shaded towards the red, obtained by Jevons (A., 1913, ii, 813) by the introduction of silicon tetrachloride vapour into active nitrogen, and ascribed by him to a nitride of silicon, has been reinvestigated. The measurements have been repeated and extended to all possible heads; the intensity minimum observed by Jevons must represent the region of the null-line, the unusual prominence of which is ascribed to the low temperature of active nitrogen. That author's data must refer to $Si^{28}N$ heads; new photographs clearly show that these heads are accompanied, at theoretically anticipated positions, by satellites corresponding with $Si^{29}N$ and $Si^{30}N$, the former isotope being slightly more abundant than the latter, a result confirmed by Aston. Hence SiO or any compound other than SiN is definitely excluded as the emitter of the bands. Further, the results yield definite, but not conclusive, evidence against the existence of half-quantum numbers for SiN; such existence, however, would be expected in view of the close analogy between SiN and BO. Jevons' arrangement is revised, and correct initial (n') and final (n'') vibrational quantum numbers are assigned. The following wave-number equation is developed for the null-lines of the $Si^{28}N$ bands: $\nu=24234{\cdot}17+1016{\cdot}30n'-17{\cdot}773n'^2+0{\cdot}410n'^3-0{\cdot}00487n'^4-1145{\cdot}00n''+6{\cdot}570n''^2$. The internuclear distance for the vibrationless SiN molecule is computed to be $1{\cdot}56\times10^{-8}$ cm. In addition to these SiN bands, herein called A bands, an extensive new system of weaker bands, shaded towards the red, and presumed also to be due to SiN, has been observed; they are quenched in the same manner as the A bands by small

amounts of oxygen. The heads (for which an equation is given) are in pairs of about equal intensity; numerical values of the coefficients and the spacing of the structure lines are of the same order of magnitude as for the *A* bands. The intensity distribution of both systems of bands has been examined. A. A. E.

Determination of Mass of H-Particles. G. STETTER (*Z. Physik*, 1925, **34**, 158—177).—The mass of the hydrogen particle emitted by paraffin on bombardment by an α-particle was determined by a method similar in principle to Aston's mass-spectrograph, but the high velocity of the particles made it necessary to use much stronger electrical and magnetic fields to deflect the particles. The deflection was measured by observing the scintillations on a zinc sulphide screen with a microscope. The apparatus was calibrated by using α-particles from polonium, of known velocity. The result obtained was within 1% of the theoretical value for the hydrogen nucleus. E. B. L.

Mass Spectra of Light Elements. J. L. COSTA (*Ann. Physique*, 1925, [x], **4**, 425—456; cf. this vol., ii, 619).—The following results were obtained by the bracketing method, with a new modification of the mass-spectrograph, giving results correct to 0·03%, using the mass 4·000 of helium as standard of comparison: the masses of the atom and of the molecule of hydrogen are in the ratio of 1 : 2, the value for the neutral atom being 1·0079±0·0005; the values 6·009 and 12·000 are found for the lithium isotope 6 and the carbon atom, respectively; by comparison with the doubly ionised nitrogen atom, the lithium isotope 7 has a mass between 7·010 and 7·013 if the atomic weight of nitrogen be 14·008. W. H.-R.

Fundamental Atomic Weights. E. MOLES (*Z. physikal. Chem.*, 1925, **117**, 157—158).—A previous paper (this vol., ii, 346) is slightly amended. L. F. G.

Determination of the Variation of the Mass of the Electron with Velocity, using Homogeneous β-Rays. R. A. R. TRICKER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 384—396).—A method of determining the variation in the mass of the electron is described, using the homogeneous β-rays from thin layers of radium-*B* with velocities up to 0·8 of the velocity of light. In previous investigations, less homogeneous rays have been employed, with corresponding loss of accuracy. The rays are sent first through an accelerating and then through a retarding electric field, in a special magnetic focussing apparatus, and the deflections produced are measured. The results obtained agree better with the theory of relativity than with Abraham's theory of the rigid electron. The maximum error in the observed deflections is about 2%, whilst the theories differ by about 5%. The published measurements are preliminary only. S. B.

Transformation of Atoms into Radiation. O. STERN (*Trans. Faraday Soc.*, October 1925, advance proof).—Eddington's theory implies the transformation of mass into radiation. If this

is true the reverse process, radiation into matter, must be conceivable. In another paper (unpublished) the author deduced the conditions of equilibrium between the two processes by means of semipermeable membranes. A new deduction has now been made substituting the assumption that the energy and the entropy of a hollow space containing black radiation and an ideal gas in equilibrium represent the sum of the values that these quantities would possess if gas and radiation were each alone present. R. A. M.

"Meta-stationary" Atomic and Molecular States. A. SMEKAL (*Z. Physik*, 1925, **34**, 81—93).—Meta-stationary states may exist for a very short time as a result of absorption of radiation or of collisions. In these states the energy of the atom or molecule is not quantised and Ehrenfest's adiabetic principle is not applicable; they may be of fundamental importance in the scattering of radiation and in regard to dispersion. E. B. L.

Action of Atoms in Collision. N. BOHR (*Z. Physik*, 1925, **34**, 142—157).—Interactions between atomic systems are characterised as those which exhibit "reciprocity" and those which do not. The former class can be accounted for adequately by the quantum theory without sacrificing the conservation of energy as hitherto understood. In the latter class, the interactions can only be related by probability laws and the conservation of energy be taken as true in a statistical sense. Reference is made to the work of Bothe and Geiger (*ibid.*, 1925, **33**, 639) on the scattering of *X*-rays as indicating that the above treatment does not lead to a satisfactory solution of the problem. E. B. L.

Law of Photochemical Equivalents and the Place of the Quantum Theory in Relation to the Atomic Theory and Energetics. D. BERTHELOT (*Trans. Faraday Soc.*, October 1925, advance proof).—A *résumé* of the author's work (A., 1911, ii, 86; 1914, ii, 402; 1915, ii, 329; 1924, ii, 320). There are two factors of radiant energy, the capacity factor (radiant energy or action) and the tension factor (frequency or photochemical potential). Einstein's law is a special case of the law of equivalent capacity, which applies to every form of energy; Planck's constant is analogous to Faraday's electrochemical constant. The discontinuity of matter imposes discontinuity on the capacity factors by which the diverse forms of energy manifest themselves; thus there are three fundamental invariants of capacity, the electron, thermon, and radion. All verifications of the law of photochemical equivalents have hitherto been mere approximations. These views are developed by considering the kinetics of electrochemical, thermochemical, and photochemical reactions. R. A. M.

Derivation of Planck's Law from Einstein's Equation. A. S. EDDINGTON (*Phil. Mag.*, 1925, [vi], **50**, 803—808).—A deduction of Planck's law is given which does not involve the assumption of Boltzmann's formula. The latter is derived in the course of the argument. A. B. M.

Distribution of Electrons in Atoms. J. D. M. Smith (*Phil. Mag.*, 1925, [vi], **50**, 878—879).—A claim for priority addressed to citers of the work of Stoner (cf. this vol., ii, 85). A. B. M.

Quantitative Apprehension of the Principle of Correspondence and the Calculation of the Intensities of Spectral Lines. I. I. Tamm (*Z. Physik*, 1925, **34**, 59—80).—The principle of correspondence was originally merely qualitative. If the magnitudes calculated according to the quantum theory are equated to those calculated from classical theory, the formulæ can be tested and the principle made precise. This has been done. The equations obtained enable the relative intensities of the Zeeman components of any spectral line to be calculated. The addition rule of Ornstein, Burger, and Dorgelo (A., 1924, ii, 361, 433; this vol., ii, 251, 340) is a simple corollary. The Bohr frequency condition is a necessary consequence. E. B. L.

Structure of Magnesium. H. Collins (*Chem. News*, 1925, **131**, 212—215).—Speculative.

Origin of Band Spectra. M. Duffieux (*Ann. Physique*, 1925, [x], **4**, 249—318).—Owing to the Döppler–Fizeau effect, the thermal agitation of radiating atoms or molecules produces a slight widening of the emitted rays, the extent of which, under suitable conditions, depends only on the temperature and the mass of the particle emitting the radiation. The following deductions are made from measurements of the width of rays by an interference method. The 102 lines examined in the second spectrum of hydrogen are all emitted by the H_2 molecule. The first positive group of the nitrogen spectrum is emitted by the N_2 molecule, whilst the second positive group and the negative group of nitrogen, as well as the 3883 and 4212 bands of the cyanogen spectrum, are due to the nitrogen atom. In the spectrum of carbon monoxide, the bands 6079, 5610, 5198, 4835, 4511, and 4393 are due to the oxygen atom, and the band 4123 is due to either the oxygen or carbon atom and not to the molecule of the compound. The negative bands of nitrogen, and those of cyanogen and carbon monoxide agree well with the laws of succession deduced from Schwarzschild's theory, in spite of its dependence on the assumption that the bands are produced by molecules. The second positive and the negative groups of nitrogen are probably due to the neutral and ionised atom, respectively, whilst for the cyanogen bands the nitrogen atom is probably in a different state of ionisation. W. H.-R.

Structure and Distribution of Band Spectra. M. H. Deslandres (*Compt. rend.*, 1925, **181**, 387—392).—The formula $\nu=qd_1/rs\pm q'd_1/r's'$ is tested by means of Coblentz's measurements of the infra-red absorption bands of methane, acetylene, ethylene, chloroform, carbon tetrachloride, ethane, carbon dioxide, carbon monoxide, hydrogen sulphide, sulphur dioxide, carbon disulphide, and crystalline sulphur. The agreement is satisfactory. The bands for which r has the value 1 are the strongest. E. B. L.

Intensities of Band Lines. H. HÖNL and F. LONDON (*Z. Physik*, 1925, **33**, 803—809).—Laws are obtained for the intensities of lines in band spectra with a zero branch, representing the more precise application of quantum theory to the formula deduced from the principle of correspondence. E. B. L.

Excitation of the Band Spectrum of Helium. T. R. MERTON and J. G. PILLEY (*Proc. Roy. Soc.*, 1925, **A**, **109**, 267—272).—The conditions are discussed for the excitation of the band spectrum of helium, now generally ascribed to the helium molecule. Experiments are described which show that it is possible to produce marked intensity changes within this spectrum by altering the type of discharge. More especially, conditions have been found under which a green band (between 5387 and 5277 Å.), normally so weak that it has not previously been described, becomes a conspicuous feature of the spectrum. Excitation of high-pressure helium by a continuous discharge or by continuous high-frequency oscillations results almost exclusively in the appearance of the line spectrum of helium. Discontinuous discharges produce also the band spectrum. In explanation of the present, and of former, observations, it is suggested that the energy required to excite the band spectrum must be greater than that required for the arc spectrum. With continuous, or low-frequency, discharges, the exciting electrons in the positive column do not acquire sufficient velocity to produce the bands. They can only do so with discontinuous high-frequency discharges, when the resistance of the gas in the positive column will rise to high values in the intervals between discharges. The green band mentioned above can apparently be excited by slower electrons than the rest of the bands. The use of a hydrogen discharge tube in place of a very small spark-gap is described. S. B.

Band Spectra Associated with Carbon. R. C. JOHNSON (*Nature*, 1925, **116**, 539—540).—The conditions associated with the appearance of the Swan bands lead to the tentative suggestion that they are due to a CH or $(CH)_2$ molecule, whilst the triplet system is due to a molecule of greater hydrogen content, possibly CH_4. The CH band, at 4315 Å., and associated heads can be completely isolated from all other carbon spectra under suitable conditions. The author believes that the Ångström bands, the third positive bands, and possibly Cameron's new band spectrum arise from a neutral CO molecule, whilst Fowler's high-pressure bands probably arise from a more complex molecule. A. A. E.

Measurements of the Rotation Spectrum of Hydrogen Chloride in the Long-wave Ultra-red. M. CZERNY (*Z. Physik*, 1925, **34**, 227—244).—The absorption spectrum has been measured in the region 42 to 100 μ, and seven absorption maxima have been found with a constant difference of about 20/cm. The position of the bands can only be explained on the band theory by using half integral instead of integral quantum numbers. The comparison of this simple rotation spectrum with the rotation–oscillation spectrum in the shorter wave ultra-red shows good agreement. The isolation

of the radiation required was obtained by means of concave mirrors, a wire grating (used by Rubens), a celluloid film covered with lampblack, and a quartz lens. The radiation was received on an exceedingly sensitive micro-radiometer. E. B. L.

Vibration of the Carbonate Ion. S. CHAPMAN and A. E. LUDLAM (*Phil. Mag.*, 1925, [vi], **50**, 822—824).—An attempt is made to modify Kornfeld's theory of the infra-red frequencies of vibration of the carbonate ion (this vol., ii, 12) in order to obtain a better agreement with observation. No modification, however, which neglects to take account of the ions surrounding the carbonate ion appears likely to remove the difficulty. A. B. M.

Infra-red Absorption Spectra. L. MÁRTON (*Z. physikal. Chem.*, 1925, **117**, 97—128).—A method of measuring infra-red absorption spectra is described. Measurements of the absorption in a range extending from the visible to 4 or 5 μ were carried out with the following substances: hexane, *cyclo*hexane and homologues, benzene and homologues, aliphatic aldehydes and ketones, chloroform, carbonyl chloride, and thiocarbonyl chloride. The closing of a ring shifts the bands towards the infra-red, and also increases intensities. Homologues differ chiefly in the intensities of the bands, the positions of which remain nearly the same, but some divergence of the principal bands occurs on passing from lower to higher homologues. Unsaturation results in a shift towards the violet. The theory of band spectra is considered mathematically, and a formula for calculating wave-lengths is derived which gives results agreeing well with the observed data. L. F. G.

Flame Spectra and Chemical Reaction. (Miss) C. E. BLUKER (*Trans. Faraday Soc.*, October 1925, advance proof).—Previous measurements of the relative intensities of several members of the first and second subordinate series in the flame spectra of rubidium and cæsium (*Z. Physik*, 1924, **27**, 195) showed no such variation of relative intensity with temperature as should be expected on the basis of temperature radiation. Extension of the measurements to sodium and potassium flame spectra gave analogous results. It is suggested that, although the variation of relative intensity in the principal series of flame spectra may be explained on the temperature radiation basis, in the case of the subordinate series the effects are produced by the oxidation of the alkali metal atoms. A. E. M.

Spectroscopic Determination of the Electron Affinity of the Halogens. E. VON ANGERER and A. MÜLLER (*Physikal. Z.*, 1925, **26**, 643).—The absorption spectra of the ionised vapour of potassium fluoride, sodium and cæsium chlorides, potassium and cæsium bromides, and potassium iodide have been examined at two different temperatures, 1050° and 2200°, and the electron affinity of the halogens has been calculated from the long-wave limit, which is the same at each temperature. The values obtained

for the above salts in cal./mol. are 94·0, 86·6, 89·6, 79·1, 81·3, and 71·3, respectively. M. S. B.

Duration of Fluorescence of Mercury Vapour. R. N. GHOSH (*Physical Rev.*, 1925, [ii], **26**, 376—379).—Saha and Sur's explanation (A., 1924, ii, 803) of the after-glow of nitrogen is extended to the case of the fluorescence of mercury vapour. The fluorescing molecules are diatomic, and are given off by the liquid when the temperature is either rising or constant. Activation of each molecule occurs by absorption of energy corresponding with 6·7 volts. A. A. E.

Polarised Fluorescence in Solutions of Dyes. F. WEIGERT and G. KÄPPLER (*Z. Physik*, 1925, **33**, 801—802).—It is suggested that in the experiments of Lewschin and Vavilov (see this vol., ii, 629, 739) the light was not sufficiently intense to show the increase in polarisation with increasing concentration. E. B. L.

Permanent Modifications in Fluorescent Liquids. (MLLE.) M. ASTERBLUM (*Bull. Inter. Acad. Polonaise*, 1924, **A**, 7—8, 297—318).—Exposure of glycerol solutions of fluorescein to ultra-violet light results in a change in the colour of the fluorescence from green to blue. The intensity of fluorescence diminishes and after prolonged exposure the solution no longer gives out light. The solution does not recover its initial properties on long keeping. Indication of the formation of modifications on illumination is afforded by the appearance of a new band between 4900 and 4470 Å. in the fluorescence spectrum and the diminution in intensity of the band at 5500 Å. characteristic of normal fluorescence. On prolonging the action of the exciting light the new band in turn disappears. The absorption spectrum of the modified solutions shows a decreased absorption in the region 4900 Å. and an increased absorption in the region below 4600 Å. Purely chemical processes, *e.g.*, oxidation by the air, action of alkaline impurities, etc., may bring about similar changes. The maximum wave-length of the light capable of producing this modified fluorescence is about 2540 Å. Glycerol solutions of methylene-violet, corallin, crocein, æsculin, erythrosin, eosin, and rhodamine lose their fluorescent properties on exposure to the action of ultra-violet light. The rate at which these modifications are formed depends on the concentration, in general the rate being greater the more dilute the solution. Solutions of erythrosin, eosin, and rhodamine in benzyl alcohol are much more sensitive to the action of light than are the corresponding glycerol solutions. J. S. C.

Chemiluminescence. H. KAUTSKY (*Trans. Faraday Soc.*, October, 1925, advance proof).—The adsorption compounds of rhodamine and rhodaminesulphonate with colourless oxidation products of siloxen are strongly coloured and fluorescent. Addition of potassium permanganate solution to the adsorption compounds promotes a strong chemiluminescence which is not exhibited when the adsorbent alone is oxidised in the same manner. The fluores-

cence and chemiluminescence spectra of the adsorption compounds are identical. The intensity of the chemiluminescence decreases with decreasing temperature, whilst that of the fluorescence increases in the normal manner. It is concluded that the energy of oxidation of the adsorbent is transmitted to the dyes, since they are adsorbed in the planes of the adsorbent and are thus in the direct neighbourhood of places of reaction. The results offer justification of the view that whereas in chemiluminescence the energy of a chemical reaction causes the radiation, in fluorescence it is the adsorbed light which has the same effect, and that therefore it should be possible to force a fluorescent substance to give chemiluminescence by using suitable reactions to activate its molecules.

A. E. M.

Scintillations in Zinc Sulphide. J. STALONY-DĄBROVSKI (*Rocz. Chem.*, 1925, **5**, 193—214).—The luminescence produced by thoria in thin layers of zinc sulphide is investigated. It is found that each scintillation, on examination through a lens magnifying up to 40 times, consists of a small bright spot of light surrounded by a diffuse aureole, the shape of which depends on the location of the thorium atom in the layer, and the diameter of which varies from 0·1 to 0·3 mm. The duration of the scintillations is determined in three ways, the first method being that of Wood (A., 1905, ii, 664), depending on the measurement of the length of the arcs of light appearing on the screen during its rapid rotation. In this way, the duration of the scintillations is shown to be of the order of 1/200 sec. and not, as Wood found, 1/20000 sec., the greater part of the arc being invisible at the high speeds of revolution used by him. In the second method, the number, N, of scintillations appearing per minute on a fixed screen of 1 sq. mm. surface is determined. Before this screen is placed a revolving opaque glass disc, possessing a window in the form of an arc of angle α, and the number of scintillations per minute, $N_{\alpha\beta}$, is again counted, being less than N but greater than $N\alpha/2\pi$, the number which would appear if the scintillations were of infinitely short duration. The duration of the scintillations, t, is given by the formula $t=(N_{\alpha\beta}-N\alpha/2\pi)/Nn$, where n is the number of revolutions per second of the disc. The minimal values of t found were 1/29 sec. The third method is more convenient than the preceding ones, and gives more accurate results. A streak of radioactive matter is disposed radially on a glass disc, and is covered on the other side by a large sector of black paper. This disc is placed before a screen of zinc sulphide, of area 0·5 sq. cm., and revolved, the speed being reduced until the sparks cease to be visible, when $t=\beta/2\pi n$, where β is the angle between the streak of radioactive matter and the edge of the sector. In this way, t was found to be 1/6 sec., results of the same order being obtained using various samples of zinc sulphide. A disc phosphoroscope is also described, in which half the revolving disc is within a box containing the source of illumination, the other half showing bands of phosphorescence strikingly similar to those obtained using thoria as the excitant, *i.e.*, a bright band

followed by a larger diffuse region; this suggests that the mechanism of luminescence is the same in both cases. R. T.

Electrification by Friction between Solids and Gases. E. PERUCCA (*Z. Physik*, 1925, **34**, 120—130).—A stream of mercury vapour at a pressure less than 10^{-5} mm. was directed against a plate of iron, which was raised to a negative potential of about 500 volts. When platinum was used in place of iron the potential only reached about 300 volts and the platinum became covered with mercury. When the collector was nickel-plated, there was no electrification. E. B. L.

Mechanism of Breakdown of Damp Liquid Insulators. A. GYEMANT (*Z. Physik*, 1925, **33**, 789—800).—The moisture is supposed to exist as an emulsion and the spherical particles to be elongated under the electrical stress. When they form a continuous chain, the insulation breaks down. A formula is obtained relating voltage and water content and verified experimentally for damp transformer oil. E. B. L.

Spectrochemistry of Thiochromans, Δ^3-Thiochromens, and Thiochromanones. F. KROLLPFEIFFER (*Ber.*, 1925, **58**, [*B*], 1677—1680; cf. Krollpfeiffer, this vol., i, 1305).—The following data, *inter alia*, are recorded: thiochroman, $d_4^{17\cdot3}$ 1·1267, $n_{He}^{17\cdot3}$ 1·61600; 6-methylthiochroman, $d_4^{15\cdot4}$ 1·0907, $n_{He}^{15\cdot4}$ 1·60227; 6 : 8-dimethylthiochroman, $d_4^{15\cdot1}$ 1·0801, $n_{He}^{15\cdot3}$ 1·59667; 4-methyl-Δ^3-thiochromen, $d_4^{14\cdot6}$ 1·1310, $n_{He}^{14\cdot6}$ 1·63315; 4 : 6-dimethyl-Δ^3-thiochromen, $d_4^{12\cdot9}$ 1·1032, $n_{He}^{12\cdot9}$ 1·62082; 6-methyl-4-ethyl-Δ^3-thiochromen, $d_4^{15\cdot6}$ 1·0893, $n_{He}^{15\cdot6}$ 1·61014; 4-phenyl-6-methyl-Δ^3-thiochromen, $d_4^{99\cdot7}$ 1·0941, $n_{He}^{99\cdot7}$ 1·62734; 4 : 6 : 8-trimethyl-Δ^3-thiochromen, $d_4^{18\cdot3}$ 1·0829, $n_{He}^{18\cdot3}$ 1·60637; thiochromanone, $d_4^{13\cdot7}$ 1·2487, $n_{He}^{13\cdot7}$ 1·64313; chromanone, $d_4^{99\cdot3}$ 1·1291, $n_{He}^{99\cdot3}$ 1·54598; 6-methylthiochromanone, $d_4^{99\cdot5}$ 1·1376, $n_{He}^{99\cdot5}$ 1·59171; 6 : 8-dimethylthiochromanone, d_4^{100} 1·1204, n_{He}^{100} 1·58634; tetrahydrobenzothiochromanone, $d_4^{100\cdot5}$ 1·1536, $n_{He}^{100\cdot5}$ 1·60589; 5 : 6-benzothiochromanone, $d_4^{98\cdot9}$ 1·2162, $n_{He}^{98\cdot9}$ 1·68556. H. W.

Determination of the Principal Refractive Indices of Doubly Refracting Substances by Means of Federov's Plate. C. PERRIER (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 22—29).—An outline is given of the theory of a method for measuring the principal refractive indices of both uniaxial and biaxial doubly refracting crystals. T. H. P.

Rotatory Dispersion of Derivatives of Tartaric Acid. II. Acetyl Derivatives. P. C. AUSTIN and J. R. PARK (*J. Chem. Soc.*, 1925, **127**, 1926—1934; cf. Austin and Carpenter, A., 1924, i, 1164).—In solution in dry acetone or ethyl acetate, diacetyltartaric anhydride does not exhibit mutarotation, but is dextrorotatory showing "simple" dispersion. In the presence of water, the solution slowly becomes lævorotatory owing to hydrolysis of the anhydride ring, and the formation of diacetyltartaric acid, which may be isolated from the solution. The final readings depend on

the amount of water, owing either to association with water molecules or to ionisation of the acid. Diacetyltartaric acid has been obtained with 1½ mols. of benzene of crystallisation; the benzene is readily lost on heating, leaving the anhydrous acid (m. p. 118°), of which the solution in acetone is strongly lævorotatory with "simple" rotatory dispersion, the anomalous dispersion of tartaric acid being eliminated by acetylation of the hydroxyl groups. Although both acid and anhydride show simple dispersion, the solution during the mutarotation shows anomalous dispersion owing to the difference between the dispersion constants of the final and end products in agreement with the theory of Arndtsen (*Ann. Chim. Phys.*, 1858, **54**, 421). W. H.-R.

Optical and Magnetic Rotation Dispersion, Dispersion, Density, and Absorption Spectra of Chemically Homologous Compounds. A. KRETHLOW (*Z. wiss. Phot.*, 1925, **23**, 233—282).—The law of Verdet, that the specific magnetic rotation of a dissolved substance should be independent of the concentration, was found not to hold for camphor in benzene solution, nor for 3-methylamyl bornylenecarboxylate; the magnetic rotation increases with decreasing concentration. Wiedemann's law, that the magnetic rotation is proportional to the natural rotation, was tested for five derivatives of methylenecamphor, and for the bornylenecarboxyl esters of 3-methylpentinenol, 3-methylpentenol, and 3-methylpentanol. The law was found not to hold for any of these eight substances; with decreasing wave-length, the natural rotation increases more rapidly than the magnetic. The optical constants of the compounds were studied for a series of different wave-lengths. The simple Drude equation was investigated for the eight compounds. The value of λ_0 was not constant, but showed a marked progression which was the same in each homologous series, but was different for different series. The characteristic frequencies calculated from the dispersion were found not to coincide with those of the rotation. Hagenbach's law, that in homologous series the rotation dispersion curves, $f(\lambda)$, of the individual homologues only differ from one another by a constant c, holds very well for the two series investigated. The Hagenbach constant provides a satisfactory means of testing whether substances belong to homologous series or not. Ordinary dispersion behaves in this respect differently from natural rotation. Although with dispersion a constant is obtained, it cannot be used for ascertaining homologous series. The theories of Lorentz and Livens and of Oseen do not agree with experimental facts. The Cotton phenomenon, that with yellow-coloured substances anomalous rotation in the visible region can be caused by an absorption band in the ultra-violet, agrees with the results of investigation of twenty-four compounds. No regularity in the absorption spectra of compounds of homologous series was observed in six series investigated. W. C.

Theory of Rotatory Polarisation. R. DE MALLEMANN (*Ann. Physique*, 1925, [x], **4**, 456—458; cf. this vol., ii, 840).—Theoretical.

Mistakes in earlier papers are pointed out and corrected. The rotatory power is independent of the choice of axes used to describe the symmetry of the molecule, but in anisotropic liquids or gases a structural rotatory power exists which is absent in ordinary liquids or gases. W. H.-R.

Diffusion of Light by Active and Inactive Molecules. R. DE MALLEMANN (*Compt. rend.*, 1925, **181**, 371—374).—Theoretical. Optical activity is treated from the point of view of the Tyndall effect, which, except for the rotation of the plane of polarisation, is the same for optically active as for inactive substances. Simple equations are deduced for the diffusion of light through inactive substances, which are extended to optically active substances. Criticism is made of an observation by Gans (*Z. Physik*, 1923, **17**, 372). F. G. S.

Diffusion of Light by Methane and its Gaseous Homologues. J. CABANNES and J. GAUZIT (*J. Phys. Radium*, 1925, [vi], **6**, 182—198).—The light diffused by saturated paraffin hydrocarbons in the gaseous state is not completely polarised. The factor of depolarisation, which for methane (illuminated by sunlight) is 0·015, varies but little as the series is ascended up to *n*-hexane. It is concluded that this depolarisation is due to the carbon atom not possessing exactly the symmetry of the regular tetrahedron. The intensity of the light diffused transversely by ethane, propane, and butane is in accordance with the values predicted by Rayleigh's formula when this is corrected for the anisotropy of the molecules. The experimental value for methane exceeds the theoretical value by nearly 10%. E. E. W.

Molecular Scattering of Light in Liquids. K. S. KRISHNAN (*Phil. Mag.*, 1925, [vi], **50**, 697—715).—The intensity and imperfection of polarisation of the light scattered transversely by 65 different liquids has been measured. The liquids in glass bulbs were illuminated by a horizontal beam of sunlight. The bulbs were blackened except for suitable small windows and were immersed in a small rectangular tank of distilled water, which was also blackened, leaving similar openings. The scattered light was compared in intensity with that scattered by a block of Jena glass, using an Abney rotating-sector photometer. The Jena glass block was used as a secondary standard, being finally compared with a freshly prepared bulb of ethyl ether. The imperfection of polarisation of the scattered light was measured by Cornu's method. Some of the liquids are feebly fluorescent, as is shown by variations in the results when coloured filters were used in the incident beam and in the scattered beam. The relation between depolarisation and chemical constitution is briefly discussed. Comparison of the intensity of scattered light with that calculated from the Einstein–Smoluchowski formula, with a correction factor for imperfect polarisation, shows a satisfactory agreement except for liquids of high refractive index. A. B. M.

Measurement of the Coefficients of the Absorption of Light by Fluorescent Substances. S. PIENKOVSKI and A. JABLONSKI (*J. Phys. Radium*, 1925, [vi], **6**, 177—181).—The fall of intensity of the fluorescence formed by a beam of parallel monochromatic rays passing through the liquid is measured photographically. From this the coefficient of absorption of light can be calculated. The method is applicable both to visible and to ultra-violet light if it is monochromatic. Results obtained for fluorescein were found to be in good agreement with those obtained by other methods.

E. E. W.

Valency Theories and the Magnetic Properties of Complex Salts. L. A. WELO and A. BAUDISCH (*Nature*, 1925, **116**, 606—607).—An application of theories of electron-sharing (cf. Sidgwick, T., 1923, **123**, 725) to salts which have been studied magnetically. In certain diamagnetic salts, iron and cobalt attain the configuration of the diamagnetic element krypton; in certain salts of ruthenium and rhodium, the metallic atom attains the configuration of xenon, whilst in their diamagnetic salts, iridium and quadrivalent platinum attain the configuration of radon. The nearly diamagnetic substances potassium permanganate and potassium dichromate yield the configuration of argon if each oxygen atom removes 2 electrons and each potassium atom receives 1 electron. A different treatment is accorded in the case of salts giving magneton numbers which are not zero, the existence of stable configurations other than those of the rare gases being assumed. Chromium, nickel, and copper are examined from this point of view. A. A. E.

Repulsive Action of Mutually Equal and Mutually Differing Groups in Saturated Organic Compounds. J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 371—385).—A large number of measurements of the increase in conductivity of boric acid caused by the addition of various polyhydroxy compounds and hydroxy-acids (due to the formation of double compounds when the hydroxyl groups are situated close together) are adduced as evidence of the repulsive action of various groups in organic compounds, and supported by measurements of the heats of combustion and dissociation constants of the corresponding acetone compounds. In pentacyclic compounds where such repulsive action is inoperative owing to the ring structure, only *cis*-diols cause an increase in conductivity as in *cis-cyclo*pentane-1 : 2-diol, mannitan, and the tartrimides, the action being independent of the nature of the remainder of the ring. In the α-glycols the mutual repulsion of the hydroxyl groups forces them closer together as their number increases, this being evidenced by the increasing effect on the conductivity of boric acid on passing from ethylene glycol (most unfavourable position) to glycerol, erythritol, mannitol, dulcitol, and sorbitol, whilst in mannitan the position of the two hydroxyl groups on the same side of the five-membered ring has a larger effect than the six hydroxyl groups in mannitol. This mutual repulsion causes polyhydroxy compounds (*e.g.*, sugars) to assume configurations very different from the conventional space

formulæ, as is evidenced by the fact that mannitol combines easily with 3 mols. of acetone, the hydroxyl groups in the middle of the chain being favourably placed. Evidence for the mutual repulsion of hydroxyl groups is found in the fact that ethyl and benzylamine mesotartrates only yield *cis*-ethyl- or benzyl-tartrimide when heated below 115°, whilst at 165° the *trans* form is produced. The corresponding *cis*-methyltartrimide cannot be obtained, since at the necessary temperature (140—145°), the *trans* form is exclusively produced. Heats of combustion (the figures given being new determinations) for fumaric and maleic acids, mesaconic and citraconic acids, *d*- and *i*-ethyltartrimide (671·1 and 672·7, respectively), *d*- and *i*-benzyltartrimide (1237·8 and 1240·7, respectively), *cis*- and *trans*-hydrindene-1 : 2-diols (1098·5 and 1096·7, respectively), and *cis*- and *trans*-1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-diols (1251·0 and 1249·4 cal./mol. at constant pressure, respectively) show that the *cis* form has always the larger value, indicating the lesser stability of this form. The repulsion of two methyl groups is indicated by the higher heat of combustion of *i*- (*cis*) *s*-dimethylsuccinic anhydride (681·0) than of the *trans* form (679·2 cal./mol.). In the tartaric acids and their esters, the repulsion of the carboxyl and carbethoxy groups causes the hydroxyl groups to approach more closely together in the active and racemic forms than in the *meso* form, as is evidenced by the greater increase produced in the conductivity of boric acid in the former cases. The mutual repulsion of phenyl groups is demonstrated by the greater dissociation constant for the acetone compound of racemic hydrobenzoin (K_{25}=8·55) than for the *meso* form (K_{25}=0·44), in agreement with the boric acid conductivity measurements and by the easy transition of *iso*stilbine (*cis*) into the *trans* form. The ready transformation of *allo*- into ordinary cinnamic acids and the heats of combustion of a large number of substituted cinnamic and coumaric acids are cited as evidence of the mutual repulsion of the phenyl and carboxyl groups. The action of dilute acids on the oxide of 1-phenyl*cyclo*hexane-1 : 2-diol yields primarily the *trans* form of the diol, but this immediately reverts to the *cis* form, in opposition to steric effects, due to the repulsion of the phenyl and the 2-hydroxyl group, a result confirmed by the greater heat of combustion of the *trans* (8136 cal./mol.) than of the *cis* form (8132 cal./mol.). Boric acid conductivity measurements on the tartramides show that the carbamide group and the hydroxyl group repel each other with greater force than they do like groups. Thus the mean positions of molecules are greatly dependent on all the groups present and on their interaction one with another; rotatory power cannot be a simple function of the groups present, and the principle of optical superposition cannot be strictly valid (cf. Patterson and Patterson, A., 1915, ii, 78). J. W. B.

Spectrochemistry in the Ultra-red. IX. Origin of the Absorption Bands Incorrectly Attributed to the Groups $-CH_3$ and $-CH_2-$. G. B. Bonino (*Gazzetta*, 1925, **55**, 576—582).—It has been shown (Bonino, A., 1923, ii, 711; this vol., ii,

838) that (*a*) even compounds not containing carbon exhibit an absorption band at 3·4 μ, (*b*) in its variation from compound to compound, the maximum absorption coefficient of this band quantitatively follows the variation in the number of hydrogen atoms and is independent of the number of carbon atoms present. On the basis of the Julius hypothesis, that the absorption band in question is due to the oscillation of the $-CH_3$ or $-CH_2-$ groups about the positions of equilibrium to which they are constrained by the valency-bonds which connect them to the rest of the molecule, although the effect of the small difference in the masses of $-CH_3$ and $-CH_2-$ on the position of the absorption maximum would be inappreciable, the value of K in the formula, $\nu=(K/m)^{\frac{1}{2}}/2\pi$ (Kratzer, A., 1921, ii, 142) would be twice as great for $-CH_2-$ as for $-CH_3$. Again, if the hydrogen atoms of ethane are substituted by halogen atoms, the above formula shows that $\lambda_{max.}$ (λ at the absorption maximum) would increase with the number of substituted halogen atoms; but experiment shows that all such halogen derivatives have $\lambda_{max.}$ 3·4 μ (approx.). If the Julius hypothesis is accepted, it must be assumed that the valency-attraction between the carbons in pentachloroethane is seven times that between the carbons in ethane, a conclusion contrary to all known facts. The hypothesis also fails when confronted by the facts that completely halogenated compounds give no band at 3·4 μ and that the position of the corresponding band for the compound $CX_3{\cdot}CX_3$ is the same as that of the corresponding band for the compounds $CX_2{:}CX_2$. It therefore appears that the absorption band at 3·4 μ in the spectra of compounds containing hydrogen linked to carbon is due to the vibration of hydrogen atoms about the positions of equilibrium to which their valency bonds constrain them (cf. Ellis, A., 1924, ii, 218, 219). W. E. E.

X-Ray Methods of Supplementing and Correcting Crystallographic Data. K. Yardley (*Phil. Mag.*, 1925, [vi], **50**, 864—878).—The limitations of the usual goniometric and *X*-ray methods of determining the dimensions and symmetry of the unit cell of a crystal are discussed, and it is shown how one method may supplement the other. *X*-Ray measurements are recorded of potassium hydrogen chloromaleate, ammonium chlorofumarate, and ammonium hydrogen fumarate, and are used to correct existing crystallographic data. A. B. M.

Reflection of *X*-Rays by Alkali Halide Crystals. (Miss) A. H. Armstrong, W. Duane, and R. J. Havighurst (*Proc. Nat. Acad. Sci.*, 1925, **11**, 218—221).—It is shown that crystals of cæsium iodide and of potassium iodide are wont to exhibit abnormal peaks in their *X*-ray spectra, and that these peaks are probably due to rays reflected by small displaced crystals in the main mass. R. W. L.

Reflection of *X*-Rays in Potassium Bromide Crystals. H. Kulenkampff (*Physikal. Z.*, 1925, **26**, 657—658).—Early experiments by Duane and his colleagues seemed to show that

alkali halide crystals reflect the lines of the *K*-series of the halogen atoms. This has not been confirmed by later work. The author has examined, both by the revolving crystal method and by the Seemann method, potassium bromide crystals which, on account of their small size, were not likely to contain structural irregularities, and has found no selective reflection of noticeable intensity indicated on a photographic plate. M. S. B.

Compton Effect with Hard *X*-Rays. D. L. Webster and P. A. Ross (*Proc. Nat. Acad. Sci.*, 1925, **11**, 224—226).—A short preliminary note indicating the scope of the research and citing the evidence obtained with rays scattered by glass and by graphite which is in good quantitative agreement with the predictions of Compton's theory. R. W. L.

Wave-lengths of Scattered *X*-Rays. S. K. Allison and W. Duane (*Physical Rev.*, 1925, [ii], **26**, 300—309).—The scattering of molybdenum $K\alpha$ rays by aluminium and lithium has been examined, and isolated experiments have been performed using beryllium, carbon, sodium, sodium chloride, magnesium, and sulphur as scatterers. The shift of the maximum intensity of the modified band is in agreement with Compton's quantum theory of scattering. For lithium, the width of the modified band is greater than that permitted by Compton's equation. Experiments in which tungsten primary rays were employed were less trustworthy, but the radiation was shifted as expected. Ross' observation, that the relative intensity of the shifted peak is greater for a given element than in the scattering of molybdenum rays, was confirmed. A. A. E.

Directed Quanta of Scattered *X*-Rays. A. H. Compton and A. W. Simon (*Physical Rev.*, 1925, [ii], **26**, 289—299).—As a result of measurements of the direction of *X*-ray scattering on stereoscopic cloud expansion photographs, it is held proved that a large proportion of the scattered *X*-rays proceed in directed quanta of radiant energy. The conclusion supports the view that energy and momentum are conserved during the interaction between radiation and individual electrons, but appears irreconcilable with the view of the statistical production of recoil and photoelectrons proposed by Bohr, Kramers, and Slater. A. A. E.

Non-existence of the Clark–Duane Secondary Spectra from Faultless Crystals. A. P. Weber (*Z. Physik*, 1925, **33**, 767—776).—Photographs were taken of *X*-rays reflected from faultless crystals of potassium bromide, rubidium alum, and copper sulphate, using the Seemann knife-edge method; the intensities of the lines were measured by means of a Moll photometer. No secondary lines appeared. E. B. L.

Asymmetric Emission of Electrons Produced by *X*-Rays. II. W. Sertz (*Physikal. Z.*, 1925, **26**, 610—615; cf. this vol., ii, 168).—Previous work has been extended to determine whether the asymmetrical emission of electrons from a metal film placed in

a beam of X-rays is confined to electrons from the outer levels, or extends to those from the X-ray levels. With a copper film asymmetrical emission of electrons from the K- and L-levels occurs, the asymmetry being the greater in the case of the L-electrons. The asymmetry of emission is less with silver than with copper. With lead the asymmetry is slight, although the ratio of the electron-emission from the surface from which the X-rays emerge to that from the incident surface increases in the region of high electron velocities. F. G. T.

X-Ray Investigation of Black ("Metallic") Phosphorus. G. Linck and H. Jung (*Z. anorg. Chem.*, 1925, **147**, 288—292).—The density of "metallic" phosphorus is d_4^{20} 2·699. The X-ray diagram yields the lattice constants a=5·96 Å., α=60·47°, corresponding with eight atoms per unit rhombohedral cell. The Δ-parameter is approximately 0·17. A. G.

Crystal Structure of Manganese. A. Westgren and G. Phragmén (*Z. Physik*, 1925, **33**, 777—788).—X-Ray photograms show that α-manganese which is stable at the ordinary temperature is cubical; at higher temperatures, it changes into a β-form, likewise cubical but slightly denser. Electrolytic manganese is tetragonal, but has the same density as α. Carbon dissolves in manganese in the same way as in iron, not by replacing atoms of the metal, but by lying between them. E. B. L.

Structure of Aragonite. S. I. Tomkeieff (*Min. Mag.*, 1925, **20**, 408—434).—Based on the X-ray measurements of W. L. Bragg (A., 1924, ii, 109), a new structure (leptonic) model is proposed for aragonite, although this does not explain the intensities of the X-ray spectra. The new model, which belongs to the space-group C_{2h}^1, explains the ready transformation of aragonite into calcite and also the shapes of the etch-figures developed by the action of acid on the different crystal-faces. L. J. S.

"Somatoid" Forms. V. Kohlschütter and C. Egg (*Helv. Chim. Acta*, 1925, **8**, 457—469).—The occurrence is discussed of minute particles of definite shape and structure which are deposited from mixed solutions and do not consist of a pure crystalline form. These "somatoid" forms depend for their characteristic shapes on the presence of impurities which influence crystal habit, twinning, and rate of crystallisation, and are regarded as definite physico-chemical units of individual character. The phenomenon is discussed with reference to the deposition of calcium carbonate from solutions of the hydrogen carbonate in a current of air and in presence of a variety of added impurities such as salts of the alkali metals, magnesium, strontium, and the heavy metals, and colloidal substances such as dyes. The first influence of the salts is to retard crystallisation and to favour the less stable forms—the faces of higher indices, the less stable crystal system, and finally a hydrated calcium carbonate. The dyes cause first a modification of crystal habit and then the deposition of definite shapes characteristic of the individual dye used, these effects being attributed to interference

with crystallisation by adsorption on to the surface of the growing crystal. The "somatoid" forms are also obtained in the presence of cobalt and nickel salts which yield colloids in solution, and the particles may be either modified crystal growths or complex aggregates consisting partly of colloidal material and not essentially crystalline in origin. The influences which contribute to their formation, such as lattice forces, retardation of diffusion by colloidal material, and the forces in the surface layer, are discussed in detail.

G. M. B.

Alterations of the Habit and of the Modification of Calcium Carbonate by Substances in Solution. V. KOHLSCHÜTTER and C. EGG (*Helv. Chim. Acta*, 1925, **8**, 470—490; cf. preceding abstract).—Calcium carbonate is deposited from a calcium hydrogen carbonate solution below 30° in the form of primary calcite rhombohedra, but above 30° aragonite is obtained. With increasing concentrations of other salts present, such as sodium or potassium chloride, negative rhombohedra are deposited which are more and more acute, crystallisation being slower and the number of crystals fewer. Still higher concentrations of various salts cause the hydrate $CaCO_3,6H_2O$ to separate. The surface forces and energy relations involved in the production of these different crystals are discussed in detail.

G. M. B.

Crystalline Structure of Perowskite. G. R. LEVI and G. NATTA (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 39—46).—*X*-Ray examination by the Debye–Scherrer method indicates for perowskite a face-centred cubic lattice. In the conditions employed, however, this method gives less exact data than the optical and other physical data employed in determining the true symmetry of crystals. Laue's method confirms the view that the structure of perowskite is virtually that of a face-centred cube, the elementary cell having the side 7·68 Å. and containing 8 mols. of $CaTiO_3$. The crystallographic and optical results indicate that the pseudo-cube of perowskite is composed of the two rhombic forms (001) and (110), and of the Laue diagrams corresponding with the three pairs of faces of the pseudo-cube two are similar and the third is different. The fact that the symmetry of the photograms is apparently of higher order than that of rhombic crystals is possibly the result of superposition of differently oriented lamellæ.

T. H. P.

Structure of Kaolin. Theory of the Structure of Silicates. M. DOMINIKIEWICZ (*Rocz. Chem.*, 1925, **5**, 252—290).—The space configuration of quartz is, on the basis of its crystal form, of its property of rotating the plane of polarised light, and of the tendency of oxy-silicon compounds, *e.g.*, silicoformaldehyde, to form rings containing six silicon atoms, assumed to consist of spirally disposed rings each containing alternately six silicon and six oxygen atoms. On this assumption, the structural formulæ of various silicic acid derivatives are deduced. The difference between ortho- and meta-silicates depends only on different quantitative relationships between the metal and silicic acid, with the probability that

for salts of bivalent metals two silicic acid nuclei are joined by the metal. For the aluminosilicates only this type of formula can be considered, and the structure of semi-hydrated kaolin, $H_{24}Al_{24}Si_{24}O_{96}$, containing four silicic acid nuclei joined by –O·Al·O– groups is given. From this follows directly, by hydration, the structure of kaolin. This hydration is an ionic reaction, taking place at the eight –Si·O·Al– groups of the two inner saturated rings, and at the four free :Si:O groups in the two outer unsaturated rings. At these eight inner hydration points various other addition processes may occur, giving rise to other minerals connected genetically with kaolin, such as margarite, prismatine, nephelite, etc. R. T.

Crystallographic Investigation of Diopside from Saulera (Val d'Ala). M. Luciano (*Mem. Accad. Lincei*, 1924, [v], **14**, 886—898).—Measurements of crystals of diopside from Saulera give : $a : b : c = 1{\cdot}0931 : 1 : 0{\cdot}5892$, $\beta = 105° 47{\cdot}5'$, d 3·289. Contrary to Strüver's statement, these crystals differ distinctly from those of Testa Ciarva. T. H. P.

Crystal Structure of Silver Phosphate and Silver Arsenate. R. W. G. Wyckoff (*Amer. J. Sci.*, 1925, [v], **10**, 107—118).—Crystals of silver phosphate and arsenate have been studied by the Laue and the powder methods of *X*-ray analysis. Two molecules are contained in the unit cube. The atomic arrangement is a new one, and the corresponding space-group is probably Te—4. The position of the oxygen atoms could not be established in either crystal. The length of the edge of the unit cube is 6·00 Å. for silver phosphate and 6·12 Å. for the arsenate. S. B.

Crystal Structures of the Sulphides of Mercury. H. E. Buckley and W. S. Vernon (*Min. Mag.*, 1925, **20**, 382—392).—*X*-Ray examination of precipitated black mercuric sulphide (corresponding with metacinnabarite) shows the structure to be of the zinc-blende type with the edge of the unit cell $a = 5{\cdot}854$ Å. Cinnabar examined by the powder method gives spacings corresponding with a hexagonal space-lattice (D_3^4) with three molecules per unit cell of dimensions $a = 4{\cdot}160$, $c = 9{\cdot}540$ Å. The mercury atoms are arranged on a simple rhombohedral lattice, whilst the sulphur atoms form spirals (of radius 0·87 Å.) running parallel to the vertical axis, corresponding with the optical activity of cinnabar. L. J. S.

Crystallographic Data for Some Organic Compounds. G. Greenwood (*Min. Mag.*, 1925, **20**, 393—405).—Details are given for the following menthyl and glyoxaline derivatives : menthyl bromomethylenephenylhydrazonecarboxylate, menthyl bromomethylene-*p*-tolylhydrazonecarboxylate, 4 : 5-dibromo-1-methylglyoxaline hydrochloride (monoclinic), glyoxaline-4(5)-sulphonic acid (tetragonal), 2-methylglyoxaline-4(5)-sulphonic acid (monoclinic), 4(5)-bromoglyoxaline-5(4)-sulphonic acid (monoclinic), 4(5)-bromo-2-methylglyoxaline-5(4)-sulphonic acid (orthorhombic), 5-bromo-1-methylglyoxaline-4-sulphonic acid (monoclinic), and also for triphenylphosphine oxide, *p*-toluenеazobenzylformaldoxime (this vol., i, 1193), a fission product of lupulon, and

5-carboline. The range in symmetry of the glyoxaline compounds is noted. L. J. S.

Significance of the Magnetism of the Rare Earths. F. HUND (*Z. Physik*, 1925, **33**, 855—859).—From a consideration of the distribution of the electrons the magneton numbers are calculated for the elements with atomic numbers 54 to 68, and are in good agreement with the numbers calculated from experiments on the magnetic properties of the elements. E. B. L.

Magnetic Researches. XXVII. Magnetic Properties of some Paramagnetic Chlorides at Low Temperatures. H. R. WOLTJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 536—543).—The dependence of the magnetic susceptibilities of anhydrous chromium, cobalt, and nickel chlorides on field strength and temperature has been studied, the magnetisation being determined from the attraction exerted on a small quantity of the substance in a non-homogeneous magnetic field. Down to the temperature of liquid nitrogen, the susceptibility is independent of field strength, but at the temperature of liquid hydrogen the susceptibility of chromium chloride decreases, whilst that of cobalt and nickel chlorides increases with the field. For a given field strength, the susceptibility of chromium chloride increases with falling temperature and of cobalt chloride decreases slightly; that of nickel chloride is independent of temperature except for weak fields, where it decreases slightly. Down to 64° Abs. all obey Weiss' law, $\chi(T-\theta)=C$, where χ is the susceptibility, T the absolute temperature, C a constant, and θ has the values 32·5°, 20°, and 67° for the chlorides of chromium, cobalt, and nickel, respectively.
M. S. B.

Further Experiments with Liquid Helium. Magnetic Researches. XXVIII. Magnetisation of Anhydrous Chromium, Cobalt, and Nickel Chlorides at Very Low Temperatures. H. R. WOLTJER and H. K. ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 544—549; cf. preceding abstract).—The magnetisation curves of the three chlorides have been determined at the temperatures of liquid hydrogen and liquid helium, *i.e.*, below the Curie temperature. None of the chlorides shows hysteresis or residual magnetism. Chromium chloride is ferromagnetic to this extent, that its susceptibility decreases with increasing field strength. The magnetisation curves for nickel and cobalt chlorides are at first convex to the axis of magnetic field, becoming linear for higher fields. At very low temperatures the connexion between magnetisation and field strength for all the chlorides appears to be independent of temperature. M. S. B.

Orientations of Crystals in Electrodeposited Metals. R. M. BOZORTH (*Physical Rev.*, 1925, [ii], **26**, 390—400).—When examined by the Debye–Scherrer X-ray method, electrodeposited films of copper, zinc, and cadmium are found to have the crystals oriented at random, whilst those of iron, nickel, and cobalt have special orientations. In the case of iron, the (111) planes tend to

lie parallel to the surface, as do also the (100) or (211) planes of nickel. Cobalt is less markedly, and silver only slightly, oriented. The production of orientation is ascribed to the tension present in the foils, presumably due to hydrogen being deposited with the metal; the metallic atoms take up positions farther apart than normally, but as successive layers are added, the hydrogen diffuses from the innermost layers, leaving the metal in a state of stress.

A. A. E.

Very Thin, Transparent Metal Films. C. MÜLLER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 464—470).—Extremely thin films of nickel, gold, platinum, silver, and iron have been obtained by a modification of the method of electro-deposition on a thicker base, followed by the solution of the latter. The exact details of the process are not given, but it is stated that the metal film is coated with a thin protective layer which is very soluble, so that in the freeing of the film from its support it is exposed to the solvent only in the last stages of the process. Greater homogeneity of the film is thus obtained. Films of gold and nickel of 0·01 μ thickness, and of the other metals of 0·04 μ thickness, were obtained. The strength and elasticity of the nickel films are considerable; a 0·04 μ foil, 6 cm. in diameter, has an elasticity of 1 mm., and a thicker foil, 0·25 μ in thickness, supported by a gauze, withstood the pressure of a 25 cm. mercury column. The thickness of the heavier foils was estimated from their weight and bulk density, and that of the thinner foils by the amount of current used in their deposition compared with that required for thicker foils of equal area. The thickness of the thinner foils corresponded with a layer of 30 atoms only. The transparency of the films was high, permitting the photographing through them of a finely ruled scale. Those of gold showed a maximum transparency near 5500 Å. In reflected light, gold films of 0·04 μ thickness appeared golden-yellow, those of 0·02 μ a deep rose. The surface of the thinnest films, under high magnification, appeared glassy and structureless, and their polarising effect was negligible. When heated in an oxidising atmosphere, a nickel foil, 0·03—0·04 μ thick, increases greatly in transparency. The reconversion of this film to its original condition by heating in hydrogen shows this to be due to oxidation, and not to loss of nickel. The current-carrying capacity of the films, owing to their large radiating surfaces, is high. A nickel foil, 0·04 μ thick, will carry 0·3 amp. per cm. width without oxidising. Applications of these foils, based on their elasticity and conductivity, are suggested.

F. G. T.

Plasticity of Single Crystals. W. P. DAVEY (*J. Physical Chem.*, 1925, 29, 1211—1214).—A consideration of the positions of the planes of maximum atomic density (cf. A., 1923, ii, 768) indicates that plastic, ductile, and malleable metals have face-centred cubic structures, whilst relatively non-plastic metals have body-centred cubic structures. Iron is fairly plastic, but has the latter structure. Crystals of simple cubic structure have practically no plasticity. Single metal crystals which are ductile in the cold along certain

axes have a "hexagonal close-packed" structure; primary slip occurs in the (001) planes when the axial ratio exceeds 1·735 (*e.g.*, zinc), and in the (100) planes when it is less than this number. A single zinc crystal stretched beyond its elastic limit exhibits "block-slip" along the (100) planes to a much greater extent than along the (001) planes, in agreement with the above theory. S. K. T.

Heat of Formation of Lead Carbonate. A. L. MARSHALL and B. BRUŽS (*J. Physical Chem.*, 1925, **29**, 1184—1186).—The heats of the reactions (1) $PbO+CO_2=PbCO_3$ and (2) $PbO+PbCO_3=PbO,PbCO_3$ have been determined. The method used consisted in dissolving lead oxide, lead carbonate (as cerussite), and $PbO,PbCO_3$ in dilute nitric acid, using a calorimeter similar to that described by U. Fischer (*Z. anorg. Chem.*, 1912, **78**, 57). From the heats of solution thus measured, the heats of reaction have been calculated. The values of ΔH given for (1) and (2) are −21,100 and −340 cal., respectively. The values of ΔH calculated by the authors from the data given by Thomsen ("Thermochemische Untersuchungen," III, 333, 442) and by Berthelot ("Thermochemie," II, 345) for the reaction $PbO+CO_2=PbCO_3$ are −22,200 cal. and −19,400 cal., respectively, the new value −21,100 cal. being approximately their mean. L. S. T.

Method of Determining Molecular Weight. G. RASTELLI (*Gazzetta*, 1925, **55**, 552—554; cf. Barger, T., 1904, **85**, 286; Rast, A., 1921, ii, 623).—Two solutions, one of a standard substance and the other of an unknown, of equal concentration, each contained in a calibrated glass tube of 2 mm. uniform internal diameter, ending in a bulb, are allowed to evaporate into a bulb containing an absorbent medium. After some hours, the amounts, a (from the solution of the standard) and b, of the solvent, which have left the two solutions, are read from the respective changes in the lengths of the columns of solution. Then $M_2=M_1b/a$, where M_1 and M_2 are the known and the unknown molecular weights, respectively. The method affords moderately accurate results. W. E. E.

Cryoscopic Measurements with Benzene. E. R. JONES and C. R. BURY (*J. Chem. Soc.*, 1925, **127**, 1947—1951; cf. Brown and Bury, this vol., ii, 32).—The use of benzene for cryoscopic measurements has been studied, using dry benzene in the presence of phosphoric oxide or alumina, and moist benzene in the presence of the salt hydrate pair $Na_2SO_4,0-10H_2O$, and also saturated with water. In calculating the molecular weights, little error is introduced by neglecting the water content of the benzene, provided that it is kept constant during the experiments. Azobenzene, triphenylmethane, picric acid, and trinitrotoluene show no definite evidence of solvation when dissolved in benzene, although they crystallise with 1 mol. of benzene of crystallisation. W. H.-R.

Resistance of Platinum Films in Presence of Hydrogen. A. W. GAUGER (*J. Amer. Chem. Soc.*, 1925, **47**, 2323—2325).—The electrical resistance of thin platinum films deposited on glass by thermal evaporation of the metal in a vacuum decreases with time,

the temperature coefficient of resistance being the reverse of that for the bulk metal. In two experiments out of three, the presence of hydrogen increased the resistance of the film. The deposition of the films is slow in starting at the ordinary temperature, but is rapid when once started; at liquid air temperatures, the deposition is rapid, but at high temperatures no film will form. The results, which were not reproducible at will, indicate that such films consist of numerous small aggregates of metal. S. K. T.

Optical Constants of Magnesium and Zinc Crystals. M. E. GRABER (*Physical Rev.*, 1925, [ii], **26**, 380—389).—By means of the crystelliptometer (polarimetric method) the optical constants of magnesium and zinc have been measured between 4160 and 6500 Å., and 4550 and 6500 Å., respectively, values of the refractive index, index of absorption, and reflecting power for the horizontal and vertical positions of the crystal being tabulated. A. A. E.

Characteristics of Tungsten and the Candle Power of a Black Body. C. ZWIKKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 499—502).—Measurements have been made between 1200° and 3400° Abs. of the following properties of tungsten: spectral emissivity and brightness temperature (both for $\lambda=0{\cdot}665$), colour temperature, electrical resistance, total radiation, brightness, thermionic emission, rate of vaporisation, thermal conductivity, and (for the range 1800—2400° Abs.) of the Thomson effect. The electron emission is given by $i=60{\cdot}2T^2e^{-b/T}$ amp./cm.^{2}, where $b=52230$. The rate of evaporation was determined from the decrease in diameter of a glowing tungsten filament maintained at a constant temperature, and is expressed by the formula

$$\log m=11{\cdot}92-4{\cdot}84\times10^4/T-0{\cdot}368\log T-0{\cdot}00016T.$$

The colour temperature of tungsten at a temperature T is defined as the temperature of a black body giving the same energy distribution in the visible spectrum as the tungsten. The ratio of the candle power B_1 of the black body at T_c to the candle power B_2 of tungsten at S is given by $B_1/B_2=e^{(C/2{\cdot}3\lambda)(1/S-1/T_c)}$, where T_c and S are the colour and brightness temperatures, respectively, and C is a constant. Measurements of the candle power of a black body, in conjunction with determinations of the brightness of a tungsten filament, give 0·00146 watt per international candle as the lowest value of the mechanical equivalent of light. F. G. T.

Specific Heat of the Hydrogen Molecule. A. PREDVODITELEV (*Z. Physik*, 1925, **34**, 178—183).—A formula is obtained by considering the hydrogen molecule as a rotating dipole, without introducing quantum theory, and is in satisfactory agreement with experiment, particularly for low temperatures. A relationship is deduced between the energy of rotation and the b. p. E. B. L.

Ratio of Specific Heats of Hydrogen. J. R. PARTINGTON and A. B. HOWE (*Proc. Roy. Soc.*, 1925, **A**, **109**, 286—291).—The ratio of the specific heats of hydrogen has been redetermined, and is

given as 1·4113±0·0002. The previous determinations of the specific heats of hydrogen are discussed. S. B.

Heat Capacity of Solid Aliphatic Crystals. E. O. SALANT (*Proc. Nat. Acad. Sci.*, 1925, **11**, 227—231).—On the basis of the assumptions inherent in the Debye and Einstein functions of a linear oscillator, and in the Lindemann m. p. formula, the author proceeds to develop an expression for the atomic heat for a compound $C_xH_yO_zN_w$ by a modification of the formal expression of the Neumann–Regnault–Kopp law. Values obtained in this way compare well with the known data and are given for formic acid, oxalic acid, methyl, ethyl, and *n*-butyl alcohols, glycerol, dextrose, acetone, and carbamide. R. W. L.

Residual Affinity and Co-ordination. XXIV. Heats of Chelation of Dithiolated Metallic Halides. G. T. MORGAN, S. R. CARTER, and W. F. HARRISON (*J. Chem. Soc.*, 1925, **127**, 1917—1925).—*Dimethyldithioethylene zinc chloride*, $C_4H_{10}S_2,ZnCl_2$, m. p. 131°, is prepared by passing chlorine into a suspension of zinc dust in ether, followed by addition of the disulphide to the filtered solution. It is unstable in the presence of moisture. *Dimethyldithioethylene zinc iodide*, m. p. 169°, is similarly prepared, using iodine in place of chlorine. *Dimethyldithioethylene cadmium chloride* and *bromide* are prepared by the action of the disulphide on dry alcoholic solutions of the halide; neither melts below 285°. *Dimethyldithioethylene cuprous iodide* is prepared by saturating an aqueous solution of copper sulphate with sulphur dioxide, and then adding the organic sulphide and potassium iodide. It is unchanged by cold water and has m. p. 156° (decomp.). The heats of reaction of dimethyldithioethylene with metallic halides are determined as follows: cupric chloride 14·85 cal., cuprous iodide 5·88 cal., zinc chloride, bromide, and iodide, 13·21, 15·35, 14·23 cal., respectively; cadmium chloride, bromide, and iodide, 12·16, 11·27, 9·96 cal., respectively; mercuric chloride, bromide, and iodide, 13·23, 11·33, and 4·83 cal., respectively; stannic chloride, bromide, and iodide, 28·06, 19·40, and 16·58 cal.; 12·0 cal. for the combination of 3 mols. of dimethyldithioethylene with 2 mols. of bismuth iodide to form the scarlet complex $3SMe\cdot C_2H_4\cdot SMe,2BiI_3$. W. H.-R.

Heats of Formation of Quinonechloroimines and Quinonedichlorodi-imines. (MLLE.) S. BLASZKOVSKA (*Bull. Inter. Acad. Polonaise*, 1924, **A**, 9—10, 409—428).—In an extension of previous work by Swientoslawski (A., 1909, ii, 862) the thermal values of the processes whereby the hydrochlorides of aromatic diamines and aminophenols react in aqueous solution with chlorine water or bleaching powder to precipitate quinonechloroimines have been evaluated. The following results have been obtained:—benzidine: $C_{12}H_8(NH_2)_2,2HCl+3Cl_2=C_{12}H_8N_2Cl_2+6HCl+58{\cdot}40$ Cal., $C_{12}H_8(NH_2)_2,2HCl+3/2Ca(OCl)_2=C_{12}H_8N_2Cl_2+3/2CaCl_2+3H_2O+80{\cdot}21$ Cal.; dianisidine: $C_{12}H_6(OMe)_2(NH_2)_2,2HCl+3/2Ca(OCl)_2=C_{12}H_6(OMe)_2N_2Cl_2+3/2CaCl_2+3H_2O+89{\cdot}72$ Cal.; *p*-aminophenol: $OH\cdot C_6H_4\cdot NH_2,HCl+2Cl_2=O:C_6H_4:NCl+4HCl+39{\cdot}92$ Cal.; *p*-amino-*p'*-hydroxydiphenyl: $OH\cdot C_{12}H_8\cdot NH_2,HCl+2Cl_2=$

$O{:}C_{12}H_3{:}NCl+4HCl$ +30·99 Cal. The formation of small quantities of decomposition products renders the thermal data obtained for picramic acid untrustworthy. It is not possible to determine the heats of formation of the corresponding bromine derivatives, the main reaction being always accompanied by a bromination of the nucleus.

From the present data and those of Swientoslawski (*loc. cit.*) on *p*-phenylene- and *p*-naphthylene-diamines a mean value of 21·92 Cal. is obtained for the difference between the heats of reaction using bleaching powder and chlorine water. Replacement of the benzene nucleus by diphenyl causes a mean decrease of 9·47 Cal. in the heat of reaction. Comparison of the thermal data for benzidine and dianisidine shows that the introduction of electropositive methoxy groups into the nucleus results in an increased thermal effect. 3 : 3′-*Dimethoxydiphenoquinone*-4 : 4′-*dichlorodi-imine* is formed as a reddish-brown, amorphous, unstable precipitate on treating solutions of dianisidine dihydrochloride with bleaching-powder solution. 4 : 6-*Dinitro*-o-*benzoquinone*-2-*chloroimine* is formed as a yellow precipitate on treating a solution of picramic acid in presence of hydrochloric acid with chlorine water in the cold. The substance, which has not yet been obtained pure, is very soluble in acetone, acetic acid, and alcohol. J. S. C.

Elasticity Modulus, Temperature, and M. P. W. Widder (*Physikal. Z.*, 1925, **26**, 618—622).—Examination of data for numerous metals shows that the elasticity modulus is a linear function of the temperature, $E_t=E_{t_0}[1-\varepsilon_{t_0}(t-t_0)]$. If it be assumed that the elastic modulus vanishes at the m. p., the temperature coefficient of the modulus at t_0 is given by $\varepsilon_{t_0}=1/(t_m-t_0)$, where t_m is the m. p. It is also shown that, for many metals, the ratio of the temperature coefficient of the elasticity modulus to the coefficient of linear expansion at the same temperature is approximately constant. The value of this constant is about 60. The divergences from this approximate relation are most marked with lead, cadmium, tin, manganese, and antimony. F. G. T.

Halides of the Fourth Group as Homopolar Compounds on the Basis of an Additive Relationship in M. P. A. Hantzsch and H. Carlsohn (*Ber.*, 1925, **58**, [*B*], 1741—1746; cf. Hantzsch, this vol., ii, 359; Paneth and Rabinovitsch, this vol., ii, 760).—The m. p. of the halides of the fourth group can be calculated from the m. p. of the *n*-valent element (M) and that of the halogen (X) according to the following empirical formula: m. p. of halide= (m. p. of M+$n\times$m. p. of X)/(n+1). It appears therefore that the atoms can be little changed by the union to form molecules; this hypothesis directly contradicts the deformation theory of Fajans and Joos (A., 1924, ii, 750). The applicability of the rule to the halides of titanium, germanium, and silicon cannot be directly shown, since these elements are associated in the "free" state as indicated by their high m. p. Since, however, the m. p. of the chlorides, bromides, and iodides of silicon, titanium, germanium, and tin lie approximately on a straight line when the m. p. of the

halides of one of these elements as abscissæ are plotted against the m. p. of the halides of another of the elements just named as ordinates, the m. p. of the halides may be regarded as normal and, by application of the rule, the m. p. of "unassociated" titanium, germanium, or tin may be calculated. The possibility of "chemical association" of the halides is regarded as excluded if the relationship, Abs. m. p./Abs. b. p.=0·62, is fulfilled. H. W.

Rare-gas Nature of Pseudo- and Non-electrolytes as Basis for the Calculation of their M. P. and B. P. H. CARLSOHN (*Ber.*, 1925, **58**, [*B*], 1747—1752; cf. Paneth and Rabinovitsch, this vol., ii, 760).—If association is taken into account, it is shown that the m. p. and b. p. of pseudo- and non-electrolytes are exactly directly proportional to the m. p. and b. p. of the rare gases corresponding with them. The halides of the elements of the fourth group, the hydrides of the metalloids, and organic halides are non-electrolytes constituted similarly to the rare gases. Association is little or non-evident in the solid inorganic compounds or molten organic derivatives. H. W.

Thermochemical Researches on Diazo Compounds. W. SWIENTOSLAWSKI (*Rocz. Chem.*, 1925, **5**, 214—231).—The methods employed by the author (cf. A., 1920, i, 336) for the thermochemical investigation of diazo compounds are described and illustrated by the cases of aniline and *p*-bromoaniline. From these, and from previously published results (*loc. cit.*), the following conclusions are reached. Substitution in the benzene ring of electronegative groups has not a constant effect on the heats of various reactions of substituted anilines. Thus, where q_{am}, q_{dz}, q_n, and q_{is} are respectively the heats of formation of amine hydrochloride, of diazonium chloride, and of *n*- and *iso*-diazohydrate sodium salts, i_n and i_{is} the heats of isomerisation of the diazonium into the *n*- and *iso*-diazohydrate forms, and A and B the heats of diazotisation of amine and of coupling of *n*-diazohydrate with solid β-naphthol, the effect of electronegative substituents is to diminish q_{am}, q_{dz}, and A, and to enhance q_{is}, q_n, and B, whilst i_n and i_{is} remain unchanged. These differences may be considerable, q_{am} varying from 7·60 to 1·81 cal., A from 19·97 to 12·47 cal., q_n from 3·77 to 5·65 cal., and q_{is} from 8·80 to 11·00 cal. B increases inversely with A, so that $A+B+i_n=50$ cal. is constant, and independent of substitution, the derivatives of *o*- and *p*-aminobenzoic and of sulphanilic acids deviating, however, from this rule. The mean values of i_n and i_{is} are +0·5 and −2·3 cal., and in all cases $q_n<q_{is}$, the difference being from 5 to 6 cal. Contrary to Hantzsch's statement, $i_{is}-i_n$ gives a negative mean value of about 3 cal., although in the case of the isomerisation of salts heat is evolved, since $q_n<q_{is}$, so that $(q_{is}+i_{is})-(q_n+i_n)=+3$ cal., the salt of *p*-sulphodiazobenzene being, however, an exception to this rule. R. T.

Thermochemical Researches on the Diazo Derivatives of Aminophenols. W. SWIENTOSLAWSKI and (MLLE.) Z. BŁASZKOVSKA (*Rocz. Chem.*, 1925, **5**, 233—251; cf. preceding abstract).—Certain reactions of picramic acid and of *p*-amino-*p*′-hydroxydi-

phenyl are examined thermochemically. The heats of formation of the hydrochlorides are, respectively, 0·746 and 6·0 cal., of formation of sodium salts 10·20 and 6·41 cal., of diazotisation 25·56 and 19·91 cal. The product of diazotisation of picramic acid is a quinonediazide which yields with sodium hydroxide a normal diazohydrate salt, 9·34 cal. being evolved. The heat of coupling of the quinonediazide with β-naphthol is about 41 cal. In the case of the aminohydroxydiphenyl, the heat of formation of the sodium salt of the diazohydrate is 24·13 cal., and of coupling with β-naphthol about 27 cal. Picramic acid exhibits greater divergences from the properties of other amines than the aminohydroxydiphenyl.

R. T.

Density and Atomic Weight of Helium. E. P. BAXTER and H. W. STARKWEATHER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 231—234).—The technique developed by the authors for determining the density of oxygen has been applied to measure the density of helium. The average value for the density of helium is given as 0·17845 at 0° and 760 mm. at sea level lat. 45°. R. W. L.

Vapour Pressure. I. Nitroanilines. J. F. T. BERLINER and O. E. MAY (*J. Amer. Chem. Soc.*, 1925, **47**, 2350—2356).—The vapour pressures of the isomeric nitroanilines have been determined by Nelson and Senseman's method (A., 1922, i, 245) using a U-tube levelling type of isoteniscope. All three isomerides decompose to some extent before their b. p. at atmospheric pressure are reached, *p*-nitroaniline decomposing completely, whilst the *o*-compound is only slightly decomposed. Below the decomposition temperatures, the observed vapour pressures agree closely with those calculated from the latent-heat equation. Determinations of the vaporisation entropies at a concentration of 0·00507*M* per litre of vapour indicate that the molten nitroanilines are not normal liquids. R. B.

Hypothesis of Molecular Association. Y. ROCARD (*J. Phys. Radium*, 1925, [vi], **6**, 199—201).—Duclaux (*ibid.*, 1924, [vi], **5**, 331) maintains that the equation of state can be deduced equally well by substituting the idea of molecular association for van der Waals' conception of internal pressure, but it is now shown that this association theory leads to the expression $\eta=\alpha\sqrt{T}(1-0{\cdot}31be^{cT_0/T}/V)$ for the viscosity of a gas, and that this is not in agreement with the result of experiment. On the other hand, postulation of the existence of cohesive forces leads to an expression for the variation of the viscosity of a gas with temperature and pressure which is in excellent agreement with the facts (A., 1924, ii, 653). E. E. W.

Statistical Basis of Volmer's Equation of State for Adsorbed Substances, and the Concentration Formula. S. C. KAR (*Physikal. Z.*, 1925, **26**, 615—618).—Theoretical. By a quantised statistical treatment based on the assumption that adsorbed molecules behave as a surface film, an equation of state of the same form as Volmer's equation (cf. this vol., ii, 539) is obtained. The treatment leads to a concentration formula different from Volmer's, but

identical with Langmuir's (A., 1918, ii, 430), and to an interpretation of the constant in that formula. F. G. T.

Cause of Surface Tension. E. H. KENNARD (*Nature*, 1925, **116**, 463—464).

[Cause of Surface Tension.] N. K. ADAM (*Nature*, 1925, **116**, 464—465).

Surface Tension Crystal *v.* Saturated Solution. The Concentration Cell: Finely Divided Salt | Supersaturated Solution | Saturated Solution | Large Crystals. L. SOEP (*Phil. Mag.*, 1925, [vi], **50**, 675—680).—Equations are deduced relating the surface tension between a crystal surface and the corresponding saturated solution with the *E.M.F.* of the above cell, and further relating these quantities with the molecular heat of solution. A. B. M.

Scattering of Light by Liquid Boundaries, and its Relation to Surface Tension. III. C. V. RAMAN and L. A. RAMDAS (*Proc. Roy. Soc.*, 1925, **A**, **109**, 272—279).—The surface-scattering of light by water and twenty-eight other liquids have been compared. It is found, in general, that the intensity of the surface opalescence increases when the surface tension is diminished or the refractive index increased. The effect of greasing the surface of the water has also been studied. With amounts of oleic acid just sufficient to stop camphor movements, the surface opalescence is approximately doubled. With excess of oleic acid over this quantity, the increase in brightness is far greater—perhaps a thousandfold. The surface is, however, no longer continuous, but contains microglobules of oil. These phenomena are correlated with recent work on surface films.

Experiments with liquid carbon dioxide show that the opalescence increases rapidly near the critical temperature, as would be expected. The scattering phenomena at the interface between carbon disulphide and methyl alcohol near the critical solution temperature are similar. S. B.

Behaviour of Crystals and Lenses of Fats on Surface of Water. I. Mechanism and Rate of Spreading. A. CARY and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, **A**, **109**, 301—317).—An experimental study has been made of the "surface spreading" on water and dilute acid solutions of long-chain organic compounds terminating in a polar group, including acids, phenols, nitriles, etc. It has been found that unimolecular films spread from crystals as well as from liquid lenses, a definite equilibrium surface tension characteristic of each material being finally established. The rate of attainment of equilibrium is very much slower for the films formed by crystals than that for liquid films, and this observation has been utilised in examining the mechanism of the spreading. Equilibrium for the liquid films is reached too rapidly for dynamical experiments. A crystal of myristic acid, or other solid, was placed in contact with the surface, and the change in the surface tension

produced was measured by the ring method. It was found that the spreading could be separated into two stages, one during which the surface is covered with a unimolecular film under zero compression, the surface tension remaining constant meanwhile, and a stage during which packing of this expanded film occurs until equilibrium between surface solution and recondensation is attained. During this stage, the surface tension is altered, the changes obeying a unimolecular equation. The results indicate that for long-chain substances there is a limit at the ordinary temperature to the expansibility of a film, and that the molecules are unable to separate completely on the surface.

Experiments have also been conducted on the rate of spreading of the films from liquids on a free water surface. The rate is found to depend on the size of the liquid drop, but invariably a comparatively rapid extension for the first few cm. is succeeded by a slower but constant rate of spreading. The mean life of a molecule on the surface of a crystal in contact with water is calculated to be of the order of 10^{-7} sec. S. B.

Behaviour of Crystals and Lenses of Fats on Surface of Water. II. Effect of Temperature on the Equilibrium Pressure. A. Cary and E. K. Rideal (*Proc. Roy. Soc.*, 1925, **A, 109**, 318—330).—The surface tension of $N/100$-hydrochloric acid has been measured when the surface is saturated with a film in equilibrium with organic compounds in bulk over a temperature range including the m. p. of the compounds. The results and conclusions are as follows. When working with highly insoluble solid compounds, there is a definite temperature below which no effect on the surface tension could be observed with the most prolonged contact between crystal and surface. Between this temperature and the m. p. the surface tension falls linearly with rise of temperature. At the m. p., there is a sudden change in the slope of the surface tension–temperature curve, but the changes are still linear. With certain compounds (*e.g.*, stearic acid and octadecyl acetate), the surface tension above the m. p. of the bulk material increases rapidly with rise of temperature over a definite range, but above this range the decrease is resumed. Other compounds do not exhibit this double break, the surface tension decreasing steadily above the m. p. These phenomena are explained on the hypothesis, put forward by other workers on other grounds, that all films can exist in two states of aggregation—"condensed" and "expanded." The passage from a partly condensed to an expanded film is considered to take place at a definite temperature. If this temperature is below the m. p., then the surface tension–temperature curve will only show one break, at the m. p. If the transition temperature is above the m. p., the curve will have two breaks, one at the m. p., and the other at this transition temperature of the film. The phenomena are discussed from the point of view of the phase rule, the film being treated as a separate phase. By an application of the Clapeyron equation, the results of the experiments enable the latent heat of fusion of the compounds to be calculated. S. B.

Behaviour of Crystals and Lenses of Fats on Surface of Water. III. Effect of Polar Group on Equilibrium Pressure. A. CARY and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, **A**, **109**, 331—338).—The measurements described in the preceding abstract have been extended to include long-chain compounds with more complex polar heads. The results suggest that the slope of the surface tension–temperature curve up to the m. p. is determined by the hydrocarbon chain, whilst the slope between the m. p. and the film "transition" temperature is dependent on the polar group. Similar measurements have been made on mixtures of two compounds. With mixtures of octa- and hexa-decyl acetates, it was found that the relative proportions of the two compounds did not influence the results. Up to the m. p., the effect on the surface tension is the same as that of the component capable of producing the greater effect when present alone. Above the m. p., complex but interesting phenomena are observed. The influence of impurities is also described. S. B.

Measurement of Viscosity. J. DUCLAUX and J. ERRERA (*J. Phys. Radium*, 1925, [vi], **6**, 202—204).—In order to avoid the errors introduced by the usual method of employing capillary viscosimeters for measuring the viscosity of liquids of low viscosity, an apparatus is devised which replaces the capillary by a cylinder of porous pot. It is shown experimentally that the rate of flow is proportional to the pressure, and that the results obtained by this method for ethyl ether, acetone, and other liquids of low viscosity are more accurate than those obtained with capillaries of 0·41 mm. and 0·26 mm. diameters. E. E. W.

Determination of the Coefficient of Viscosity of Water. P. LEROUX (*Ann. Physique*, 1925, [x], **4**, 163—248).—The absolute viscosity of water has been measured at different temperatures by the rotating cylinder method, the water being contained between two concentric cylinders, of which the outer was rotated at known velocity and the resulting twisting moment on the inner cylinder measured. The following values are given for the absolute value of η: 0·01704 at 1·5°, 0·01648 at 2·5°, 0·01551 at 4·1°, 0·01419 at 7·5°, 0·01276 at 10·9°, 0·01175 at 14°, 0·01121 at 16°, 0·01069 at 18°, 0·01018 at 20°, 0·00949 at 23·2°, 0·00883 at 26·4°, 0·008198 at 30°, 0·007500 at 34·3°, 0·006554 at 41·6°, and 0·006220 at 44·5°. No irregularity exists in the neighbourhood of 4°, and the values of η are independent of the speed of rotation of the outer cylinder, showing that water has no rigidity. The different methods of determining viscosity are critically discussed, and the elaborate precautions used in the present work are described. W. H.-R.

Relation between Viscosities of Liquids and their Molecular Weights. D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, **21**, 151—159).—See this vol., ii, 498.

Physical Properties of Water. D. B. MACLEOD. (*Trans. Faraday Soc.*, 1925, **21**, 145—150).—See this vol., ii, 498.

Equal Viscosities. W. Herz (*Z. anorg. Chem.*, 1925, **147**, 293—294).—It is shown for about forty organic liquids that the ratio of the temperature at which the viscosity has the value 0·0040 C.G.S. unit, to the critical temperature, is approximately constant. The recorded ratios vary from 0·515 to 0·692 and the critical temperatures from 214° to 397°. A. G.

Viscosities of Liquids at their B. P. D. B. Macleod (*Trans. Faraday Soc.*, 1925, **21**, 160—167).—An attempt has been made to determine to what extent the b. p. of liquids may be regarded as corresponding temperatures. On the basis of previous determinations (this vol., ii, 492), the association factors of a number of liquids have been calculated and show a fairly close agreement with those given by Ramsay and Shields. Taking pentane as standard (b. p.=0·6578 T_c), the viscosities of other liquids have been compared (1) at the same reduced temperature, and (2) at the b. p. both with and without reduction of the free space to the same value as that given by pentane, viz., 0·1690. It has thus been shown that the viscosity at the b. p. bears no relation to the molecular weight. These quantities are, however, found to be proportional when the comparison is made under conditions of equal free space. It follows that the condition of equal free space corresponds very closely with that given by equality of reduced temperature on the basis of van der Waals' equation. M. S. B.

Diffusion of Iodine in Pure and Mixed Solvents. J. Gróh and I. Kelp (*Z. anorg. Chem.*, 1925, **147**, 321—330; cf. this vol., ii, 28).—The diffusion coefficient of iodine has been measured in benzene, chloroform, and carbon disulphide, in which the solutions are violet, and in ethyl alcohol and ether, in which the solutions are brown, owing, it is believed, to solvation. The coefficients in the first group of solvents are nearly equal after correction for the viscosities of the solutions. In ether, the coefficient is smaller, as was to be expected; in alcohol, it is greater, indicating that hitherto unsuspected factors are involved. The addition to carbon disulphide or chloroform of sufficient alcohol or ether (2 mols. per litre) to produce brown iodine solutions diminishes the diffusion coefficient. A. G.

Densities and Compressibilities of Organic Liquids and Solutions: Polymerisation of Water. T. W. Richards and H. M. Chadwell (*J. Amer. Chem. Soc.*, 1925, **47**, 2283—2302).—The densities of aqueous solutions of ethyl alcohol, urethane, ethyl ether, and methyl acetate, and of solutions of urethane in water, alcohol, ethyl ether, and benzene have been measured at 20°. The compressibilities of some of these solutions and solvents were also determined. The contractions observed in the formation of these solutions (excepting the first) are approximately proportional to the compressibilities of the solutes in the liquid state. Since urethane and water have comparable compressibilities, the large decrease in volume which occurs when urethane dissolves in water is attributed to depolymerisation of some of the water molecules. Equi-molar quantities of different substances have the same

depolarising effect. At 20° water appears to contain about 28% of "polyhydrol" (cf. Sutherland, A., 1906, ii, 603). In aqueous alcohol solutions, the alcohol polymerides, which are probably less bulky than those of water, appear to dissociate. S. K. T.

Vapour Pressure of Organic Solutions and Application of Dühring's Rule to Calculation of Equilibrium Diagrams. E. H. Leslie and A. R. Carr (*Ind. Eng. Chem.*, 1925, **17**, 810—817).—Dühring's rule agrees with experimental data satisfactorily enough for technical application. This has been proved by Baker and Waite (*Chem. Met. Eng.*, 1921, **25**, 1137) for aqueous solutions of salts. The vapour pressures of *n*-hexane, *n*-heptane, and *n*-octane, and of binary mixtures of these three substances, have now been determined in an apparatus similar to that used by Baker and Waite (*loc. cit.*) between 92·3 and 760 mm. It is found that the rule holds good for these binary mixtures of organic liquids. It is evident that by applying the rule the complete vapour pressure curve for any liquid can be plotted from two observations only. This facilitates technical investigations. Various applications are discussed. W. A. S.

Vapour Pressures of Hydrogen Chloride above Aqueous Solutions. I. S. Mitsukuri, T. Rokkaku, and T. Watase (*Sci. Rep. Tôhoku*, 1925, **14**, 251—258).—The partial pressure of hydrogen chloride in equilibrium with dilute hydrochloric acid solutions has been determined by passing air through a series of three saturators in a thermostat for several days and condensing the water vapour and hydrogen chloride in a bulb surrounded by ice. The conductivity of the condensate was measured and from these data the partial pressure of the gas over the original solution was calculated. The values obtained are much lower than those calculated from the vapour pressures of concentrated solutions of hydrochloric acid or from the *E.M.F.* of the cell $H_2|HCl|AgCl|Ag$, whereas Dunn and Rideal's values (A., 1924, ii, 306) were much higher. The authors reject the results of Dunn and Rideal on the ground that the method used involves a violent surface distillation, and they consider that the published data for concentrated hydrochloric acid solutions are also too high. A. R. P.

Equilibrium in the Liquid System Iron–Copper–Manganese with Varying Small Proportions of Carbon. F. Ostermann (*Z. Metallk.*, 1925, **17**, 278—282).—Pure copper and iron are miscible in all proportions in the liquid state, but in the presence of small quantities of carbon there is a more or less extensive range in which the metals are immiscible. On the addition of manganese, which alloys with both copper and iron in all proportions and has a great affinity for carbon, this range of immiscibility disappears. [Cf. *B.*, 1925, 852.] A. R. P.

Law of Depression of Freezing Points in Metallic Alloys. K. Honda and T. Ishigaki (*Sci. Rep. Tôhoku*, 1925, **14**, 219—233).—Measurements of the depression of the f. p. of many metals on the addition of a small amount of a second metal indicate that dilute

solutions obey the law of van 't Hoff whether a solid solution is formed or not. The atomic depression of the solvent is independent of the solute. [Cf. *B.*, 1925, 884.] A. R. P.

Properties and Structure of Some Alloys of Aluminium and Chromium. F. T. Sisco and M. R. Whitmore (*Ind. Eng. Chem.*, 1925, **17**, 956—958).—Aluminium may be readily alloyed with chromium (up to 5%); photomicrographs of the alloys show scattered crystals of great hardness which probably have the composition $AlCr_3$. [Cf. *B.*, 1925, 852.] C. I.

Mechanical Properties and Structure of Some Alloys with a Restricted Range of Mixed Crystals. Silver-rich Binary Solid Solutions containing Magnesium, Aluminium, Tin, Zinc, Cadmium, and Manganese. F. Saeftel and G. Sachs (*Z. Metallk.*, 1925, **17**, 155—161, 258—264, 294—298).—Pure silver which has been hardened by cold work begins to soften at 100° and is completely soft at 600°, having a hardness of 25 and a tensile strength of 12·8 kg. per sq. mm. and giving an elongation of 48% before breaking. By adding magnesium, aluminium, tin, zinc, cadmium, or manganese in such quantities that the whole is retained in solid solution, the hardness and ductility increase, the tensile strength remains nearly constant, whilst the malleability decreases considerably, the reduction being nearly proportional to the amount of the second element added. The limiting amounts of zinc and aluminium retained in solid solution at the ordinary temperature are 20·4% and 5·7%, respectively, and the mixed crystal range in the silver-rich magnesium–silver alloys extends uninterruptedly to the compound MgAg. [Cf. *B.*, 1925, 853.] A. R. P.

Hardness of Ternary Alloys of Lead, Bismuth, and Cadmium. C. Di Capua (*Gazzetta*, 1925, **55**, 582—594).—A detailed study of the hardness–composition curves corresponding with certain sections of the f. p. diagram of this system shows that the ternary eutectic mixture possesses a minimum hardness, whereas the binary eutectic mixtures of the constituents (A., 1924, ii, 268, 553) are always characterised by a maximum hardness. This result is also met with in the ternary systems bismuth–tin–cadmium (where the minimum in question disappears on reheating) and lead–tin–bismuth (see following abstract). W. E. E.

Hardness of Ternary Alloys of Lead, Bismuth, and Tin. C. Di Capua (*Gazzetta*, 1925, **55**, 594—604).—Alloys of lead, bismuth, and tin or cadmium (cf. preceding abstract) show anomalies in the hardness–composition diagrams in that the binary eutectic mixtures show maxima, whilst the ternary eutectics show minima. These anomalies are eliminated by reheating. The reheating, moreover, increases the concentrations of the saturated solid solutions of lead and bismuth in tin. W. E. E.

Expansion of Glasses. Boric Anhydride. M. Samsoen (*Compt. rend.*, 1925, **181**, 354—356).—The linear coefficient of thermal expansion of boric oxide, determined by dilatometric

methods, is about 15×10^{-6} up to 240°, but then rapidly increases, again becoming constant at about 200×10^{-6}, between 250° and 334°. An approximate determination gave an average value of 200×10^{-6} over the region 1100—250°. [Cf. *B.*, 1925, 849.] A. COUSEN.

Partition of Silver between Lead and Zinc. W. A. NAISH (*Trans. Faraday Soc.*, 1925, **21**, 102—113).—See this vol., ii, 506.

Solubility of Slightly Soluble Chlorides in Concentrated Chloride Solutions. J. KENDALL and C. H. SLOAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2306—2317).—The solubility of silver chloride in concentrated aqueous solutions of sodium, lithium, and magnesium chlorides, and of lead chloride in solutions of the chlorides of hydrogen, bivalent mercury, alkali, and alkaline-earth metals has been determined at 25°. In both series, the electrode potential varies in accordance with the rule previously given (cf. A., 1922, ii, 34), irrespective of the formation of double salts. New *compounds* of the type $X,PbCl_2$ were isolated, where $X=\frac{1}{2}LiCl$, $\frac{1}{2}NaCl$, KCl, $SrCl_2$, $BaCl_2$, $HgCl_2$, $CaCl_2$, and $MgCl_2$, the last two compounds containing $6H_2O$. S. K. T.

Solubility Relations of Isomeric Organic Compounds. III. Mutual Solubility of the Three Dinitrobenzenes. D. H. ANDREWS (*J. Physical Chem.*, 1925, **29**, 1041—1047).—The mutual solubilities of the dinitrobenzenes, as indicated by f. p. observations, are recorded, and the results compared with those derived from calorimetric data. These solutions deviate but little, if at all, from the ideal, and this is taken to imply that the crystals of each isomeride which separate from ternary mixtures are pure, and that the mixing of the liquids is not attended by an appreciable change in volume or heat content. (For the method of experiment and the interpretation of the time–temperature curves, see this vol., ii, 852).

The solubilities of the three isomerides in different solvents have been interpolated from the observations of various workers and are given for reference. These also deviate but little from the ideal curve, which can therefore be used as a criterion of accuracy for such determinations.

The preparation of *p*-dinitrobenzene by diazotising *p*-nitroaniline in nitric acid solution and subsequent treatment with sodium nitrite and copper sulphate is outlined. L. S. T.

Solubility Relations of Isomeric Organic Compounds. IV. Mutual Solubility of *o*-, *m*-, and *p*-Nitroanilines and of *o*-, *m*-, and *p*-Chloronitrobenzenes. G. T. KOHMAN (*J. Physical Chem.*, 1925, **29**, 1048—1056; cf. preceding abstract).—The mutual solubilities of the three nitroanilines and of the three chloronitrobenzenes are recorded. As with the previous systems, the isomerides form solutions which are practically ideal, although calorimetric data for the chloronitrobenzenes are not available. It is probable that many such ternary systems will be found to be ideal, the solubility diagram affording the basis for a method of analysis.

The behaviour, on melting, of *o*-nitroaniline and of *m*-chloro-

nitrobenzene in binary mixture indicates the existence of an unstable form. A new method for the preparation of *m*-chloronitrobenzene from *m*-nitroaniline by diazotising in hydrochloric acid solution and subsequent treatment with cuprous chloride, giving 80—90% yield, is also described. L. S. T.

Solubility Relations in Isomeric Organic Compounds. V. Construction of the Ideal Ternary Solubility Diagram, and its Use in Analysis. G. T. KOHMAN and D. H. ANDREWS (*J. Physical Chem.*, 1925, **29**, 1317—1324).—A discussion of the construction and interpretation of solubility diagrams for ternary systems in which ideal or nearly ideal solutions (*e.g.*, those consisting of *o*-, *m*-, and *p*-isomerides) are formed. The use of these diagrams in the analysis of such mixtures is described. S. K. T.

Formation of Metallic Deposits by Molecular Radiation. I. ESTERMANN (*Z. Elektrochem.*, 1925, **31**, 441—447).—When a narrow stream of vapour from a heated metal impinges on a cold surface in a high vacuum, condensation takes place only below a critical temperature (*e.g.*, —50° to —110° for cadmium on glass) which varies with the density of the stream and the material of the surface. From the critical temperatures, the dimensions of the apparatus, and the temperature of the hot metal, the adsorption pressure of the condensed metal may be calculated. This quantity is of the order of 10^{10} times the vapour pressure of the metal at the same temperature. The heats of adsorption may further be calculated; they are approximately 3500 cal./mol. for cadmium on glass, 3000 cal./mol. for cadmium on copper, 500 cal./mol. for cadmium on silver, and 2500 cal./mol. for mercury on silver. These values are from one-fifth to one-seventh of the heats of vaporisation. Since the work required to separate one atom from another is about one-fifth to one-seventh that required to detach an atom from a crystal surface, it would appear that the condensation nucleus consists of a simple pair of atoms. W. A. C.

Adsorption of Gases by Graphitic Carbon. H. H. LOWRY and S. O. MORGAN (*J. Physical Chem.*, 1925, **29**, 1105—1115).—The charcoals used in previous work on adsorption have proved to be hydrocarbons (Lowry, A., 1924, ii, 393); pure carbon, as graphite, is now shown capable of an adsorptive capacity equal to one-third or one-fourth that of the best adsorptive charcoals. Graphites of varying degrees of fineness were prepared by the oxidation of Ceylon graphite, previously treated to reduce the ash content, and exploding the resulting "graphitic acid" to produce "pyrographitic acid" or graphite in a fine state of division (see Burns and Hulett, *J. Amer. Chem. Soc.*, 1923, **45**, 572). Three samples of graphites of different adsorptive capacities were thus obtained. Experiments on pressed and unpressed samples of adsorbent showed no difference in adsorptive capacity.

Data for the three samples are given for (1) carbon dioxide at 0°, 35°, 56·7°, 80·4°, and 100°; (2) nitrogen at 0°, 56·7°, and 100°, and (3) hydrogen at —191°, and at pressures up to 1 atm. Graphite from

"graphitic acid" which was least oxidised (C : O=3·98 : 1) adsorbed the least gas, and that from "graphitic acid" most completely oxidised (C : O=3·12 : 1), the most. There is, however, no simple relation between the amount of gas adsorbed and the degree of oxidation. Support is given to the conclusion previously advanced (Lowry, *loc. cit.*) that large adsorptive powers are due to (1) large ratios of surface to mass and (2) unsaturation of the forces holding the atoms together in the solid.

Details of a method for measuring adsorption, eliminating the use of stop-cocks, are given. L. S. T.

Adsorption Capacities of Different Charcoal Powders. F. KÖNIG (*Pharm. Zentr.*, 1925, **66**, 645—648).—The adsorption capacity of various medicinal charcoals for mercuric chloride has been measured, and found to bear no simple relation to the adsorption capacity for methylene-blue, although those samples which adsorb the former most readily are found to adsorb the latter strongly. These adsorption methods, combined with determinations of moisture, ash, soluble matter, and cyanogen compounds, are recommended for the examination of medicinal preparations. S. I. L.

Protein Films on Collodion Membranes. D. I. HITCHCOCK (*J. Gen. Physiol.*, 1925, **8**, 61—74).—The amount of protein (gelatin or egg-albumin) absorbed from an aqueous solution by a disc of collodion varies with the concentration of the protein. The results agree approximately with the hyperbolic formula proposed by Langmuir (cf. A., 1918, ii, 430) for the adsorption of a gas on a plane surface. If the p_H is varied, the absorption of protein is maximal at the isoelectric point; the absorption also varies when different quantities of inorganic salts are present, the variation being parallel to the changes in fluidity of the protein solution. The greater the permeability of the membrane to water, the larger is the amount of protein absorbed. Membranes which have absorbed protein become less permeable. Calculation of the capillary surface of the collodion from its permeability leads to the conclusion that the protein is adsorbed on the surface of the membrane. W. O. K.

Surface Concentration of Sodium Oleate and of Colloidal Sulphur. J. M. JOHLIN (*J. Physical Chem.*, 1925, **29**, 1129—1139; this vol., ii, 388, 857).—The surface tension of 0·0001% to 1% sodium oleate solutions has been measured at 25° by the capillary rise method, and the change of surface tension with time studied. For the stronger solutions, this change is rapid, and may be represented by an equation of the form $\sigma=a/t^n$. It is considered probable that this change of surface tension with time occurs only with colloidal solutions in which the solute is in a highly dispersed state similar to that in true solutions. When alkali is added in increasing amounts to the 0·1% solution, the change in σ with time fluctuates in a periodic manner. Addition of sodium hydroxide diminishes the tendency towards the formation of stable foams.

Preliminary experiments with colloidal sulphur solutions show that, under certain conditions, σ changes with time according to the same equation. L. S. T.

Structure of True Solutions and the Nature of the Changes Occurring Therein. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **37**, 230—234).—The colour changes exhibited by solutions of the oleates of cobalt, nickel, chromium, iron, copper, and manganese in aromatic hydrocarbons on warming are similar to those shown by aqueous solutions of the chlorides and other salts of these metals. Hydrate and ionic theories are inapplicable to the hydrocarbon solutions, and the author, with many references to previous work, outlines his own theories of the colour changes and the nature of true solutions in general. The colour changes are attributed to alterations in the intensity factor of the volume energy of the molecules. N. H. H.

Distribution of Particles in Colloidal Suspensions. W. W. BARKAS (*Trans. Faraday Soc.*, 1925, **21**, 66—80).—See this vol., ii, 289.

Law of Distribution of Particles in Colloidal Suspensions. Specific Volume of a Gamboge Suspension. J. R. H. COUTTS (*Trans. Faraday Soc.*, 1925, **21**, 63—65).—See this vol., ii, 290.

Colloid Systems in Nitrobenzene. F. S. BROWN and C. R. BURY (*J. Physical Chem.*, 1925, **29**, 1312—1316).—Colloidal solutions of dehydrating agents (phosphorus pentoxide, calcium chloride, silica, alumina, zinc chloride) in nitrobenzene are formed in the presence of compounds containing hydroxyl groups (*e.g.*, alcohols, organic acids) on vigorous stirring. The hydroxy compound is adsorbed by the dehydrating agent, which is peptised and passes into solution. Traces of moisture cause rapid coagulation. Sufficiently concentrated solutions of phosphorus pentoxide and calcium chloride set to gels on keeping. S. K. T.

Albumin Solutions. I. M. KOLTHOFF (*Chem. Weekblad*, 1925, **22**, 489—494).—The albumins are distinct chemical individuals, since when they are obtained from the same source in the same way, they always give the same amino-acids in the same proportions. Their amphoteric properties arise from the presence of free amino and carboxyl groups, and not from the group –CO·NH–, since diketopiperazine is entirely neutral, whilst other simple substances containing the group are not amphoteric. Adsorption is probably a purely chemical phenomenon, and although the law of mass action does not hold in its simplest form for the adsorption of acids or alkalis by proteins, yet since these substances must be polybasic and polyacidic, and the values of the coefficients of activity of multivalent ions are unknown, the law may well be found to hold and simple chemical action cannot be ruled out. Since the dissociation constants of the various acidic and basic groups in an albumin molecule probably differ but little, the ions may be regarded as spread over the whole surface of the molecule, forming with added hydrogen or hydroxyl ions a double surface layer, a knowledge of the forces within which is necessary to the understanding of the relations between electrolytes and albumins. S. I. L.

Albumin Solutions. H. R. KRUYT (*Chem. Weekblad*, 1925, **22**, 473—475).—The author considers that the solutions are true colloidal systems. S. I. L.

Solubility of Casein in Hydrochloric Acid. K. LINDERSTRØM-LANG and S. KODAMA (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **16**, [i], 1—47).—When casein is shaken for 3 days with dilute hydrochloric acid the system does not reach equilibrium. Reproducible but arbitrary solubility values are obtained by dissolving casein in a solution of sodium hydroxide and adding a known quantity of hydrochloric acid, when the casein is liberated at the isoelectric point and then partly redissolves in the excess of acid. The equilibrium may be similarly approached from the acid side, and measurements of the solubility of casein at 18° in the resulting solutions of hydrochloric acid and sodium chloride have been made. The solubility increases with the activity of the hydrogen ions and with decreasing concentration of the chlorine ions, but the results are variable. With a given total quantity of hydrochloric acid, the solubility of casein diminishes with the amount of solid phase present, owing to adsorption of acid, but with a given concentration of hydrochloric acid in solution, the solubility of casein increases with the amount of the solid phase, indicating that solid casein is a mixture of different substances. By fractionation two portions of casein with slightly different solubility were obtained. W. H.-R.

Is Casein a Homogeneous Substance? K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **16**, [i], 48—62; cf. preceding abstract).—Pure casein was prepared from milk without exposure to hydrogen-ion concentrations greater than p_H 4 or less than 7. Partial fractionation was effected by precipitating an acid solution with a base or *vice versa*. The various fractions all gave the casein reaction with rennin in a solution containing calcium salts, but showed distinct differences in the colloidal nature of the precipitate. The ratio of phosphorus to nitrogen varied between 0·0542 and 0·0194. The solubility of casein in mixtures of phosphoric acid and sodium phosphate is not independent of the quantity of solid phase, showing that casein liberated at the isoelectric point is not a single compound of phosphoric acid and protein, but a mixture of several substances. The results of Linderstrøm-Lang and Kodama (preceding abstract) with hydrochloric acid are confirmed with purer material. W. H.-R.

Physical Properties of Serum on Addition of "Water-binding" Substances. R. FÜRTH and R. PECHHOLD (*Kolloid-Z.*, 1925, **37**, 193—199).—The effect of the addition of small quantities of methyl or *iso*propyl alcohol or acetone on the physical properties of bovine serum is analogous to that produced by the addition of ethyl alcohol (cf. A., 1924, ii, 313). The viscosity shows a minimum with 0·6—1·2% of added substance, the conductivity a maximum with 0·4—0·89%, and characteristic turning points are exhibited by the refractive index with 1·2% of methyl alcohol, 5% of *iso*propyl alcohol, and 2·4% of acetone. The results are explained on the

basis of Debye's dipole theory. Dilution of the serum with small quantities of water produces characteristic alterations in the above phenomena; in particular, the viscosity minimum is destroyed. This is held to explain the discrepancy between the authors' observations and those of Hayashi (this vol., ii, 663). N. H. H.

Physical Chemistry of Colouring Matters. I. Measurement of the Electric Charge of Solutions of Colouring Matters. R. FÜRTH (*Kolloid-Z.*, 1925, **37**, 200—204).—A method is described for determining the sign of the electrical charge on particles of colouring matter. The method is especially applicable to the study of the staining of animal tissues. The disadvantages inherent to the cataphoretic method are avoided. Two electrodes composed of "half-conducting" material are connected to a source of direct current at 200—600 volts and dip in a solution of the dye. The arrangement permits only a very small current to pass through the solution, but produces a high fall of potential at the liquid/electrode boundaries. The particles cling to the electrode having the sign opposite to their own. N. H. H.

Titania Jellies. S. KLOSKY and C. MARZANO (*J. Physical Chem.*, 1925, **29**, 1125—1128).—The production of titanium dioxide jellies from sodium titanate is described. The best results were obtained with a solution of the composition HCl,TiO_2,xH_2O on addition of potassium, sodium, and ammonium carbonates as coagulating agents. Potassium carbonate gave the clearest jellies. Ferric oxide–titanium dioxide jellies were also obtained. L. S. T.

Optical Activity of Gelatin Systems. E. O. KRAEMER and J. R. FANSELOW (*J. Physical Chem.*, 1925, **29**, 1169—1177).—An extension of the work of Smith (A., 1919, i, 179), studying the optical activity of gelatin systems for p_H 2·30 to 12·31 between 10° and 50°. Gelatin, with an ash content of less than 0·05%, was used and rotations were measured for λ=5461 Å. The Tyndall effect also was measured at 23°.

Above 27·5°, the p_H–specific rotation curve shows a minimum at p_H 4·9, and another, less pronounced, at p_H 7 to 9. The apparent temperature coefficient and the change in rotation with p_H for p_H 3—11 (cf. Smith, *loc. cit.*) are both small. Below 27°, the curve changes in character, the minimum at p_H 4·9 becoming a pronounced maximum; the other minimum at p_H 7 to 9 also becomes a maximum, less pronounced, as before. That this change is quite distinct between 25° and 27·5° is shown by plotting specific rotation against temperature for a constant p_H value. The light-scattering capacities of these gelatin solutions show a pronounced maximum in the heterogeneity of the system at p_H 4·7 (approx.). The Tyndall effect and optical activity are roughly parallel at p_H values less than 5, but show little resemblance at higher values.

A qualitative parallelism is shown between gel-forming tendency and the increase in optical activity at low temperatures.

The authors conclude that (i) there is insufficient evidence for supposing that gelatin contains two related molecular species (cf.

Smith, *loc. cit.*; Lloyd, A., 1920, i, 452; Wilson and Kern, A., 1923, i, 68); (ii) gelatin systems display in many ways the characteristics of disperse systems which include the properties to which the Donnan theory of membrane equilibrium may be successfully applied; (iii) in view of (i), the so-called " mutarotation " of gelatin is an indication of colloidal changes in a system tending to gel formation. Influences which inhibit gel formation likewise prevent mutarotation. The term is thus a misnomer when applied to gelatin. The optical activity of gelatin gels shows that these are optically more or less homogeneous, *i.e.*, the structure is very fine-grained, in spite of the pronounced light-scattering capacity. L. S. T.

Elasticity of Gelatin Jellies and its Bearing on their Physical Structure and Chemical Equilibria. H. J. POOLE (*Trans. Faraday Soc.*, 1925, **21**, 114—142).—See this vol., ii, 519.

Plasticity in Relation to Gelatin. S. E. SHEPPARD (*J. Physical Chem.*, 1925, **29**, 1224—1232).—The temperature at which plasticity appears in 1% to 8% gelatin solutions depends on the concentration and the method of preparation. The growth of elastic resistance with time is most marked for the more concentrated solutions. In the region between the m. p. and setting-point curves plasticity is well developed. S. K. T.

Plasticity and Structure in Gelatin Systems. R. H. BOGUE (*J. Physical Chem.*, 1925, **29**, 1233—1238).—The change from the plastic solid to the viscous liquid state in gelatin systems is gradual and continuous; the exact value of the transition point, which depends on the concentration, is governed by the sensitiveness of the instruments used. It is not a " critical equilibrium temperature," but a point on a continuous curve. The interpretation of these facts on the basis of the fibrillar structure theory for gelatin sols is discussed. S. K. T.

Plasticity in Relation to Cellulose and Cellulose Derivatives. S. E. SHEPPARD and E. K. CARVER (*J. Physical Chem.*, 1925, **29**, 1244—1263).—The plastic properties of cellulose nitrate and acetate films and sols are recorded, and a modified Bingham plastometer is described. Cellulose plastics resemble the metals in elastic properties, although the ultimate particles are more like those of rubber than those of the metals. Unless *X*-rays reveal a crystalline structure, the fibrillar structure theory is to be preferred for these sols, the fibrils being chains of molecules held together by residual valencies. On this view, Mardles' " metastable phase " (cf. A., 1923, i, 443) might consist of a brush-like structure of broken filaments. S. K. T.

Plasticity as applied to Viscose and Artificial Silk. C. S. VENABLE (*J. Physical Chem.*, 1925, **29**, 1239—1243).—Curves are given illustrating the effect of humidity on the plasticity of viscose silk. Viscose solutions (7% to 9%) behave almost like true solutions; their viscosities diminish with increasing temperature and pass through a minimum on ageing. [Cf. *B.*, 1925, 912.] S. K. T.

Limited Significance of Hydrogen-ion Concentration as a Factor in Determining the Condition of Lyophilic Sols. H. R. KRUYT and H. C. TENDELOO (*J. Physical Chem.*, 1925, **29**, 1303—1311).—The electrolyte concentration of the medium determines the electrical condition of the colloid particles in gelatin solutions. The action of electrolytes on lyophilic colloids does not differ essentially from that on lyophobic colloids. The isoelectric point may be reached at various hydrogen-ion concentrations by adding a quantity of electrolyte just sufficient to produce discharge. The viscosity of positively charged gelatin is diminished by the addition of uni-univalent neutral salts, the diminution depending on the valency of the anions. Bi- and ter-valent cations increase the positive charge on the gelatin particles and this is accompanied by an increase in the viscosity. Emulsoid sols are to be regarded as hydrated suspensoids, the electric charge, which is one of the factors of stability, being influenced by electrolytes in all colloidal solutions in essentially the same manner. S. K. T.

Action of Electrolytes on Colloidal Nitroalizarin. S. LIEPATOV (*Kolloid-Z.*, 1925, **37**, 224—230).—With the object of throwing light on the constitution of alizarin lakes, the adsorption of various electrolytes by nitroalizarin and by its monosodium salt has been measured. In the coagulation of nitroalizarin sols by solutions of barium, calcium, cupric, aluminium, and ferric chlorides, of the sulphate and acetate of copper, and of other salts not designated, it is found that the degree of adsorption is influenced by the anion, *e.g.*, with the copper salts the more readily hydrolysable acetate is adsorbed more than the sulphate. The coagulates (lakes) vary in composition according to the concentration of salt in the solution. The principal rôle in the formation of the lakes is played by the cations. The anion is not adsorbed, and only affects the process in so far as the specific properties of the electrolyte depend on it. With free nitroalizarin, the salts of strong inorganic acids and the acids themselves, *e.g.*, barium and cupric chlorides, and hydrochloric acid, are not adsorbed at all, whereas cupric acetate is strongly adsorbed, giving lakes of variable composition. From a consideration of the properties of this and similar lakes and the effect on them of change of temperature and mineral acids, the author concludes that they are formed by a distribution of the base, cupric hydroxide, etc. between the two acids nitroalizarin and acetic acid. In the case of monosodium nitroalizarin, experiments with barium and cupric acetates show that a chemical compound of constant composition is formed, 2 mols. of the nitroalizarin reacting with 1 mol. of the acetate with the elimination of sodium acetate. These compounds have the same colours as the corresponding lakes of variable composition described above, and the latter are therefore regarded as the result of unsaturated chemical combination. N. H. H.

Action of Proteins on Gold Sols. W. REINDERS (*Chem. Weekblad*, 1925, **22**, 481—484).—The variations in the protective effect of proteins in solutions of different degrees of acidity and

alkalinity have been followed by measurements of the gold numbers and the migration velocities for different values of p_H and different concentrations of protein. The results are in accordance with the known amphoteric character of the proteins. S. I. L.

Separation Methods by Means of Specific Adsorption. A. FODOR and A. ROSENBERG (*Kolloid-Z.*, 1925, **37**, 234—236).—The disadvantages inherent to the usual biochemical methods of separating mixtures of albumin, peptone, carbohydrates, organic acids, etc., may be avoided by the use of a specific adsorption process which consists of first treating the mixture in fairly strong acid solution with talcum powder which removes organic acids, adsorbing the albumin from the filtrate, after diminishing its acid concentration, by means of kaolin, and finally removing starch from the kaolin filtrate by moist ferric hydroxide. Experiments are described which illustrate the efficacy of the process and demonstrate the influence of the constitution of oxalic, malonic, succinic, lactic, malic, glyceric, tartaric, citric, and pyruvic acids on the readiness with which they are adsorbed by talcum powder and by kaolin. N. H. H.

Velocity of Coagulation of Antimony Trisulphide. K. JABŁCZYŃSKI and A. PRZEŹDRIECKA-JĘDRZEJEVSKA (*Rocz. Chem.*, 1925, **5**, 173—177; cf. this vol., ii, 203).—The velocity of coagulation on the addition of potassium chloride of colloidal antimony trisulphide is shown to agree with the equation log tan α—log tan $\alpha_0 = kt$, where α and α_0 are the initial and the final angles of rotation of polarised light over a period of time t, and k is the coefficient of coagulation. This equation was previously shown to hold for colloidal arsenic trisulphide (*loc. cit.*). During the first 24 hrs. k changes very slightly, but later it increases, probably as a result of the loss of hydrogen sulphide, which has a stabilising influence on the colloid; k remains constant after blowing hydrogen through the hydrosol until free hydrogen sulphide can no longer be observed, its value, however, being nearly quadrupled. R. T.

Velocity of Coagulation of Mixed Colloids. K. JABŁCZYŃSKI and H. LORENTZ-ZIENKOVSKA (*Rocz. Chem.*, 1925, **5**, 178—181; cf. preceding abstract).—The velocity of coagulation of mixtures of colloidal arsenic and antimony sulphides follows the same law as for each colloid separately (cf. preceding abstract). The same result is obtained when the colloidal sulphides are prepared separately and then mixed, as when the colloids are produced together from a mixed solution. R. T.

Electrical Dispersion of Liquids. V. COFMAN (*J. Physical Chem.*, 1925, **29**, 1289—1302).—Experiments are described in which the nature of current conduction across the boundary between aqueous potassium tri-iodide solution and nitrobenzene is investigated. Other solutes and liquids were also used. A critical *E.M.F.* must be attained before any current crosses. Ions, electrons, and larger complexes of ions and solvent are involved in the process. The phenomena at the electrodes depend on the *P.D.* applied;

dispersion occurs, generally in the solvent in which the substance produced by the current is insoluble, or only slightly soluble.

S. K. T.

Rhythmic Reactions showing U-shaped Bands. G. V. STUCKERT (*Kolloid-Z.*, 1925, **37**, 238—239).—The "corrosive" action of certain substances when placed on gelatin gels contained in test-tubes has been studied. Three effects were observed: (i) reversible or irreversible solvation of the gel; (ii) penetration of the gel by the substance, with the formation of different types of fissure; (iii) rhythmic reactions. With sodium aminoacetate and sodium tungstate the effects (i) and (iii) were obtained. The middle of the gel became solvated from top to bottom, and at the bounding surface between the sol so formed and the gel, horizontal bands, lower in the middle than at the sides (and thus like a wide U), made their appearance.

N. H. H.

Simple Method for Preparing Ultra-filters. E. MÜLLER (*Kolloid-Z.*, 1925, **37**, 237—238).—An apparatus, fully figured in the original, is described, with which the uniform impregnation of ultra-filters with gelatin or collodion may be effected. The disadvantages of Bechhold's method (*Z. physikal. Chem.*, 1907, **60**, 257) are avoided.

N. H. H.

Equation of State and its Relation to the Laws of Thermodynamics. N. J. KOLTSCHIN (*Z. anorg. Chem.*, 1925, **147**, 312—320).—In Lorenz's ("Festschrift z. Jahrhundertfeier d. Physikalischen Vereins," Frankfurt a.M., 1924) deduction of gas laws from the first two laws of thermodynamics and the conditions $(\delta U/\delta v)_T=0$ and $(\delta U/\delta p)_T=0$ there is the inherent assumption that $F(p,v,T)=0$. It is now shown that from the more general equations $(p,v,T)dp+(p,v,T)dv+(p,v,T)dT=0$ and $(\delta U/\delta v)_{T,p}=0$, $(\delta U/\delta v)_{T,v}=0$ generalised forms of the equations of Clapeyron and Thomson may be derived. In order to deduce the equation of state it is necessary to add the condition $(\delta S/\delta p)_{v,T}=0$ or $S=S(v,T)$. The conditions $U=U(T)$ and $S=S(p,T)$ are not sufficient. This is due to the particular form of the work equation $dR=Ap\,.\,dv$, but a general form $dR=f_1dp+f_2dv+f_3dT$, together with the conditions $U=U(T)$ and $S=S(v,T)$, may be sufficient to deduce a differential form of the equation of state.

A. G.

Theory of Interionic Attraction in Strong Electrolytes. S. R. PIKE and G. NONHEBEL (*Phil. Mag.*, 1925, [vi], **50**, 723—728).—The theories of Milner (*ibid.*, 1912, [vi], **23**, 351; A., 1913, ii, 481) and of Debye and Hückel (A., 1923, ii, 459, 724) are compared in the light of recent experimental results, and it is shown that at present the evidence is insufficient to decide between them.

A. B. M.

Activity Coefficients and Transport Numbers of Solutions of Hydrogen Chloride in Methyl Alcohol. G. NONHEBEL and H. HARTLEY (*Phil. Mag.*, 1925, [vi], **50**, 729—749; cf. preceding abstract).—Activity coefficients and transport numbers for hydrogen

chloride in methyl alcohol solution have been determined from measurements of the *E.M.F.* of the cells H_2|HCl in MeOH|AgCl : Ag, and Ag : AgCl | HCl,(C_1) | HCl,(C_2) | AgCl : Ag. The *E.M.F.* of the former cell has been measured at 25° for concentrations from 0·0004955 (*E.M.F.*=0·3861 volt) to 0·5574 mol. HCl per 1000 g. solvent (*E.M.F.*=0·0844 volt). The transport number of the hydrogen ion for dilute solutions at 25° is 0·735±0·005. The results are discussed in conjunction with recent measurements of the activity coefficients of hydrogen chloride in aqueous and ethyl alcohol solutions. The observed values agree better with those calculated from Milner's theory than with those given by Debye's equation. The relation between the activity coefficients of hydrogen chloride in different solvents and the partial pressure of the vapour over the solutions is pointed out. A. B. M.

Dissociation Constant of Methyl Alcohol. N. Bjerrum, A. Unmack, and L. Zechmeister (*Kong. Danske Vidensk. Meddel.*, 1925, **5**, No. 11, 1—34; from *Chem. Zentr.*, 1925, i, 2680).—The dissociation constant of methyl alcohol at 18° is $10^{-17\cdot01}$, calculated from the *P.D.* between hydrogen electrodes in methyl-alcoholic hydrochloric acid and in sodium methoxide, respectively, connected by methyl-alcoholic sodium chloride solution. The dissociation constant of methyl alcohol was also obtained from the degree of alcoholysis of ammonium acetate by measuring the increase in conductivity resulting from the addition of acetic acid and methyl alcohol, respectively. For the dissociation constant of ammonia and acetic acid, it was found that $-\log K_{NH_3}=5\cdot92$ and $-\log K_{CH_3\cdot COOH}=9\cdot65-1\cdot77\sqrt[3]{C}$ at 18°. G. W. R.

Ionic Equilibria across Semi-permeable Membranes. N. Kameyama (*Phil. Mag.*, 1925, [vi], **50**, 849—864).—The results of Donnan and Allmand (T., 1914, **105**, 1941) on the distribution of potassium chloride between two aqueous solutions separated by a copper ferrocyanide membrane, one of the solutions containing also potassium ferrocyanide, are discussed from the point of view of activity coefficients and the "ionic strength principle" of G. N. Lewis. The results are in agreement with this principle, except when the potassium chloride concentration is small compared with that of the ferrocyanide. A repetition of the experimental work, however, over this range with improved methods of analysis and technique renders it probable that the deviations mentioned are due to experimental error. A. B. M.

Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. VIII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 396—402).—The equations governing membrane diffusion and osmotic equilibria previously deduced for a theoretical membrane (cf. this. vol., ii, 538) are shown to be valid for a real membrane if the mass of the latter is small compared with that of the ternary systems involved; they also hold if one of the separate systems consists of substances

of constant composition between which a phase reaction occurs when water is added or removed. J. W. B.

Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. IX. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 489—498; cf. this vol., ii, 538, 869, and preceding abstract).—Theoretical. The membrane phase rule is applied to osmotic equilibria in which two ternary systems are separated by a semi-permeable membrane. Cases are considered in which both systems contain, respectively, one and two components in common. F. G. T.

Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. X. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 564—572; cf. preceding abstracts).—Osmotic equilibria in a group of systems, separated from one another by semi-permeable membranes through which water only can diffuse, are discussed, and also the osmotic action, under different conditions, of the double membrane formed when two systems, previously in osmotic contact through a semi-permeable membrane, are separated by two membranes between which a phase is interposed. M. S. B.

Dissociation Pressures of Hydrated Double Selenates. J. FERGUSON (*J. Chem. Soc.*, 1925, **127**, 2096—2100; cf. Caven and Ferguson, A., 1924, ii, 553).—Equilibrium pressures for systems of the type $M''SeO_4,M'_2SeO_4,6H_2O \rightleftharpoons M''SeO_4,M'_2SeO_4,2H_2O+4H_2O$ have been measured, and the stabilities of the hexahydrated double selenates compared by reference to the temperatures at which the dissociation pressures reach 50 mm. of mercury. If the salts are regarded as having the structure $M'_2[M''(SeO_4)_2]$, the stability increases with decreasing molecular volume of the anion, and with increasing atomic or molecular volume of the cation, but exceptions are noted, especially in the case of cæsium. This rule is the reverse of that found for the stability of metallic ammines. The salts investigated contained ammonium, potassium, rubidium, or cæsium and copper, cobalt, zinc, nickel, cadmium, and manganese. Nickel ammonium chromate was also examined. W. H.-R.

Equilibrium in the Systems: Zinc Chloride–Pyridine: and Cadmium Chloride–Pyridine. R. B. MASON and J. H. MATHEWS (*J. Physical Chem.*, 1925, **29**, 1178—1183).—Measurements of the solubility of zinc chloride in pyridine show that only one compound, viz., $ZnCl_2,2C_5H_5N$, is formed. The curve representing the solubility of cadmium chloride in pyridine shows a break at 9°. From 0° to 9° the solubility increases rapidly, whilst from 9° to 100° there is a gradual decrease. At the ordinary temperature, the solid phase is $CdCl_2,2C_5H_5N$, whilst below 9° the stable compound is $CdCl_2,6C_5H_5N$. The new *compound* forms large, clear, transparent crystals, which at the ordinary temperature crumble to a fine powder. An analogous compound, $CdBr_2,6C_5H_5N$, has been described by Varet (A., 1891, 732). L. S. T.

Condensed Ternary System Phenol–Water–Salicylic Acid. C. R. BAILEY (*J. Chem. Soc.*, 1925, **127**, 1951—1965).—The system phenol–water has been examined, the critical saturation temperature being taken as the temperature of sudden thickening; the results in general agree with those of Timmermans (A., 1907, ii, 229). In the system salicylic acid–water, the eutectic ice–salicylic acid is determined as −0·07° and 0·103% salicylic acid. The m. p. of salicylic acid is 160·4°. The values obtained agree with those of Walker and Wood (T., 1898, **73**, 620) up to 30°, but are slightly and uniformly larger at higher temperatures. In the system phenol–salicylic acid, a simple eutectic is formed at 38·16° and 5% salicylic acid; the f. p. data agree with the presence of single molecules of the acid. The ternary system has also been examined, using synthetic and analytical methods. No liquids exist below −1·3°, the ternary eutectic composition being 6·5% phenol, 0·2% salicylic acid, and 93·3% water. Salicylic acid is much more soluble in mixtures of water and phenol than in either alone, but the results are very complex. W. H.-R.

Reversible System $PbI_2+ZnSO_4 \rightleftharpoons PbSO_4+ZnI_2$. C. G. STOFFELLA (*Boll. Chim. farm.*, 1925, **64**, 481—488).—No conversion at 15°, and only partial conversion at 100°, of zinc sulphate, in saturated solution, into zinc iodide occurs on the addition of an equimolecular amount, or more, of lead iodide. Complete conversion at 15° is attained only in extremely dilute solutions of zinc sulphate by the addition of an equimolecular amount of lead iodide. The yield of zinc iodide is best from a 1% solution of zinc sulphate at 100°. This behaviour is in accord with the solubility products of the components of the reaction, the ratio $S_{PbI_2} . S_{ZnSO_4} : S_{PbSO_4} . S_{ZnI_2}$ being 1 : 220 at 15° and 2 : 1 at 100°. F. G. T.

Precipitation Laws. P. P. VON WEIMARN (*Chem. Reviews*, 1925, **2**, 217—242).

Heats of Oxidation of Carbon Monoxide and of Hydrogen by Manganese Dioxide at 0°. J. C. W. FRAZER and C. E. GREIDER (*J. Physical Chem.*, 1925, **29**, 1099—1104).—A continuation of the work of Whitesell and Frazer (A., 1924, ii, 114). The heat changes accompanying the adsorption and oxidation of carbon monoxide by active manganese dioxide have now been measured. A large amount of heat is liberated during the admission of the carbon monoxide to the catalyst, indicating almost immediate oxidation. Equilibrium was not attained after several hours, however, owing to slow diffusion of the gases concerned: under modified conditions, thermal equilibrium was established in approximately 30 mins. It is assumed that (1) for every mol. of carbon dioxide removed, a corresponding amount of the dioxide is reduced to the oxide Mn_3O_4, and (2) all the carbon monoxide entering is oxidised. A deficiency in the amount of carbon dioxide desorbed suggests that a portion of the manganese dioxide is reduced to the monoxide, which then forms the carbonate, the catalyst showing a change from black to orange. The heats attending these reactions were evaluated

from the heat of formation, the heat of adsorption of carbon dioxide being taken equal to the measured heat of desorption. The heat data are (1) $MnO_2 \rightarrow MnO(+O)$, $-7{\cdot}0$ cal., (2) $1{\cdot}5MnO_2 \rightarrow 0{\cdot}5Mn_3O_4(+O)$, $-23{\cdot}2$ cal., (3) $MnO+CO_2 \rightarrow MnCO_3$, $5{\cdot}5$ cal., and (4) $CO(+O) \rightarrow CO_2$, $79{\cdot}7$ cal. Further results indicate that when the catalyst has been reduced with pure carbon monoxide, it is re-oxidised with difficulty. Heat treatment over-night in air at 150—160° does not restore the original activity; oxygen is more efficient in this respect. When hydrogen replaces carbon monoxide, a slow but continuous fall in pressure is observed, but the oxidation of the hydrogen is too slow for the heat of reaction to be determined. L. S. T.

Aqueous Solutions of Sodium Silicates. I. Preparation and Electrical Conductivity. R. W. HARMAN (*J. Physical Chem.*, 1925, **29**, 1155—1168).—An investigation of the system Na_2O–SiO_2–H_2O at 25°. The system has been studied from the point of view of (1) conductivity, (2) transport numbers, (3) hydrolysis, (4) sodium-ion activity, (5) silicate ion, (6) lowering of vapour pressure and of f. p., and (7) heterogeneous equilibria.

Sodium metasilicate enneahydrate, $Na_2SiO_3,9H_2O$, prepared according to Vesterberg's method (A., 1913, ii, 406), was used as the starting point and crystals of m. p. 47° (Vesterberg 48°; Erdenberger 47°) were obtained. Solutions having other values for the $Na_2O:SiO_2$ ratio were prepared by electrolytic removal of the alkali (cf. Kröger, A., 1922, ii, 212). Solutions prepared in different ways gave identical results for the conductivity and other properties. Values of Λ at 25° are given for the ratios 2 : 1, 1 : 1, 1 : 1·5, 1 : 2, 1 : 3, and 1 : 4 at concentrations $2N_w$ to $0{\cdot}005N_w$ (N_w=weight normality with regard to sodium content). The 2 : 1 and 1 : 1 solutions are excellent conductors, whilst 1 : 2, 1 : 3, and 1 : 4 are fair conductors in dilute solution, but abnormally poor in concentrated solutions (approx. $1-2N_w$). The values for 1 : 1 agree with those of Kohlrausch (A., 1894, ii, 133; 1893, ii, 166). The high conductivity of Na_2SiO_3 is attributed to the presence of hydroxyl ions formed by hydrolysis, but quantitative conclusions could not be reached. The low conductivity in concentrated solutions of 2 : 1, 1 : 1, and 1 : 1·5 is due to a decrease in hydrolytic dissociation. Hydrolysis is not sufficient, however, to account for some of the values obtained and calculations have therefore been made of the mobility of the silicate ion. Values for Λ_∞ have been assigned by extrapolation from the conductivity–log of concentration curve, and by Noyes' method (*Carnegie Inst. Pub.*, 1908, 63). The final values of Λ_∞ for ratios 1 : 1, 1 : 1·5, 1 : 2, 1 : 3, and 1 : 4 are 160, 121, 95, 91, and 88, respectively. The mobility of the silicate ion is calculated to be 60, 35, 43, and 41 for the ratios 1 : 1, 1 : 2, 1 : 3, and 1 : 4. Values of Λ_∞ derived from the curves and from the mobility data show good agreement.

It appears that the salts $Na_2O,2SiO_2$ and Na_2O,SiO_2 exist in solution and that other ratios correspond with mixtures of these salts with sodium hydroxide and " hydrated " silica.

L. S. T.

Conductivity of Solutions of Aluminium Chloride in Carbonyl Chloride at 25°, 0°, and −45°. A. F. O. GERMANN (*J. Physical Chem.*, 1925, **29**, 1148—1154).—When a current is passed through a solution of aluminium chloride in liquid carbonyl chloride, the solvent is decomposed with the formation of carbon monoxide and chlorine (*Science*, 1924, **60**, 434). The conductivity of these solutions has been examined at 25°, 0°, and −45° in a specially constructed cell. The conductivity curve resembles those which have been previously obtained for solutions in weakly ionising solvents. The variation of the temperature coefficient is also similar to that observed by Franklin (A., 1911, ii, 1052) for solutions of potassium bromide and iodide in liquid sulphur dioxide, and the interpretation suggested by Franklin is accepted by the author.

L. S. T.

Potential Difference between 0·1*N* and 3·5*N* Calomel Electrodes. J. K. GJALDBAEK (*Kong. Danske Vidensk. Meddel.*, 1924, **5**, [9], 1—17; from *Chem. Zentr.*, 1925, i, 2679).—The potential of a 3·5*N*-calomel electrode measured against a standard electrode varied from 0·31 to −0·06 millivolt, according to the method of preparation. The values after 5½ months varied from 0·45 to 0·03 millivolt. For the 0·1*N*-electrodes the potential varied between 83·5 and 83·0 millivolts. The temperature coefficient of the 3·5*N*-electrode is 0·45 millivolt, and of the 0·1*N*-electrode 0·77 millivolt per degree. The mean value of the potential between 0·1*N*- and 3·5*N*-calomel electrodes is found to be 83·13 millivolts.

G. W. R.

Decrease in Electromotive Force of Unsaturated Weston Cells. W. C. VOSBURGH (*J. Opt. Soc. Amer.*, 1925, **11**, 59—61).—A slow decrease in the *E.M.F.* of an unsaturated Weston cell is to be expected on account of the diffusion of mercurous ion and its reaction with the cadmium of the amalgam electrode giving cadmium ion and mercury. The resulting increase in the concentration of cadmium sulphate in the electrolyte must cause a decrease in the *E.M.F.* Actually, the *E.M.F.* of a number of unsaturated cells were found to decrease at the average rate of 0·03—0·04 millivolt (0·003—0·004%) in a year.

S. B.

Potentials of Copper and Zinc in Cyanide Solutions. W. M. WALKER, J. H. SORRELS, and J. M. BRECKENRIDGE (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 113—124).—The potential of copper in cyanide solutions shows somewhat unsteady values for some hours, but gradually becomes more electropositive owing to atmospheric oxidation. The most electropositive potentials found were −0·7526 volt in 0·5*N*-sodium cyanide and −0·0765 volt in the same solution containing 0·125*N*-copper cyanide; −0·8598 volt and −0·1123 volt in the corresponding potassium cyanide solutions. Zinc tends to become more electronegative. In 0·5*N*-sodium cyanide it shows −0·9156 volt, in presence of 0·175*N*-zinc cyanide −0·8731 volt. The change of potential takes place more slowly when the electrolyte is covered with paraffin oil, more rapidly when oxygen is blown

over it. The rate of corrosion of the electrodes shows similar variations. W. A. C.

Reduction Potential of Dicyanoquinhydrone. E. K. RIDEAL (*Trans. Faraday Soc.*, 1925, **21**, 143—144).—See this vol., ii, 546.

Overvoltage and Surface Forces at the Lead Cathode. S. GLASSTONE (*Trans. Faraday Soc.*, 1925, **21**, 36—41).—See this vol., ii, 301.

Electrochemical Actinometers. G. ATHANASIU (*Ann. Physique*, 1925, [x], **4**, 318—424).—The *E.M.F.* of the cells examined are not attributable to a photo-electric effect, but are due to three factors, (1) polarisation, (2) absorption of heat, and (3) chemical changes at the surface of the electrode-producing films, which may be comparatively inactive, as with zinc electrodes in zinc sulphate, or strongly actino-sensitive, as with copper in copper sulphate; in this case an *E.M.F.* of the order of 40 millivolts was obtained, the illuminated electrode being negative relative to the electrode in the dark. Greater effects can be obtained by coating metallic electrodes with films of suitable salts. Actinometers with electrodes of mercury covered with a film of mercurous halide or sulphide have been examined in monochromatic light of different wave-lengths, sulphuric acid being the electrolyte. The sensitivity is defined as the ratio of the *E.M.F.* produced to the intensity of the incident radiation. With films of mercurous halides, the illuminated electrode is positive, and the maximum sensitivity moves towards longer wave-lengths as the atomic weight of the halogen increases; the chloride and bromide are sensitive only to ultra-violet radiation, and photographic plates with this property have been prepared. With mercurous sulphide, the illuminated electrode is negative and shows a maximum sensitivity at about λ=4046 Å. The electrical conductivity of mercurous halides is increased by illumination, whilst the bromide and chloride give an orange fluorescence under the influence of ultra-violet light. Actinometers with oxidised copper electrodes in solutions of sodium or potassium chloride or sodium bromide show a marked maximum sensitivity at about λ=4046 Å., the illuminated electrode being positive. With silver electrodes coated with silver iodide, maximum sensitivity is shown at λ=4245 Å., with potassium chloride as electrolyte. If the chemical reaction involved is the decomposition of the halides, the critical wave-lengths and heats of reaction are in good agreement with the radiation theory of Lewis and Perrin. The electrical conductivities of all actino-active substances are affected by light, both effects being due to the displacement of the outer electrons, but the phenomena are distinct from the ordinary photo-electric effect. W. H.-R.

Electrolysis of Nitrobenzene with the Mercury-dropping Cathode. I. Reduction Potential of Nitrobenzene. II. Influence of Cathode Potential on Adsorption of Nitrobenzene. M. SHIKATA (*Trans. Faraday Soc.*, 1925, **21**, 42—52, 53—62).—See this vol., ii, 304.

Polarisation of Metals used as Electrodes. M. DRESBACH and H. R. HOSMER (*Amer. J. Physiol.*, 1924, **68**, 122—123).—From observations of the changes produced in the plate-filament circuit of a three-electrode tube by altering the voltage in the grid-filament circuit, polarisation values in ascending order have been obtained for amalgamated zinc–zinc sulphate; silver–silver chloride; lead; zinc; tin; uncoated silver. A. A. E.

Electrolytic Corrosion of Ferrous Metals. W. M. THORNTON and J. A. HARLE (*Trans. Faraday Soc.*, 1925, **21**, 23—35).—See this vol., ii, 303.

Effect of Superposed Alternating Current on Anodic Solution of Gold in Hydrochloric Acid. A. J. ALLMAND and V. S. PURI (*Trans. Faraday Soc.*, 1925, **21**, 10—16).—See this vol., ii, 302.

Electrochemical Corrosion Tests on Iron and Steel. H. BEENY (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 135—149).—The polished test-piece serves as anode in a 0·2% sodium chloride solution contained in a rotating gilded vessel used as the cathode. The effective surface of the cathode is made forty times as large as that of the anode, so that cathodic polarisation is minimised. Experiments show that the amount of iron going into solution as $Fe^{\cdot\cdot}$ agrees with the quantity of electricity generated, and it is inferred that the corrosion is entirely electrochemical. W. A. C.

Disintegration of Carbon Anodes in Nitric Acid. H. J. M. CREIGHTON and W. H. OGDEN (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 161—165).—In the explosive disintegration of carbon anodes, a gas is evolved which consists mainly of air. The fragments are sometimes covered with minute yellow crystals. It is suggested that the disintegration is caused by formation and decomposition of graphitic acid. W. A. C.

Physico-chemical Study of Some Organic Syntheses. C. MATIGNON (*Bull. Soc. chim.*, 1925, [iv], **37**, 825—836).—The possibility of certain reactions taking place is investigated theoretically by a consideration of the equilibrium constant, the heat of reaction, and the formula $\log K = -Q/4{\cdot}57T + 3{\cdot}50 \log T + C$. The syntheses of methyl and ethyl alcohols, formaldehyde, acetone, acetic and propionic acids from carbon monoxide and hydrogen are dealt with; also syntheses involving ethylene (butane, hexane, acetone, and propyl alcohol); and syntheses of nitrogen compounds. L. L. B.

Fundamental Factors in Corrosion. G. M. ENOS (*Ind. Eng. Chem.*, 1925, **17**, 793—797).—The rate of corrosion of various steels in the atmosphere and in distilled water was determined, the former rate averaging about ten times the latter. No definite effect of varying carbon content in the steel could be traced. Chromium–vanadium steel and nickel–silicon steel showed lower rate losses. With increase in temperature, the increase in corrosion is a function of the temperature difference above that of the ordinary for a given

steel, the slope of the curve being similar whether the corroding agent was water, dilute sulphuric acid, or ferric sulphate solution. With increase in time, the rate of corrosion suffered an initial drop and then showed a linear increase. Ultra-violet light somewhat increases the rates of corrosion. [Cf. *B.*, 1925, 765.] C. I.

Influence of Metallic Elements on the Corrosion of Iron and Steel. Y. UTIDA and M. SAITÔ (*Sci. Rep. Tôhoku*, 1925, **14**, 295—312).—Addition of chromium to iron gives an alloy that is very resistant to 10% nitric acid solutions, but is readily attacked by dilute hydrochloric acid. Nickel in iron also retards its dissolution in cold 10% nitric acid, but not to the same extent as an equal amount of chromium. Nickel steels, on the other hand, are markedly resistant to 10% hydrochloric acid, and their resistance is increased by the addition of chromium. Copper and manganese first reduce the rate of attack of 10% nitric acid on iron, but with more than 1% of these elements the resistance of the metal to this acid is much reduced. Tungsten and copper increase the resistance of iron to sulphuric and hydrochloric acids. The rate of corrosion of nickel–chromium steel in cold 10% hydrochloric acid decreases with a rise in the carbon content from 0·1% to 0·7%. [Cf. *B.*, 1925, 884.]

A. R. P.

Solution of Zinc in Hydrochloric Acid at High Pressures. W. IPATIEV and W. VERCHOVSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 1—10; from *Chem. Zentr.*, 1925, i, 2525).—The pressure developed by the reaction of zinc with hydrochloric acid in glass test-tubes placed in a closed cavity over machine oil reaches a maximum of 1125 atm. This limiting value is not conditioned by the reverse reaction, but is related to the solubility of hydrogen in the oil, the contraction of the hydrochloric acid on saturation with zinc chloride, and the compressibility of the air present in the closed cavity. The limiting value is reached when some zinc still remains undissolved in the hydrochloric acid. When copper tubes are used instead of glass test-tubes, complete solution of the zinc occurs.

G. W. R.

Catalytic Decomposition of Acetoacetic Acid by Strong Acids and Bases. H. VON EULER and A. OLANDER (*Z. anorg. Chem.*, 1925, **147**, 295—311).—Measurements have been made of the velocity of decomposition of the sodium derivative of ethyl acetoacetate in solutions of p_H 11—15·1. In the less alkaline solutions, the reaction $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H=CH_3{\cdot}CO{\cdot}CH_3+CO_2$ takes place exclusively, and the velocity constant is $3{\cdot}0—3{\cdot}4\times10^{-5}$ between p_H 11·1 and 13·2. With increasing alkalinity, the velocity of this reaction diminishes rapidly and is zero at p_H 14·2. The only reaction then taking place is $CH_3{\cdot}C(ONa):CH_2{\cdot}CO_2Na+H_2O=2CH_3{\cdot}CO_2Na$, and the velocity constant of this increases rapidly with increasing alkalinity from zero at p_H 13·2 to $1{\cdot}3\times10^{-3}$ at p_H 15·1 (12·9 *N*-sodium hydroxide). The second acid dissociation constant of acetoacetic acid is 10^{-13}. A. G.

Acid Catalysis in Lactone Formation. H. S. TAYLOR and H. W. CLOSE (*J. Physical Chem.*, 1925, **29**, 1085—1098).—An examination of Henry's results (A., 1892, 1303) indicates that the proportionality between the reaction velocity and the hydrogen-ion concentration is not exact, but that, as the concentration of the catalysing acid is increased, the reaction velocity increases faster than the hydrogen-ion concentration. The reaction has now been studied by varying the nature and concentration of catalysing acid and of the neutral salt, the temperature, and the solvent.

γ-Hydroxyvaleric acid, prepared only as required, from its lactone, was the acid used, and the reaction velocity was measured in the usual way, after addition of the catalyst, with barium hydroxide as the titrating agent. The reaction was studied in presence and absence of salts over a temperature range 0—35°. In the experiments with different solvents, *o*-hydroxymethylbenzoic acid replaced γ-hydroxyvaleric acid, since the former is easily obtainable in the crystalline state and is stable when kept dry, and was converted into its lactone as in the previous case. The marked effect of moisture on the reaction velocity indicated that water plays an important rôle, and hence the velocity of lactone formation from this acid was also studied in ether–water mixtures with hydrogen chloride as catalyst. The reaction velocity is very much greater in wet ethereal solutions containing hydrogen chloride than in aqueous solutions of the same acid strength.

The results are in good agreement with those previously obtained (A., 1917, ii, 253), and confirm the similarity there found between acid catalysis in lactone formation and in ester hydrolysis, so far as deviations from proportionality to hydrogen concentration and the influence of neutral salts are concerned. Good agreement likewise exists with the data of Garrett and Lewis (A., 1923, ii, 476), although, unlike these authors, the use of the formula for opposed reactions, $K_2=(1/t)\log[a/(a-1{\cdot}075x)]$, has now been found necessary to eliminate a slight drift in the unimolecular constant.

The results indicate that the velocity is not dependent on the acid concentration, the undissociated acid molecule concentration, or the hydrogen-ion concentration as determined by conductance methods. A proportionality between reaction velocity and the thermodynamic activity of the hydrogen ions is suggested instead.

L. S. T.

Catalysis of Oxido-reductions by Blood Pigments. W. LIPSCHITZ (*Z. physiol. Chem.*, 1925, **146**, 1—43).—Hydroxylamine is rapidly decomposed by blood pigments with the formation of ammonia, nitrogen, nitrite, and nitrate, the pigment being transformed into methæmoglobin. Fresh frog's muscle, blood charcoal, bile pigments, chlorophyll, hæmin, and serum cannot effect this change. Hydroxylamine (1 mol.) and oxyhæmoglobin (½ mol.) yield approximately ammonia (4/12 mol.), nitrogen (5/12 mol.), nitrite and nitrate (3/12 mol.). Hydroxylamine (1 mol.) and reduced hæmoglobin (½ mol.) yield ammonia (6/12 mol.), nitrogen (4/12 mol.), nitrite and nitrate (1/12 mol.). About 1/12 of the hydroxyl-

amine-nitrogen is lost, but small amounts of nitrous oxide are detected. With carbon monoxide–hæmoglobin (1 mol.) the yield of ammonia falls to 4/12 mol. Nitric oxide–hæmoglobin and –methæmoglobin also act in this way. More than 24 mols. of hydroxylamine are decomposed by 1 mol. of pigment, but the rate of the reaction gradually decreases, probably on account of decreased adsorption of hydroxylamine by the hæmoglobin. Irradiation of hæmoglobin or precipitation by alcohol or colloidal ferric hydroxide does not influence its catalytic activity, but if the globin molecule be removed by heating, ammonia formation decreases to 10% or less. P. W. C.

Catalytic Action. X. Comparative Study of the Catalytic Activity of Reduced Copper, Reduced Nickel, and Thoria. I. S. Komatsu and B. Masumoto (*Mem. Coll. Sci. Kyōtō*, 1925, [*A*], **9**, 15—21).—A comparison of the products obtained when *cyclo*hexanol is heated in presence of reduced copper, reduced nickel, and thoria, respectively, at 200° and at 300°, shows that reduced nickel acts principally as an oxidation catalyst, causing the formation of *cyclo*hexanone and phenol, whereas thoria has a dehydrating effect, giving yields of di*cyclo*hexyl ether, benzene, and tetrahydrobenzene. Reduced copper lies between the two in the nature of its activity and is the least affected by the change of temperature. With thoria at 300°, some dodecahydrotriphenylene is formed from *cyclo*hexanol. B. W. A.

Promoter Action of Thoria on Nickel Catalysts. W. W. Russell and H. S. Taylor (*J. Physical Chem.*, 1925, **29**, 1325—1341).—The promoter action of thoria on nickel catalysts in the reaction $CO_2+4H_2=CH_4+2H_2O$ was studied. The results indicate that promoter action in supported catalysts cannot be explained by surface extension or by change in the relative concentrations of the adsorbed reactants. The former explanation partly suffices in the case of unsupported catalysts. The following theory of promoter action is advanced. The unsaturated metal atoms assumed to be responsible for catalytic activity are present in pure nickel in a higher concentration the lower the temperature of reduction. These atoms coalesce as the temperature rises, but the presence of thoria in supported nickel catalysts prevents sintering (coalescence) and, by the creation of thoria–nickel interfaces, increases the concentration of these atoms. The same may also occur in unsupported nickel, but on the other hand the surface may increase because of the promoter acting as a support, or because the ratio in which the reacting substances are adsorbed is favourably altered. [Cf. *B.*, 1925, 903.] S. K. T.

Catalytically Active and Inactive Forms of Ferric Oxide. L. A. Welo and O. Baudisch (*J. Biol. Chem.*, 1925, **65**, 215—227).—The catalytic activity of different samples of magnetite varies with the mode of preparation, those made by precipitation of a mixture of ferrous and ferric sulphate being much more active than those made by precipitation of ferrous sulphate and subsequent

partial oxidation. The activity of active magnetite is not destroyed by oxidation, but both activity and magnetic properties are lost on heating at 550°. Comparison of the water absorption and *X*-ray diffraction spectra of active and inactive oxides indicates that the crystals of the former are smaller than those of the latter. It is thought that both magnetic properties and catalytic activity are related to the spatial arrangement of the atoms within the molecule.

C. R. H.

Catalytic Action of Colloidal Metals of the Platinum Group. XVII. Colloidal Cobalt. C. PAAL and H. BOETERS (*Ber.*, 1925, **58**, [*B*], 1542—1546; cf. A., 1914, ii, 642; 1915, ii, 171).—Colloidal solutions of cobalt are prepared by the action of hydrogen in the presence of palladium on sols or gels of cobaltic hydroxide (cf. this vol., ii, 1090). Reduction occurs slowly but completely, even with preparations rich in cobalt, although in the latter case the production of the sol is accompanied by that of an irreversible cobalt gel. In the solid form, the preparations of colloidal cobalt and sodium protalbate or lysalbate oxidise slowly when exposed to air, but otherwise remain colloidally soluble for long periods; preparations of colloidal cobalt with free protalbic or lysalbic acid are considerably more stable. Attempts to obtain cobalt sols by the reduction of colloidal cobaltic hydroxide by hydrazine or formaldehyde in the presence of palladium sol were unsuccessful. Colloidal cobalt could not be obtained by the reduction of colloidal cobaltic hydroxide with hydrogen at 200—210°.

H. W.

Physical State of Catalysts. R. C. SMITH (*J. Physical Chem.*, 1925, **29**, 1116—1118).—The catalytic activities of platinum, gold, and palladium have been studied in relation to the crystalline or amorphous state of the surface. Direct observations were made of the time taken for oxygen to be evolved from solutions of hydrogen peroxide, varying in strength from 0·2 to 10 volumes, placed on a plate of the metal. Polished platinum was found to decompose hydrogen peroxide (cf. Spring, A., 1896, ii, 92), but washing the metal surface with alcohol and water, or the presence of a film of grease, inhibited the decomposition. The change in the state of surface from amorphous to crystalline was also accompanied by a decrease in catalytic activity. The loss of activity pointed out by Thomas (A., 1923, ii, 64) in the case of nickel prepared at 650°, and by Vavon (A., 1914, ii, 189) in the case of platinum-black, is attributed to the formation of crystals in the finely-divided metal.

L. S. T.

Thin Films of Platinum and Nickel and Catalytic Activity. A. W. GAUGER (*J. Amer. Chem. Soc.*, 1925, **47**, 2278—2282).—The reaction $C_2H_4+H_2=C_2H_6$, both in the presence and absence of water vapour and of oxygen, is not catalysed by thin films of platinum or nickel deposited on glass wool. It is concluded that the influence of surface in catalysis is overestimated. It is probable that catalysts have electrons on other energy levels than is the case with the bulk metal, whereas the molecules in films probably have

the same electronic configuration as the latter. The active surface of a catalyst would consist, therefore, of molecules having electrons in the outer energy levels. This theory is developed briefly.

S. K. T.

Electrolysis in Liquid Sulphur Dioxide. H. P. CADY and R. TAFT (*J. Physical Chem.*, 1925, **29**, 1075—1084).—The solubilities of various substances in liquid sulphur dioxide have been examined qualitatively and also the electrolysis of certain solutions in this solvent. Amongst other substances, potassium iodate, bromate, and chlorate, and silver nitrate, are appreciably soluble; sodium thiosulphate and cyanide and potassium dichromate very slightly soluble; and potassium perchlorate and permanganate, boric acid, and sodium insoluble in this solvent. A specially-constructed cell was used in the electrolysis experiments and precautions were taken to prevent the introduction of traces of moisture which probably account for the anomalous results previously obtained. The production of a deposit at the cathode causes reduction of the current, which is never large, to a very small value. No great advantage was found in the use of silver or copper cathodes as recommended by Bagster and Steele (A., 1913, ii, 15). In none of the electrolyses attempted (potassium iodate, iodide, ferricyanide, etc.) were cathodic reduction products of the electrolyte obtained. Generally, the products possessed similar qualitative properties and are considered to be produced by the discharge of the ions of the solvent. The cathodic deposit, characteristic of so many of the solutions, gave reactions which indicated the presence of a sulphite, thiosulphate, and probably one or more salts of the thionic acids. Contrary to Bagster and Steel (*loc. cit.*), but in agreement with Centnerszwer and Drucker (A., 1923, ii, 370), no free sulphur was contained in these deposits. Anodic products are similar to those produced in the electrolysis of the substances in aqueous solution. A difficult feature encountered in this work was that retention of the solvent frequently led to misleading analytical results. The influence of current density on electrolytic oxidation and reduction is discussed and an explanation advanced.

L. S. T.

Oxidation and Reduction. H. P. CADY and R. TAFT (*J. Physical Chem.*, 1925, **29**, 1057—1074).—In order to examine the truth of the conception that oxygen and hydrogen are respectively actually formed in oxidation and reduction reactions, electrolytic reduction was attempted in a system containing no hydrogen, and oxidation in one containing no oxygen. Ammonia was adopted as a suitable medium for oxidations, and phosphorus oxychloride, $POCl_3$, for reductions. Liquid sulphur dioxide proved unsatisfactory owing to the complex character of the cathodic processes involved (cf. preceding abstract).

Qualitative results for a number of inorganic substances are given. Nearly all solutions of these substances in this solvent are coloured. Phosphorus oxychloride is readily hydrolysed; it could be freed from the traces of hydrogen chloride formed by distillation over metallic potassium provided that certain precautions are taken to

prevent explosion. In the electrolysis of solutions of potassium iodate and of ferric chloride in phosphorus oxychloride, products were obtained which showed that reduction can take place in the absence of hydrogen. With liquid ammonia as solvent, the work was confined to solutions of thallous iodide, cuprous iodide, hydrazobenzene, and methyl- and ethyl-amine hydrochlorides, and it is concluded that oxidation in the absence of oxygen is established. A table of collected physical constants of liquid ammonia and phosphorus oxychloride is given. L. S. T.

Dissociation Theory and Photochemical Thresholds. E. J. BOWEN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The theory that absorption of a light quantum causes dissociation into free atoms or radicals has been fairly fruitful, especially in reactions to which a "chain" mechanism has been ascribed. It is not yet certain whether dissociation, if it occurs, is a unimolecular process or whether collisions of activated and unactivated molecules are necessary. There is no strong evidence for the existence of a connexion between heats of linking and activation energies corresponding with absorption spectra, as the one represents merely the difference between the energies of the lowest electron orbits in the free atoms and in the molecule, whilst the other is concerned only with the molecule. Clearer conceptions depend on a more complete knowledge of the physical meaning of absorption spectra. In general, heats of linking are less than the energies of the lower limits of absorption, and are therefore (except in the halogens) much less than the activation energies. There is little to justify a connexion between the so-called photochemical threshold and either the heat of linking or the lower limit of absorption. The conception of photochemical threshold has at present little value because there is no method of measuring it. Apparently the only work which throws light on the question of the minimum energy required to make a molecule active is in the rate of bimolecular thermal gas reactions (T., 1918, **113**, 471; 1924, **125**, 1841). In each case, the heats of activation are considerably less than the electronic activations obtained from absorption spectra, and appear to be unconnected with the heats of linking. It is difficult at present to form any clear picture of what constitutes an active molecule. R. A. M.

Relation between Quantum Sensitivity and Intensity of Radiation. C. WINTHER (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—In photochemical reactions the quantum sensitivity decreases with increase of absorbed energy. The importance of measuring this variation experimentally in future photochemical work is emphasised. A. B. M.

Einstein's "Photochemical Equivalent Law." A. J. ALLMAND (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Einstein's deduction of the photochemical equivalent law is critically examined and the conditions of its validity are discussed. The available experimental work, and in particular that of Warburg, is summarised. In considering the application of the law a clear distinction must be

made between the primary and the complete reaction. The law seldom holds when applied to the complete reaction, as is shown by an examination of a variety of photochemical changes. A more complete examination of Einstein's deduction shows that the applicability of the law even to the primary reaction may fail under certain conditions, which are briefly discussed. A. B. M.

Einstein's Law of Photochemical Equivalence. N. R. DHAR and B. K. MUKERJI (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The failure of Einstein's law of photochemical equivalence to be applicable in the majority of cases is discussed. The law is more applicable to endothermic than to exothermic reactions. The abnormally large yield obtained in the photochemical combination of hydrogen and chlorine is explained as due to electron emission during the interaction of activated chlorine molecules with hydrogen to form hydrogen chloride. The electrons thus emitted activate other chlorine molecules. A. B. M.

Confirmation of Einstein's Law of the Photochemical Equivalent in a Very Simple Photochemical Reaction. F. WEIGERT and L. BRODMANN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The photochemical transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone solution has been studied quantitatively. A reaction of this type, where the change takes place in the same molecule, is particularly suitable for testing the validity of the Einstein law. The source of light was a mercury arc, and the strong spectral groups at 436, 405, and 366 μμ, respectively, were used. The concentration of the *o*-nitrosobenzoic acid produced was determined by conductivity measurements. The energy measurements were carried out by a surface bolometer of Lummer and Kurlbaum, and the proportion of the radiation absorbed by the *o*-nitrobenzaldehyde was calculated from Hyman's figures for the extinction coefficient. The efficiency ratio in all three spectral regions was found to be 0·5 within the limits of experimental error, thus proving the Einstein law for this reaction. Based on this value for the efficiency ratio, a suggestion is made as to the mechanism of the reaction. It appears probable that the orientation of the molecules with regard to the direction of vibration of the incident light is of significance. A. B. M.

Mechanism of Photochemical Reactions. M. BODENSTEIN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A critical *résumé* attempting to clarify the general position. Einstein's law of equivalence in its simple form is practically never verified, for in almost all cases the original product is unstable and further transformations occur. Although the law is valid for the initial process, the molecule may communicate its increased energy by increasing thermal motion, by fluorescence, or by effecting a chemical reaction. If the period between two collisions is about 10^{-8} sec. the fluorescence is extinguished; this fact agrees with other estimates of the life of an activated molecule. The existing data mainly apply to conditions

with short intervals between collisions, in which circumstances the competition is between chemical reaction and the communication of energy to other molecules. The mechanisms are best studied through the medium of chemical kinetics. The author discusses primary reactions in which the departure from the Einstein law is not of a high order and considers in detail the various mechanisms postulated to explain how two molecules of hydrogen iodide by absorption of one quantum result in the formation of hydrogen and iodine. He then treats the sensitisation of ozone decomposition by chlorine and the decomposition of ozone in the presence of inert gases. He concludes that the simple equivalence law is inadequate for a complete explanation of the phenomena observed even in such relatively simple systems. A critical discussion of secondary processes and "chain" reactions follows in which the syntheses of hydrogen chloride and hydrogen iodide are taken as examples.

R. A. M.

Radiation Theory of Chemical Reaction. J. Rice (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The simple Lewis–Perrin radiation theory leads in the case of unimolecular reactions to a rate of activation about 10^{-6} that determined experimentally. The simple collision theory of activation has to meet equally serious difficulties in the unimolecular reaction. The more general radiation theory postulates that the energy absorbed extends over a broad band and is not confined to the quasi-monochromatic beam (A., 1920, ii, 100; this vol., ii, 799). This postulate is a frank assumption (as the arguments hitherto advanced appear to be unsound), and it should be discussed on its merits and justified. The author analyses the assumptions involved in the revived theory and attempts to ascertain the conditions under which the generalised radiation theory may be valid. No serious numerical discrepancy as regards intensity of absorption is likely to be removed merely by quantising a classical expression unless an additional hypothesis is advanced. The simple collision theory cannot yield a unimolecular reaction (cf. Thomson, A., 1924, ii, 222), and can only account for a sufficiently rapid supply of active molecules by a hypothesis of rapid return of activation energy to the as yet unactivated mass. The G. N. Lewis–Smith (this vol., ii, 799) tubular "quant" mechanism also implies very rapid regeneration of "quants." It also involves that radiation of all frequencies above a threshold must be effective in activating. The "quant" mechanism is at variance with dispersion and interference phenomena, whilst recent work by the Copenhagen school has resulted in a correlation of the wave theory and the stationary atom theory by means of statistical conservation and the correspondence principle. Hence the author employs the latter to investigate the conditions under which the radiation theory may hold. He concludes (*a*) that absorption must go on uninterruptedly for a relatively long period, *i.e.*, the stationary state must persist for 10^{-7} sec., (*b*) that the theory requires a gas like nitrogen pentoxide to possess intense reflecting power. Condition (*a*) is not normally fulfilled, but it may be the criterion for a

unimolecular reaction. Intense reflection may explain why light of the suitable wave-length does not seem to hasten the reactions.

R. A. M.

Influence of Radiation on Chemical Reactions. L. S. ORNSTEIN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Lewis (A., 1920, ii, 100) has directed attention to the difficulty of finding the temperature coefficient of a unimolecular reaction from the radiation theory. The rate of reaction as derived from Planck resonators as well as from light quanta is too small to be observed. Franck considers that in the photochemical process excited molecules are formed by light, collisions transform the energy absorbed by the quantum absorption into chemical energy, and in the second stage newly-formed molecules lose their energy by way of quantum emission. The author shows mathematically that if Franck's view be accepted, Lewis' difficulty disappears provided the considerations are restricted to the direct chemical action of light.

R. A. M.

Elementary Processes of Photochemical Reactions. J. FRANCK (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The elementary photochemical process consists usually in the excitation of a molecule. Stern and Volmer (A., 1920, ii, 461) showed that the primary reaction is not the first elementary process, which is instanced rather by the excitation of the molecule, *e.g.*, $I_2+h\nu=I'_2$. The conversion of excitation into chemical energy occurs only by collisions of the excited molecules with other molecules during the period of excitation. Molecules which are bound together by van der Waals forces can be separated into atoms by an adiabatic process. Illumination can cause either a dissociation into normal and excited atoms or else the formation of an excited molecule, in a single photochemical elementary process. Mecke's results (*Ann. Physik*, 1924, **71**, 104) on the band spectrum of iodine provide strong support for the views set forth. R. A. M.

Formation and Decomposition of Molecules. M. POLANYI and E. WIGNER (*Z. Physik*, 1925, **33**, 429—434).—According to Born and Franck, molecules cannot be formed by simple association, nor can the reverse process take place, because the probability of the relative energy of the colliding atoms possessing the appropriate quantum of energy is vanishing small. On the assumption that the energy levels have a finite width, the authors show that the probability of the formation or dissociation of molecules, although small, is not infinitely so. E. B. L.

Activation of Hydrogen by Excited Mercury Atoms. A. C. G. MITCHELL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 458—463).—The work of Dickinson (A., 1924, ii, 841) on the reaction between hydrogen and oxygen in presence of excited mercury vapour has been extended and the influence of argon on the rate of reaction investigated. If the concentration of oxygen be kept constant, the rate of reaction increases with the pressure of hydrogen until a saturation value is reached. On addition of small quantities

of oxygen, the pressure of hydrogen being constant, the rate of reaction reaches a maximum at 0·01 mm. of oxygen and then falls to a lower limiting value. When the pressures of hydrogen and oxygen are maintained at a constant value and the pressure of argon is varied the rate of reaction falls with increasing argon concentration, addition of relatively large quantities completely stopping the reaction. J. S. C.

Reactions of Hydrogen Activated by Excited Mercury Atoms. H. S. TAYLOR and A. L. MARSHALL (*J. Physical Chem.*, 1925, **29**, 1140—1147).—Various gases react at the ordinary temperature with the hydrogen atoms produced by collisions of molecular hydrogen with mercury atoms excited by illumination with the resonance line (2536·7 Å.) of the mercury arc. This reactivity in the case of ethylene, carbon monoxide, and oxygen indicates that activation of hydrogen alone is a sufficient preliminary to catalytic reaction, activation of the compound reduced being unnecessary. The present work differs from that of previous investigators (Dickinson, A., 1924, ii, 841; Cario and Franck, A., 1922, ii, 809) in that the initial working pressures are much higher (average 0·5 atm.) and wider variations of conditions have been employed. The mercury arc system must be kept cold. Hydrogen and ethylene reacted smoothly according to the usual equation; with hydrogen and oxygen at an initial total pressure of 36 cm., the velocity of reaction was constant over the whole range of experiment. The reaction between hydrogen and carbon monoxide is complex, formaldehyde, solid polymerised products, and methane being produced. Formaldehyde is considered to be definitely the primary reaction product, and this thus represents a new synthesis at atmospheric pressure and temperature. Mixtures of hydrogen and carbon dioxide, and of nitrogen with excess of hydrogen showed no reaction under the conditions used. Hydrogen and nitrous oxide reacted more rapidly than did similar mixtures of hydrogen and oxygen. The velocities of reaction observed are about 100—40,000 times as great as in previous studies of this type, and it is suggested that the high yields may result from a chain mechanism of the kind obtaining in the photochemical combination of hydrogen and chlorine. L. S. T.

Photosensitisation and the Mechanism of Chemical Reactions. H. S. TAYLOR (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A *résumé* of earlier work on photosensitisation, and an account of a research carried out with Marshall (preceding abstract). R. A. M.

Some Conclusions from Recent Work on Photochemistry. D. L. CHAPMAN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Trautz (A., 1923, ii, 716) has shown that perfectly dry hydrogen and chlorine are unaffected by visible light. Electrolytically prepared gas cannot be dried sufficiently to ensure no reaction; probably enough oxygen is present to form a trace of water which on illumination initiates the chain of reactions. The author uses

as a working hypothesis the statement :—$Cl_2+h\nu=Cl'_2$ (active); $Cl'_2+H_2O \rightleftharpoons \frac{Cl}{Cl}>O<\frac{H}{H}$; $\frac{Cl}{Cl}>O<\frac{H}{H}+H_2=\frac{H}{Cl}>O<\frac{H}{H}+HCl$; $\frac{H}{Cl}>O<\frac{H}{H}+Cl_2 \rightleftharpoons \frac{Cl}{Cl}>O<\frac{H}{H}+HCl$, etc. Without water, an active molecule of hydrogen chloride is assumed. Water is not essential under the influence of ultra-violet light. Chapman (T., 1923, **123**, 3079), in opposition to Baly and Barker (T., 1921, **119**, 653), finds that the rate of reaction is proportional to the intensity of the light. The reaction between iodine and potassium oxalate was found by Dhar (T., 1923, **123**, 1856) to be proportional to the intensity of the light, whilst Berthoud and Bellenot (A., 1924, ii, 327) found it proportional to the square root of the intensity. The latter view is confirmed (Walters, unpublished), with the addition that the mean life of an active molecule is $>0{\cdot}02$ sec. and may be as high as 1 sec. The implications of the verification are discussed.

R. A. M.

Physical Antecedents of the Photo-activity of Chlorine. W. Taylor (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A theoretical examination of the optical properties of a medium containing activated molecules, and of the possibility of detecting their presence in photochemical reactions. Attempts to observe a change in the refractive index of chlorine when subjected to radiation containing the activating frequencies yielded negative results. A. E. M.

Photo-activation of Chlorine. E. J. Bowen (*Phil. Mag.*, 1925, [vi], **50**, 879—880).—An error in Taylor's deductions (this vol., ii, 811) is pointed out. No account was taken of the fact that the amount of light absorbed varies with the wave-length. When this is considered, the results lead to the conclusion that the Ribaud fine-structure bands are photo-active and that the rate of combination of hydrogen and chlorine is directly proportional to the number of light quanta absorbed. A similar error has been made by Coehn and Jung (this vol., ii, 142). A. B. M.

Mechanism of the Ozone–Chlorine Reaction. A. J. Allmand (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—In the photochemical decomposition of ozone in the presence of chlorine it is suggested that the activated chlorine molecules produce activated oxygen molecules by collision, and that both are then effective in deozonisation by collision with ozone molecules. Assuming that the life of an activated chlorine or oxygen molecule is long in comparison with the time taken to encounter an ozone molecule, it is shown that the reaction should be of zero order, as is observed experimentally. A. B. M.

Mechanism of Photochemical Reactions. N. R. Dhar and B. K. Mukerji (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—It is assumed that the first stage in a photochemical reaction consists of the activation of some at least of the molecules concerned. In the phenomenon of photo-sensitisation, *e.g.*, by chlorine in the

decomposition of ozone, the molecules of the sensitiser are activated by the incident light and then pass on their energy to the reacting molecules. The mechanism of photo-inhibition is discussed. In certain cases, it appears to be related to the fluorescent nature of the inhibitor molecules, which transform the active short wave-lengths of the incident light into less active light of longer wave-length. The temperature coefficients of photochemical reactions are considered, and it is shown that they may, and often do, possess values greater than unity. A. B. M.

Photochemical and Thermal Decomposition of Ozone. R. O. Griffith and A. McKeown (*Trans. Faraday Soc.*, Oct. 1925, advance proof; cf this vol., ii, 1076).—A comparison is made of the available results on the decomposition of ozone (1) by ultra-violet light, (2) by visible light, and (3) thermally, in the presence of oxygen only and with other diluent gases. The relative rates of decomposition in helium, nitrogen, and oxygen are given by the ratios 6·0 : 3·8 : 1 in ultra-violet light, and 5·3 : 4·4 : 1 in visible light. The helium : nitrogen ratio for thermal decomposition is 0·89 : 1, and the nitrogen : oxygen ratio is of about the same order as for photochemical decomposition. The catalytic effect of hydrogen is more difficult to measure, but appears to be much greater still. The temperature coefficient of the reaction increases with wave-length and is greatest in thermal decomposition. It is probable that the primary step in all cases is activation of the ozone molecule, but the subsequent course of the reaction may be different under different conditions. In the decomposition of ozone thermally or by visible light, the intermediate formation of atomic oxygen is improbable. Alternative mechanisms of the reaction are discussed. A. B. M.

Rôle of Water in the Photosynthesis of Hydrogen Chloride. R. C. W. Norrish (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Coehn and Jung's results on the catalytic action of water on the photosynthesis of hydrogen chloride by visible radiation (this vol., ii, 142) cannot be accounted for by the theories of Coehn or Cathala (this vol., ii, 812). They are, however, in accord with the hypothesis that the effect is produced by a film of water on the surface of the vessel. It is assumed that the primary photochemical reaction, $Cl_2+h\nu=2Cl$, occurs at the surface and is proportional to the concentration of water existing there, and that the chain reactions extend into the gas phase and end again at the surface. The author's results on the induction period are explained on the same basis. A small quantity of ammonia can affect the reactivity of the surface, even after the removal of all gaseous ammonia. The velocity of the dark reaction between ethylene and chlorine is increased by 30% by so treating the surface of the vessel. It is suggested that other cases of catalysis by traces of water may be due to the formation of a surface film. A. B. M.

Law of Photographic Blackening for Homogeneous *X*-Rays. W. Busse (*Z. Physik*, 1925, **34**, 11—14).—The proportionality

between blackening and intensity is found to be linear. Variations from this law must be attributed to variation in development.

E. B. L.

Formation of Polar Compounds by Photochemical Reactions. W. A. NOYES (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A discussion of the work of Moore and Noyes (A., 1924, ii, 748) on the reactions between oxygen and mercury, and nitrogen dioxide and mercury when the mercury was illuminated by wave-lengths both shorter and longer than the photo-electric threshold of mercury. It is considered probable that in such reactions leading to the formation of a highly polar compound the removal of electrons from the electropositive element by means of light may accelerate the reaction. The reaction $4Hg+2NO_2=4HgO+N_2$ is considered to take place through the scheme $Hg(liquid)+radiation=Hg^+(Hg\ liquid)+\ominus$, $\ominus+NO_2=NO_2'$, and $NO_2'+Hg=HgNO_2+\ominus$, in which the electron is made available for more than one such cycle. A. E. M.

Reactions Produced by Sunlight in the Presence of Uranium Compounds. J. ALOY and A. VALDIGUIÉ (*Bull. Soc. chim.*, 1925, [iv], **37**, 1135—1140).—In neutral solution, uranium salts on exposure to sunlight in the presence of organic compounds for periods up to a few hours yield a violet precipitate of uranoso-uranic oxide, $U_3O_8,2H_2O$, through partial reduction of the uranic salt. In acid solution, the reaction is indicated by the decolorisation of methylene-blue. The reaction is even more rapid on exposure in a vacuum. With saturated hydrocarbons, there is no reaction; with olefinic hydrocarbons, reaction takes place readily, amylene yielding amyl alcohol. Acetylenic hydrocarbons react even more readily, and in the case of acetylene the appearance of the violet compound is accompanied by the formation of aldehyde and formic acid. The reaction is sufficiently sensitive for the detection of double linkings. *cyclo*Hexane and the *cyclo*hexenes behave similarly, the former being unattacked, whilst the unsaturated compounds react readily. With benzene, no reaction occurs, but the introduction of side-chains facilitates reduction and reaction takes place with increasing readiness from toluene to xylenes and cymene. Benzoic acid is formed when only one side-chain is present. The introduction of electro-negative groups into the hydrocarbons favours reaction. Chloroform, bromoform, and iodoform react readily with formation of the hydrogen halide. With the alcohols, reaction takes place readily, yielding the corresponding aldehyde and acid, but the reaction proceeds less readily as the length of the carbon chain increases. Methyl alcohol reacts less readily than ethyl alcohol, but the slow reaction of the cyclic alcohols is probably due to their slight solubility. Reaction occurs with the aliphatic ethers, but not with phenolic ethers. With the aliphatic aldehydes, reaction proceeds more rapidly than with the corresponding alcohol, but with aromatic aldehydes the reaction is much slower. Ketones react very slowly, but fatty acids, with the exception of acetic acid, are readily decomposed and the decomposition is promoted by the

presence of hydroxyl or carbonyl groups in the molecule. Phenols do not undergo catalytic oxidation in this way; on the contrary, they prevent the catalysis in the presence of many acceptors of oxygen. Amines and amides do not react. R. B.

Relation between Velocity of Photochemical Reactions and Dielectric Constant. C. WINTHER (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—An examination of some results on the photochemical oxidation of iodoform and of the polymerisation of anthracene in several solvents shows that in general the reaction velocity decreases with increasing dielectric constant. A. B. M.

Formation of Organic from Inorganic Substances under the Influence of Light. O. BAUDISCH (*Chem.-Ztg.*, 1925, **49**, 737).—In connexion with recent work of Baly and Heilbron, the author directs attention to his previous experiments on the formation of organic nitrogenous compounds (*e.g.*, formhydroxamic acid) by the action of ultra-violet light on mixtures of alkali nitrates and simple aldehydes or alcohols or on alkali nitrate solutions through which carbon dioxide is passed. Similar results have also been obtained by illuminating mixtures of formaldehyde and nitric oxide.
W. T. K. B.

Activity of Various Radiations in Photosynthesis. R. WURMSER (*Compt. rend.*, 1925, **181**, 374—376).—The assimilation of carbon dioxide by marine algæ (*Ulva lactuca*) has been studied under slight illumination. The radiant energy absorbed was measured by the product of the intensity and the absorbing power of the chlorophyll, corrected for absorption due to its colourless constituents. The assimilation is evaluated as the chemical work in cal. involved in the reduction of the absorbed carbon dioxide to carbon. The efficiency, which is the ratio of assimilation to absorbed energy, is between 60 and 100 for red light (cf. *ibid.*, 1923, **177**, 644). This result agrees with that of Warburg and Negelein (A., 1923, ii, 718), but their conclusion that the efficiency is inversely proportional to the frequency is criticised. The ratio of the efficiency for radiation of wave-length 590—490 μμ to that of wave-length 700—590 μμ is 1·15. The greater efficiency of green light is connected with the fact that its frequency is such that $2h\nu$ corresponds exactly with the energy required to reduce a molecule of carbon dioxide.
F. G. S.

Photolysis of Methylene-blue, Sensitised by Zinc Oxide. E. BAUR (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Investigation of the photolysis of methylene-blue, sensitised by zinc oxide, offers corroboration of the idea that photolysis is molecular electrolysis (Baur, A., 1918, ii, 284). The zinc oxide, in absorbing energy, is converted into a "phototrope" one-half of which oxidises a substance in its neighbourhood, whilst the other reduces it. The scheme of the photolysis of methylene-blue is considered thus:

$$ZnO \begin{cases} \oplus + \text{methylene-blue} \longrightarrow \text{oxidation products} \\ \ominus + \text{methylene-blue} \longrightarrow \text{leuco-compound.} \end{cases}$$

A. E. M.

Photochemical Sensitisation. A. BERTHOUD (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A discussion of various interpretations of the photochemical sensitising process. It is suggested that light may render a sensitiser chemically active and in consequence provoke a more or less complex chain of reactions at the end of which the sensitiser is regenerated (cf. preceding abstract). The hypothesis has been examined in connexion with the rate of addition of bromine to cinnamic acid and to stilbene, and is supported by the results.

A. E. M.

Becquerel Effect on Copper Oxide Electrodes. W. J. D. VAN DIJCK (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—For copper oxide electrodes in *N*-solutions of potassium nitrate, zinc nitrate, and sodium bromate subjected to wave-lengths between 5700 and 8600 Å. the Becquerel effect becomes zero at the same potential for all wave-lengths. It is concluded that the analogy with vacuum cells does not hold and that the effect does not consist in the neutralisation of positive ions in the liquid by the ejection of electrons from the electrode. Experiments with specially prepared electrodes show that cupric oxide and possibly cuprous oxide are light-sensitive. The Becquerel effect is then explained by the transport of oxygen resulting from the balance of the light reactions. $2CuO \rightleftharpoons 2Cu+O_2$; $2Cu_2O \rightleftharpoons 4Cu+O_2$ and $4CuO \rightleftharpoons 2Cu_2O+O_2$.

A. E. M.

Absorption of Light by Solutions of Electrolytes. H. VON HALBAN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—An examination of the validity of Beer's law. The molecular extinction coefficients of solutions of sodium nitrate, sodium picrate, and sodium dinitrophenoxide are constant only up to 0·5*N*-concentration, above which the variations are greater than the observational error. Addition of potassium, sodium, and calcium chlorides to potassium nitrate solutions has a powerful effect on the absorption of light by the nitrate ions. The influence of calcium chloride is greater than that of either the sodium or potassium salt. At 0·048*N*-concentration potassium and sodium nitrate show the same molecular extinction coefficient. The light absorption by a 0·048*N*-barium nitrate solution showed differences from that of the alkali nitrates in the same sense as those induced by adding calcium chloride to potassium nitrate solutions, and it is deduced that bivalent cations influence the light absorption of the univalent anion even in diluted solutions. Similar departures from Beer's law were found by adding various salts to solutions of sodium picrate and sodium dinitrophenoxide. A. E. M.

Action of Ammonia and of a Solution of Potassamide in Liquid Ammonia on certain Halides of Molybdenum and Tungsten. F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1925, **47**, 2317—2323).—Molybdenum and tungsten dibromides and tungsten dichloride yield slightly soluble ammonobasic halides on treatment with liquid ammonia. Molybdenum tribromide and pentachloride, and tungsten pentabromide and hexachloride dissolve in liquid

ammonia to give red solutions, the first named also giving a precipitate of ammonobasic bromides. Dilution of the solutions yields amorphous precipitates of indefinite composition. Molybdenum pentachloride absorbs 8 mols. of ammonia gas, giving a derivative of unknown composition. "Nitridation" takes place when an ammonia solution of molybdenum dibromide is kept for some days. *Potassium ammonomolybdite*, $Mo(NK)_2NH_2$, is precipitated by adding excess of potassamide solution to molybdenum tribromide solution and keeping for some weeks. Free potassium is formed owing to reduction of the potassamide and "nitridation" of the molybdenum; hydrogen and nitrogen are simultaneously formed. The compound reacts vigorously with water and is soluble in dilute sulphuric acid; it loses $0{\cdot}5NH_3$ at 120—130° in a vacuum. The *sodium* salt is prepared using molybdenum pentachloride and sodamide. *Potassium ammonotungstite*, $(?)W(NK)_2NH_2$, is precipitated as above, using tungsten pentabromide. It is pyrophoric, blackens in air, and reacts violently with water. If excess of halide is used in these precipitations, ammonobasic mixtures are obtained.

S. K. T.

Apparently Anomalous Protection against Oxidation. S. E. Sheppard (*Nature*, 1925, **116**, 608—609).—When a strip of copper, brass, or bronze is dropped into a solution of potassium persulphate, it is blackened readily and completely, whereas if it is slowly lowered into the solution, blackening either does not take place or is merely a patchy tarnish. The oxide layer forms a soft, velvety pile which consolidates when rubbed to a smooth and semi-lustrous layer. The phenomenon is evidently associated only with the difference in the time of exposure of the metal to the air–solution interface, and normal blackening can be caused by mechanical or chemical protection of the metallic surface as it passes the interface, where molecular oxygen is accumulating as a result of reactions expressed by the equations: (i) $K_2S_2O_8+H_2O=2KHSO_4+O$; (ii) $O+O=O_2$. In explanation of the oxygen interference, the formation of cuprous peroxide, Cu_2O_3, is postulated; alternatively, both cuprous and cupric peroxides may be formed, with subsequent mutual reduction.

A. A. E.

Is Orthoboric Acid, H_3BO_3, Volatile in Steam? R. Anschütz and K. Riepenkröger (*Ber.*, 1925, **58**, [*B*], 1734—1735).—Orthoboric acid is volatile with steam only if the temperature is sufficiently high to cause dissociation into water and metaboric acid; the latter then volatilises and subsequently recombines with the condensed water to give orthoboric acid. If a solution of orthoboric acid in water is distilled under atmospheric pressure, the distillate does not contain orthoboric acid.

H. W.

Corrosion of certain Metals by Carbon Tetrachloride. F. H. Rhodes and J. T. Carty (*Ind. Eng. Chem.*, 1925, **17**, 909—911).—Pure, dry carbon tetrachloride vapour reacts vigorously with aluminium yielding hexachloroethane, $2Al+6CCl_4=2AlCl_3+3C_2Cl_6$. Other metals are only slightly corroded by prolonged

exposure to the dry liquid or its vapour, but in presence of water hydrogen chloride is formed by the interaction of the water with carbon tetrachloride (the metals acting as promoters) and corrosion proceeds accordingly. [Cf. *B.*, 1925, 852.] C. I.

Preparation of "Phosgeno Salts." A. F. O. GERMANN and C. R. TIMPANY (*J. Amer. Chem. Soc.*, 1925, **47**, 2275—2278).—An enclosed apparatus is described for the preparation of quantities of the pure metallic salts of the "phosgeno acid," $COAl_2Cl_8$, which are soluble in volatile solvents. Reactions of the type $COAl_2Cl_8 + CaCl_2 = CaAl_2Cl_8 + COCl_2$ are utilised. Vapour pressure measurements confirm the formula $CaAl_2Cl_8,2COCl_2$ for the calcium salt (cf. Germann and Gagos, A., 1924, ii, 861). A method of analysing these salts is also described. S. K. T.

Combustion of Carbon. III. H. F. SMITH (*Ind. Eng. Chem.*, 1925, **17**, 930—931; cf. this vol., ii, 888, 987).—Further experimental evidence is adduced to support the view that carbon monoxide is the initial product of the combustion of carbon at high temperatures. [Cf. *B.*, 1925, 835.] C. I.

Phosphates of Zirconium and Hafnium. G. VON HEVESY and K. KIMURA (*Z. angew. Chem.*, 1925, **38**, 774—776).—The pure phosphates, prepared by adding a solution of disodium hydrogen phosphate in 6*N*-hydrochloric acid to a solution of the oxychlorides in 6*N*-hydrochloric acid, were dried below 80°. Analytical results and general considerations point to the formula $MO_2,P_2O_5,2H_2O$ (M=Zr or Hf), but when heated at 700° they lose 2 mols. of water. Hafnium phosphate is less soluble than zirconium phosphate in hydrochloric acid, and the separation of the two should be carried out in concentrated acid. The solubility at 20° of hafnium phosphate is 0·00012 and 0·00009 mol. per litre of 10·21*N*- and 5·94*N*-hydrochloric acid, respectively, whilst of zirconium phosphate it is respectively 0·00023 and 0·00012 mol. per litre of 10·00*N*- and 6·01*N*-hydrochloric acid. Zirconium and hafnium may be separated as phosphates, but, even when working in strong acid solution, a large excess of phosphate should be used in the precipitation, which should also be carried out in the cold. W. T. K. B.

Properties of Stannous Iodide. P. FREUNDLER and (MLLE.) Y. LAURENT (*Bull. Soc. chim.*, 1925, [iv], **37**, 1133—1135).—Concentrated aqueous solutions of stannous chloride and sodium iodide deposit orange crystals of the monohydrate, SnI_2,H_2O, which on drying at 100° is converted into stannous oxide; the anhydrous iodide, obtained by spontaneous desiccation in the cold, or by warming a mixture of stannous chloride (1 mol.), sodium iodide (2 mols.), and hydrogen chloride (0·5 mol.), is stable at 100°. No double compound could be obtained in this case, but with potassium chloride in neutral solution the double compound, $SnI_2,KI,3H_2O$, described by Personne and Boullay, is obtained. The same compound is obtained in acid solution in the cold, but from warm solutions anhydrous stannous iodide is deposited, the temperature of transformation depending on the concentration of the potassium

iodide. In acid solution, the potassium double compound is readily oxidised, especially in sunlight, giving a dark brown solution which loses iodine on warming and probably contains a periodide. Under similar conditions, stannous iodide prepared from sodium iodide oxidises very slowly with separation of colloidal stannic acid. In view of these facts, the colloidal complex in *Laminaria flexicaulis* is now regarded as containing, at least temporarily, the complex iodine–rubidium–sodium (cf. this vol., ii, 22). The existence of rubidium iodide in association with protoplasm is further supported by the presence of rubidium and iodine in the equivalent proportions, by the absence of iodine and rubidium from the salts resulting from spontaneous desiccation, and by the similar behaviour of the compound obtained from *L. flexicaulis* and the rubidium–stannous iodide complex, $2SnI_2,RbI$ (Auger and Karantassis, this vol., ii, 814), on exposure to sunlight. R. B.

Lead Bromate and Diacetato-diplumbo-bromate. E. GÜNZEL and E. MARCUS (*Z. angew. Chem.*, 1925, **38**, 929—930).—Lead bromate is quite insensitive to shock or friction. A hot solution of lead acetate and acetic acid, when treated with potassium bromate, gives no precipitate on cooling, but lead bromate crystallises out after cooling and seeding. A mixture left over-night without seeding yielded a solid which on drying exploded with fatal results; the solid was found to be a mixture of lead bromate and diacetato-diplumbo-bromate (cf. Weinland and Paul, A., 1924, ii, 45), the latter being a readily detonated substance. Preparation in presence of acetic acid is therefore dangerous. S. I. L.

Doubly-refractive White Phosphorus. D. VORLÄNDER, W. SELKE, and S. KREISS (*Ber.*, 1925, **58**, [*B*], 1802—1806).—Optically isotropic white phosphorus becomes converted into a doubly refractive variety (cf. Bridgman, A., 1914, ii, 647) when strongly cooled. The transition temperature of the two forms, determined from time–temperature curves and by observation with a specially-constructed polarisation microscope, is —68° (Bridgman, *loc. cit.*, records —76·9°). The crystalline form of the doubly-refractive variety is indistinct, but appears to be either monoclinic or rhombic. Attempts to obtain well-defined crystals from carbon disulphide or other solvents at low temperatures showed that phosphorus remains permanently undercooled under these conditions and that production of the doubly-refractive variety does not occur (cf. Bridgman, *loc. cit.*). A corresponding, doubly-refractive form of arsenic could not be observed above —190°. H. W.

Effect of Sodium Chloride on Hydrogen-ion Concentration and Stability towards Alkali of Chromic Chlorides. K. H. GUSTAVSON (*Ind. Eng. Chem.*, 1925, **17**, 945—952).—The addition of progressive amounts of sodium chloride to solutions of chromic chloride causes an initial increase in the value of p_H, followed by a later decrease with greater sodium chloride concentration. The latter effect is due to the increase in concentration of the chromium salt by hydration of the sodium chloride. The former change is

best marked in dilute solutions of lesser acidity. It is considered that it is due to changes in the composition of the internal sphere in the chrome complex, different modifications of the basic aquo-chromic chlorides existing analogous to the normal chlorides $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2$, and $[Cr(H_2O)_4Cl_2]Cl$. Addition of sodium chloride will favour the formation of compounds with chlorine co-ordinatively attached, and the increase in chlorine ions is evidenced by decrease in the electric charges of the cation and by an increase in p_H. If sodium chloride is replaced by magnesium chloride, this effect is masked by the greater hydration tendency of the magnesium salt. The point at which precipitation occurs during addition of sodium hydroxide is not a function of p_H, but is proportional to the ratio of chlorine to chromium in the complex cation. C. I.

Synthetic Potassium and Sodium Chromosilicates. (MLLE.) H. KARFIOL (*Rocz. Chem.*, 1925, **5**, 182—192).—Synthetic chromosilicates of sodium and potassium are prepared by the fusion of mixtures in various proportions of chromium sesquioxide, sodium, or potassium chloride and carbonate, and silica. The fused mass, after being heated for 10 hrs., is extracted with water. In the case of mixtures with potassium, the residue thus obtained had so low a potassium content that most of them appeared to be compounds of chromium sesquioxide and silica in various proportions, the potassium present being probably an impurity. The only product of this type which appeared definitely to be a chromosilicate had a composition corresponding with the formula $K_2Cr_4Si_{13}O_{33}$. The crystalline nature of these substances could not be determined, owing to the extremely small size of the particles. The sodium chromosilicates obtained are of very complicated composition, and seem to be additive compounds of sodium silicate and oxide to chromosilicates of the same type as the known series of aluminosilicates, $R_2Al_2Si_nO_{2n+4}$. All the sodium chromosilicates prepared are isomorphous, in spite of considerable differences in composition, the proportions of chromium sesquioxide to sodium metasilicate being as 1 : 2, 3, 4, 5, 6, 7, and 8. R. T.

Decolorisation of Carbon Disulphide Solutions of Iodine by Red Phosphorus. R. N. TRAXLER and F. E. E. GERMANN (*J. Physical Chem.*, 1925, **29**, 1119—1124).—The work of Sestini (J., 1871, **24**, 1005) on the action of moist red phosphorus on iodine in carbon disulphide has been repeated and verified. After decolorisation had occurred, the phosphorus was found to contain hydriodic and phosphorous acids, but no free iodine. The presence of these acids is ascribed to their insolubility in carbon disulphide, and not to adsorption. Decolorisation when dry phosphorus is added occurs only in dilute solution; more concentrated solutions give phosphorus tri-iodide. Dry red phosphorus and red phosphorus which had been heated for 2 hrs., when shaken with iodine in carbon disulphide, lost 18·5% of its original weight before losing its activity towards iodine. The reddish-brown solutions resulting from this addition yielded red crystals of phosphorus tri-iodide, m. p. 55°. The low

m. p. (55° instead of 61°) was probably due to the presence of the compound $P_4S_3I_2$ (m. p. 119·5°) derived from the sulphur in the carbon disulphide. The preparation of phosphorus tri-iodide using carbon disulphide freshly purified with mercury is recommended. L. S. T.

Ferric Acid and Ferrates. L. Losana (*Gazzetta*, 1925, **55**, 468—497; cf. Baschieri, A., 1906, ii, 857; Frémy, *Compt. rend.*, 1841, **12**, 23; Rossel, *J. Amer. Chem. Soc.*, 1895, **17**, 760).—The authors have attempted to prepare the following ferrates: potassium, thallium, silver, mercurous, barium, strontium, calcium, mercuric, copper, lead, zinc, nickel, cobalt, manganese, magnesium, ferrous, aluminium, ferric, chromium, thorium. Potassium ferrate was prepared by oxidising with chlorine a suspension of ferric hydroxide in aqueous potassium hydroxide (Merz, *J. pr. Chem.*, 1867, **101**, 269). Barium and calcium ferrates (Frémy, *loc. cit.*) and strontium and magnesium ferrates were obtained by double decomposition from the potassium salt; with three exceptions, the ferrates of the other metals were obtained by double decomposition of the nitrates, with an aqueous suspension of very finely divided barium ferrate. In the cases of the ferrates of silver, barium, strontium, calcium, copper, lead, zinc, nickel, and cobalt, the analysis was obtained and the thermal decomposition also studied. Those of iron (ferrous and ferric), aluminium, and thorium decompose on drying and only the combining ratios of their constituents were determined. Manganese, thallium, and bivalent mercury do not give definite compounds; magnesium ferrate was not obtained. Barium ferrate ($+4H_2O$) and strontium ferrate ($+2H_2O$) are stable over concentrated sulphuric acid in a vacuum, and controlled thermal decomposition shows that they can exist as anhydrides, but calcium ferrate ($+2H_2O$) and copper ferrate ($+H_2O$), which decompose in a vacuum over sulphuric acid, do not give anhydrides. The temperatures of decomposition of the ferrates studied are diverse. All lose oxygen continuously except barium ferrate, which possibly gives the intermediate compound, $BaFeO_3$. W. E. E.

Co-ordination Chemistry. Chloroferrates of Substituted Ammonium Bases. H. Remy and H. J. Rothe (*Ber.*, 1925, **58**, [*B*], 1565—1571).—According to the author's "law of homopolar combination" of atoms (A., 1921, ii, 501) compounds containing atoms with the co-ordination number 5 or 7 are to be expected among the chloro compounds of ferric iron if they are capable of existence. From analogy with osmium and ruthenium, the existence of the ions $[FeX_4]'$, $[FeX_5]''$, $[FeX_6]'''$, and $[FeX_7]''''$ may be foreseen and stable compounds of the type $M'_2[FeX_5]$ and $M'_4[FeX_7]$ may be expected if the inherent instability of the corresponding complex ions is neutralised by combination with cations of suitable size and form. Such a series is found in the chloroferrates of substituted ammonium bases. The latter invariably also yield compounds, $M'[FeX_4]$, but their region of existence is nearly always smaller than that of the penta- and hepta-chloro

salts and their stability is generally less. Unfortunately, they are not sufficiently stable to permit measurements of molecular weight or conductivity. The following salts are described: *methylammonium tetrachloroferrate*, $[MeNH_3][FeCl_4]$, m. p. about 211°; *methylammonium heptachlorohemiaquoferrate*, $[MeNH_3]_4[FeCl_7+H_2O]$, m. p. 161°; *dimethylammonium tetrachloroferrate*, m. p. (indef.) 97—104°; *dimethylammonium pentachloroferrate*, $[Me_2NH_2]_2[FeCl_5]$, m. p. 98°; *dimethylammonium heptachloroferrate*, m. p. about 48°; *trimethylammonium tetrachloroferrate*; *trimethylammonium pentachloroferrate*, m. p. 143·5°; *tetramethylammonium tetrachloroferrate*, m. p. above 308°; *ethylammonium tetrachloroferrate*, m. p. about 85°; *ethylammonium heptachloroferrate*, m. p. 117°; *propylammonium tetrachloroferrate*; *propylammonium heptachloroferrate*, m. p. 118° after softening at 110°; *butylammonium tetrachloroferrate*, m. p. 60·5°. H. W.

Iridium Halides. F. KRAUSS and H. GERLACH (*Z. anorg. Chem.*, 1925, **147**, 265—287).—Attempts to prepare tetrahalides of iridium were unsuccessful. The formation of the trichloride from iridium and chlorine is accelerated by light and by the presence of carbon monoxide. Iridium tetrahydroxide readily reacts with chlorine when heated, yielding the trichloride, and with gaseous hydrogen chloride and bromide at the ordinary temperature, forming the *substances* $[X_2Ir(OH)(OH_2)],2H_2O$. When heated, these lose their water of crystallisation, and the resulting *compounds* $[X_2Ir(OH)(OH_2)]$ yield the acids $[X_2Ir(OH)_2]H$ when dissolved in water. By further treatment of the substances

$$[X_2Ir(OH)(OH_2)],2H_2O$$

with gaseous hydrogen chloride or bromide the *compounds* $[X_3IrOH_2]$ are obtained. The compound $[Cl_3IrOH_2]$ loses its water at 310°; the bromine compound could not be dehydrated without decomposition, and when heated yielded the *dibromide* at 440° and the *monobromide* at 485°. The *tribromide* was prepared by heating the dibromide in a bomb tube with bromine. Iridium and iridium tetrahydroxide are not acted on by iodine, but hydrogen iodide readily reacts with the tetrahydroxide forming the *substance* $[I_3IrOH_2],2H_2O$. When heated this loses water to form the *compound* $[I_3IrOH_2]$, which, when further heated, yields the *monoiodide* and probably the *di-iodide*. The *acid* $[I_3IrOH]H$ is probably formed when the substance $[I_3IrOH_2],2H_2O$ is dissolved in water. A. G.

Preparation of Auric Chloride. M. PETIT (*Bull. Soc. chim.*, 1925, [iv], **37**, 1141—1147).—The preparation of anhydrous auric chloride is best effected by the action of gaseous chlorine on gold leaf. In the apparatus described, the gold leaf is placed in a boat inside a tube (*A*) sealed on to a small flask. A current of chlorine at about 60—80 mm. in excess of atmospheric pressure is passed through the tube, leaving by a second tube, whilst a third tube at the bottom of the flask is connected with a test-tube in which the auric chloride is collected. The tube (*A*) and the adjacent side of

the flask are heated electrically, and at 245—250°, the optimal temperature, 0·15 g. of auric chloride is obtained per hr. (79% yield). R. B.

Preparation of Beryllium. A. Stock, P. Praetorius, and O. Priess (*Ber.*, 1925, **58**, [*B*], 1571—1580).—Technical beryllium oxide is purified from aluminium oxide by conversion into the basic acetate, which is dissolved in chloroform and finally distilled. Larger quantities of material are more conveniently obtained by slowly adding a solution of basic beryllium chloride to a solution of sodium carbonate through which a brisk current of carbon dioxide is passed; basic beryllium carbonate is thereby dissolved, whereas aluminium and iron hydroxides remain. Dissolved iron in the solution is removed by hydrogen sulphide. After addition of a quantity of hydrochloric acid sufficient to precipitate a fraction of the beryllium carbonate together with a little aluminium and iron which still remain, the bulk of the beryllium is precipitated as the basic carbonate, which is converted into the hydroxide. The fluorides, $NaBeF_3$, $BaBeF_4$, and $BaBe_2F_6$, are prepared by dissolving the requisite amounts of beryllium oxide or hydroxide, sodium carbonate, and barium carbonate in hydrofluoric acid and ultimately heating the products before the blowpipe.

The electrolyte is contained in an Acheson graphite crucible, which serves as anode; it rests on asbestos inside a copper cylinder, the intervening space being filled with kryptol. The cathode is composed of an iron rod with internal water cooling. The crucible is filled initially with kryptol and electrically heated at 700—800°. The contents are removed and sodium beryllium fluoride is introduced, followed gradually by the fluoride, $BaBeF_4$. When the requisite temperature (1350°) is attained, the cathode is cleaned and reinserted and actual electrolysis begins, during which the fluoride $BaBe_2F_6$ is added in small portions at frequent intervals. After 3 hrs., the process is interrupted and the beryllium is removed adhering to the cathode. A second and third run can be accomplished if the electrolyte is enriched by addition of the volatile sodium beryllium fluoride. The yield of beryllium is 45—51%, the current efficiency 75—80% in the first period, 60% in the second and third periods. Almost half of the fluorides is lost by volatilisation at the high temperature required for electrolysis. Beryllium is thus obtained in a compact, crystalline form, d^{18} 1·842. It contains only traces of sodium or barium, its purity depending otherwise on that of the materials used. The iron content varies from 0% to 0·4%. The purity of the metal is most accurately determined by measurement of the hydrogen evolved when a known weight of it is dissolved in air-free, dilute hydrochloric acid. Traces of aluminium are determined by a modification of Atack's method (A., 1915, ii, 842), using sodium alizarinsulphonate. H. W.

Colloidal Cobaltic Hydroxide. C. Paal and H. Boeters (*Ber.*, 1925, **58**, [*B*], 1539—1541).—Colloidal solutions of cobaltous hydroxide are obtained by the alternate addition of small quantities of solutions of cobalt chloride and sodium hydroxide to solutions

of sodium protalbate or lysalbate, but the protective action of the latter substances is less marked than with nickel hydroxide, and turbidity ensues when more than 10% of cobalt is present. During dialysis, the cobaltous hydroxide is oxidised by the air to colloidal cobaltic hydroxide, which can be obtained in the solid, colloidally soluble form by evaporation of the dialysed solution; stable preparations do not contain more than 10% of cobalt. If colloidal cobaltic hydroxide is directly prepared by the method described above, but in the presence of hydrogen peroxide, the stable, colloidally soluble, solid form can be obtained with more than 20% of cobalt. H. W.

[**Ultra-balance.**] F. Holtz (*Ber.*, 1925, **58**, [*B*], 1924; cf. Holtz and Kuhlmann, this vol., ii, 319).—A reply to Kuhlmann (this vol., ii, 706). H. W.

Elimination of Surface Devitrification on Laboratory Quartzware. F. C. Vilbrandt (*Ind. Eng. Chem.*, 1925, **17**, 835—837).—The surface "devitrification" or frosting that gradually develops on fused silica laboratory vessels is frequently caused by the deposition of "slag" particles in the surface of the material. The phenomenon has been investigated by repeatedly evaporating water in fused silica dishes, by repeatedly incinerating wet filter-papers in crucibles, and by repeatedly quenching hot fused silica tube in water. In each case surface "devitrification" occurred. The deterioration was progressive; the ware gradually became brittle and eventually very fragile. The corroded surface layer is removed by hydrofluoric acid, and only by that acid. Vessels treated with hydrofluoric acid (by momentary immersion in the solution, which contains a little sulphuric acid) become clear and smooth again, and their life is prolonged. W. A. S.

Calculations for and Calibration of the Haber–Löwe Gas Interferometer. G. Werner (*Z. angew. Chem.*, 1925, **38**, 905—911).—Equations are deduced for determining the percentage composition of gas mixtures, involving the scale reading of the interferometer, the refractive indices of the component gases, the absolute temperature, the pressure, and a constant for the instrument. Dry air, free from carbon dioxide, is used as standard, and any impure gas or mixture can be used for the same purpose after its relative refractive index (taking that of air as unity) has been determined. A single, short experiment enables the difference in refraction to be determined, by means of which the analysis of a gas mixture can be carried out independently of temperature and pressure. Mixtures of gases having widely different refractive indices can be analysed by using as standard a gas (*e.g.*, carbon dioxide) the refractive index of which lies between the two. W. T. K. B.

Cryostat for Precision Measurements at Temperatures extending to −180°. J. E. Walters and A. G. Loomis (*J. Amer. Chem. Soc.*, 1925, **47**, 2302—2306).—A cryostat is described, based on that of Henning (*Z. Instrumentenkunde*, 1913, **33**, 33), which

maintains for 3 hrs. any required temperature between 0° and −180° to within ±0·01°. Aged liquid air is allowed to flow through a copper spiral immersed in petroleum or butane (for temperatures to −140° and to −180°, respectively) contained in a Dewar vessel, the rate of flow, controlled by a water head, being such that the bath tends to cool slowly. Change in the temperature of the bath is revealed by the gradual deflection of a galvanometer in the resistance thermometer circuit; the needle is constantly restored to zero by the momentary passage of a current through a resistance coil in the cryostat liquid. S. K. T.

Porous Electrode for Oxidations or Reductions. M. KNOBEL (*Ind. Eng. Chem.*, 1925, **17**, 826).—Knobel (A., 1923, ii, 608) and Schmid (A., 1924, ii, 324) have described a hydrogen electrode consisting of a platinised, but still porous, graphite tube. Similar electrodes can readily be prepared for use in electrolytic oxidation or reduction. The graphite tube (one end is closed) is electroplated with lead, copper, zinc, nickel, iron, or silver, a current of air being blown through the electrode in order to keep it porous. The metallic layer should be 1—2 mm. thick, because it does not adhere well to the graphite. [Cf. *B.*, 1925, 855.] W. A. S.

Mineralogical Chemistry.

Rare Gases of Volcanic Exhalations. A. PIUTTI and E. BOGGIO-LERA (*Mem. R. Accad. Lincei*, 1924, [v], **14**, 871—884). —In the various volcanic gases of different Italian localities examined, the ratio argon : nitrogen is constantly less than in the atmosphere, a value as low as 0·381 being obtained in one case. The ratio (helium+neon) : argon varies within wide limits, but, as with the gases of thermal springs, is always higher than with air. For the gases of any one volcanic region, the content of neon and helium increases as the temperature at which the gases issue falls. In no instance were more than traces of neon found. T. H. P.

Albite and other Authigenic Minerals in Limestone from Bengal. E. SPENCER (*Min. Mag.*, 1925, **20**, 365—381).—Small crystals of albite, together with crystals of quartz, mica, pyrite, rutile, and tourmaline, occur in certain zones in limestone beds near Raipura in Gangpur State. The albite crystals are twinned on the Roc Tourné type and are dark grey in colour due to carbonaceous inclusions. Analyses (I by K. B. SEN) show the mineral to be practically pure albite :

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	Ign.	Total.
I. ...	66·95	19·72	0·50	0·88	0·66	9·95	0·52	0·63	99·81
II. ...	67·10	19·95	0·55	0·70	0·50	10·30	0·60	0·85	100·55

A review, with bibliography, is given of the literature on the occurrences of small crystals of felspars in limestones, and it is

concluded that the crystals have grown in place and are not the result of metamorphic processes. L. J. S.

Chlorophaeite in Dolerites near Edinburgh. R. CAMPBELL and J. W. LUNN (*Min. Mag.*, 1925, **20**, 435—440).—Chlorophaeite occurs as irregular patches in the dolerites (tholeiites) of Dalmahoy and Kaimes Hills near Edinburgh. On freshly-fractured surfaces it is bright olive-green with glassy lustre, but on exposure it soon changes, through dark-green, to black with pitchy lustre. This change in colour is not due to the action of light, but to oxidation. The material is mostly optically isotropic with n 1·498; hardness 1·5, d 1·81. Analysis by W. H. HERDSMAN gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.
32·95	0·62	5·40	12·37	9·18	0·33	4·75	3·05	1·68	0·36

H_2O (at 105°).	H_2O (+105°).	Total.
23·90	5·20	99·79

Several other occurrences of chlorophaeite in Scotland are noted. L. J. S.

Analytical Chemistry.

Use of the Quinhydrone Electrode for the Determination of p_H in Soils. C. BRIOUX and J. PIEN.—(See i, 1227.)

Standardisation of Solutions used in Iodometry. II. S. POPOFF and J. L. WHITMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2259—2275).—An electrometric study of the reaction between solutions of iodine in potassium iodide and of sodium thiosulphate shows that when the mixed liquids after titration are of large volume and the iodide concentration is therefore low (below 1%) a loss of iodine occurs. This loss is inappreciable when the iodide concentration is within 1% to 8% and the titration time, in the dilute solution, does not exceed 10 mins.; or when the 1% of iodide is replaced by its equivalent (0·06N) of hydrochloric acid, or by sulphuric acid up to 0·6N. Sunlight has no influence when the solutions contain up to 4% of iodide, although it vitiates the results when certain mineral acids are present. One % of iodide and 0·2N-acids may be used safely in diffused light. When the iodide concentration is less than 1% the order of mixing the solutions slightly influences the results. The conditions necessary for the accurate standardisation of thiosulphate solutions against iodine or potassium permanganate, dichromate, or bromate, are detailed. S. K. T.

Diphenylamine Reaction [for Nitrates]. L. EKKERT (*Pharm. Zentr.*, 1925, **66**, 649—650).—The development of a coloration on addition of diphenylamine to a solution in sulphuric acid is not specific for nitric acid, but arises from the presence of many other oxidising agents. The colorations developed by the common oxidising agents when a solution in concentrated hydrochloric acid is treated with diphenylamine in glacial acetic acid, diluted, and

portions are shaken with chloroform and ether, are tabulated. Concentrated phosphoric acid gives even stronger colorations than sulphuric or hydrochloric acid. S. I. L.

Quantitative Kjeldahlisation of Nitrates with Phenolsulphonic Acid and Potassium Sulphate. B. M. MARGOSCHES and E. SCHEINOST [with V. WOYNAR] (*Ber.*, 1925, **58**, [*B*], 1850—1857).—Kjeldahlisation of sodium or potassium nitrate by sulphuric acid in the immediate presence of phenol and potassium sulphate gives low values for nitrogen. If, however, addition of potassium sulphate is delayed until the first main reaction is completed (about ½ hr. after commencement of the heating with a small luminous flame), accurate results are obtained. The success of the process appears to depend on the quantitative conversion of the nitrate into mononitrophenolsulphonic acids, since the corresponding polynitro compounds cannot be accurately kjeldahlised. The immediate addition of potassium sulphate disturbs the regular course of mononitration owing to the very considerable development of heat which it causes. Addition of compounds which are formed during the reaction (*e.g.*, potassium hydrogen sulphate) and do not evolve any considerable amount of heat when added to concentrated sulphuric acid is harmless even in the initial stages of the process. H. W.

Replacement of Monohydric by Dihydric Phenols in the Kjeldahlisation of Nitrates. B. M. MARGOSCHES and E. SCHEINOST (*Ber.*, 1925, **58**, [*B*], 1857—1860; cf. preceding abstract).—Experiments with quinol, resorcinol, pyrocatechol, pyrogallol, phloroglucinol, and hydroxyquinol show that only resorcinol and phloroglucinol are suitable in place of phenol as fixing agents for nitrate nitrogen in the kjeldahlisation of nitrates in the absence of an accelerator. Complete kjeldahlisation of potassium nitrate can be effected in 4 hrs. in the presence of phloroglucinol and molybdic acid. Salicylic, *m*-hydroxybenzoic, and gallic acids are unsuitable. H. W.

Electrolytic Determination of Moderate Amounts of Arsenic. J. MOIR and J. S. JAMIESON (*J. South African Chem. Inst.*, 1925, **8**, 16—18).—The apparatus is a modification of Thorpe's electrolytic apparatus with substitution of the generator cell by a narrow cylinder, and of the porous pot by an alundum crucible. A cadmium electrode is used (activated by reversal of the current and subsequent deposition of porous cadmium on restoring the normal direction) and platinum anode. The pressure of the anode liquid (1 : 5-sulphuric acid) prevents outward diffusion of the arsenical liquid. The cross tube is filled with lead acetate cotton wool, and the gas exit connected with silver nitrate tubes; the contents of these are titrated with dilute iodine solution after addition of a large excess of potassium iodide. [Cf. *B.*, Nov. 27th.] D. G. H.

Simple Apparatus for the Determination of Carbon Dioxide. G. WITTIG (*Ber.*, 1925, **58**, [*B*], 1925).—An apparatus for the rapid,

accurate determination of carbon dioxide in carbonates is described and figured. H. W.

Detection of Sodium as Oxalate. L. W. WINKLER (*Pharm. Zentr.*, 1925, **66**, 669—670).—The conditions under which a precipitate is obtained on addition of a potassium oxalate solution to solutions containing various sodium salts are described. The test is best carried out in an alcohol–water solution containing 30% of alcohol by volume; a solution containing 2 mg. of sodium per c.c. gives an oxalate precipitate in 10 mins. S. I. L.

Sodium Rhodizonate as a Reagent for Barium, Strontium, and Lead. I. M. KOLTHOFF (*Pharm. Weekblad*, 1925, **62**, 1017—1020).—Solutions of sodium rhodizonate decompose on keeping in air. Fresh neutral solutions can be employed to detect lead, strontium, and barium in neutral solutions, but the utility of the reagent is limited. The sensitiveness to barium and strontium is much increased by addition of alcohol, 2 mg. of barium and 10 mg. of strontium per litre being detectable. S. I. L.

Separation from Calcium of Magnesium, Iron, Aluminium, and Phosphoric Acid. W. F. JAKÓB (*Rocz. Chem.*, 1925, **5**, 159—172; cf. this vol., ii, 69).—The addition of ammonium citrate to solutions containing calcium, in the presence of magnesium, tervalent metals, and phosphates, causes the calcium oxalate precipitated by the addition of ammonium oxalate to crystallise in octahedra of the approximate composition $CaC_2O_4,2{\cdot}5H_2O$. In this form, calcium oxalate does not tend to form solid solutions with magnesium oxalate, isomorphous with the monohydrate obtained in the absence of citric acid. Citric acid, further, owing to its tendency to the formation of complex ions, to a certain extent inhibits the precipitation of impurities such as iron, aluminium, phosphates, and magnesium. 200—300 C.c. of a faintly acid solution containing from 0·02 to 0·3 g. of calcium are treated with 20—25 c.c. of 10% ammonium citrate solution and warmed to 40—50°. A slight excess of 3% ammonium oxalate solution is then added, and the precipitate of β-hydrate collected, and boiled with dilute feebly acid citrate solution, thereby converting the precipitate into the stable monohydrate, and incidentally freeing it from impurities. The calcium is then determined as oxide. R. T.

Detection of Minute Quantities of Material at Very Great Dilution. F. L. HAHN (*Festschr. Physikal. Verein, Frankfurt a.M.*, 1924; from *Chem. Zentr.*, 1925, ii, 75).—Tincture of alkanet which contains hydroxyanthraquinones gives colour changes with many metals, including magnesium, which can be recognised by alterations in the absorption spectra. 1 : 2 : 5 : 8-Tetrahydroxyanthraquinone (quinalizarin) gives a bluish-violet solution in alkalis, which changes to a cornflower-blue in the presence of small quantities of magnesium and gives a blue precipitate with larger quantities. Ammonium salts mask or hinder the reaction. The test is sensitive to 1 μg./c.c. in the cold and 0·5 μg./c.c. when hot. The diphenylamine reaction for nitrates is not specific. A nitrate

is reduced to nitrite by lead salts and metallic lead and then detected by the diazo reaction. The reagents must be absolutely free from nitrate. The water is boiled with zinc dust and distilled. The lead and lead salt are obtained by strongly heating lead formate. A little of the solution to be tested is heated with some of the powder for 15—30 mins. at 100°, poured off from the lead, and treated with the diazo reagent (sulphanilic acid or α-naphthylamine in acetic acid). Using 1—2 c.c. solution, 1 mg. of nitrate per litre gives a strong red and 0·1 mg. a distinct rose coloration. The diazo reagent is made more stable by using more than the usual amount of acetic acid and adding a suitable quantity of marble. If kept in a bottle filled with a stopcock tube, the quantity required may be obtained by the pressure of the carbon dioxide. A powder form of the reagent is obtained by mixing sulphanilic acid with acetnaphthylamide. This is boiled with acid or alkali just before using. The action of copper as an accelerator in the reaction between ferric salts and thiosulphate (resulting in ferrous salts and tetrathionate) can be used as a delicate qualitative and quantitative method for copper (cf. A., 1924, ii, 412). The disappearance of the ferric iron is followed by means of thiocyanate and the sensitiveness of the reaction raised to 0·03 μg. in 25 c.c. A. C.

Permanent Standards as a Possible Source of Error in Iron Determinations. E. S. HOPKINS (*Ind. Eng. Chem.*, 1925, **17**, 832).—The determination of small amounts of iron in water by the procedure given in "Standard Methods of Water Analysis" (American Public Health Association) is liable to error for two reasons: (i) the cobalt chloride used in making up the standard solution may not be pure, and (ii) the Nessler tubes used may not be of an appropriate shape or capacity, the tints observed in different concentrations being differently related to one another in different sizes and shapes of tubes. The colour standards should be checked against actual iron solutions. W. A. S.

Separation of Tantalum from Niobium, and Detection and Determination of Tantalum in Niobium Compounds. A. R. POWELL and W. R. SCHOELLER (*Analyst*, 1925, **50**, 485—498).—Tantalum and niobium may be separated by a method depending on the differential hydrolytic dissociation between oxalotantalic and oxaloniobic acids in the presence of tannin in slightly acid solution, and the method may be modified to allow of the detection and determination of small quantities of tantalum in niobium compounds. The two elements may be identified in admixture by the characteristic colours of the precipitates produced. [Cf. *B.*, Dec. 11th.] D. G. H.

Determination of Urobilin and Urobilinogen. A. J. L. TERWEN.—(See i, 1351.)

Determination of Uric Acid in Blood. M. DELAVILLE and C. M. JONES.—(See i, 1344.)

General, Physical, and Inorganic Chemistry.

Excitation of the Hydrogen Spectrum by Electron Impact. P. M. S. Blackett and J. Franck (*Z. Physik*, 1925, **34**, 389—401).—The four possible modes of explaining the atomic spectra are: (1) The molecule is directly split up by the impact into a normal and an excited atom. (2) The molecule is excited by the impact and dissociated into a normal and an excited atom by collision while still in the excited state. (3) Normal free atoms produced by the discharge may be excited by the impact of an electron. (4) Atoms may also be excited by absorption of radiation, by collision with positive ions, and by successive collisions with electrons. The experiments show that electrons possessing sufficient kinetic energy can dissociate, in one elementary act, a normal hydrogen molecule into a normal atom and an excited atom. The broadening of the Balmer lines due to the Döppler effect is greater in this case than when free atoms are excited, owing to the great velocity with which the atoms separate in dissociation. A suggestion is made, with some reserve, that the impact of electrons may result in dissociation into two normal atoms, the excess energy being radiated as a continuous emission stretching from the far ultra-violet down to long wave-lengths. E. B. L.

Absorption of the Balmer Lines in Hydrogen. R. V. Jolowicz (*Phil. Mag.*, 1925, [vi], **50**, 1089—1096).—Attempts have been made to observe absorption of the Balmer lines by hydrogen subjected to bombardment by electrons. Electrons from a glowing filament were accelerated by an electric field through a grid into a field-free space between the grid and a metal plate. A beam of light passed through the tube between grid and plate into a spectroscope, and was observed directly and also photographed. Experiments were carried out both with white light and with light from a hydrogen tube. Neutral glass wedges were used for the comparison of intensities (Nicholson and Merton, A., 1916, ii, 461). No trace of absorption was observed even with a specially designed apparatus in which a column of hydrogen 25 cm. long was subjected to electron bombardment. It is concluded either that the number of hydrogen atoms with electron moving in the second orbit is too small to produce absorption effects under the conditions of experiment, or that the ionisation is molecular, unaccompanied by dissociation. A. B. M.

Fine Structure of Hydrogen Lines. G. Hansen (*Physikal. Z.*, 1925, **26**, 678—680).—The structure of H_α is the simplest case to which the relativistic fine structure can be applied. The author has used a long tube (cooled in the centre by liquid air) containing electrolytic hydrogen through which direct current is passed. The

measurements were made by a Lummer–Gehrcke plate and a registering photometer. For H_α, in the short-wave group the records indicate a definitely unsymmetrical distribution of intensity among the components in the sense that the shorter wave is more intense. The effect is shown under widely diverging conditions. The value of $\Delta\nu$ definitely increases for the lines $\alpha \rightarrow \beta \rightarrow \gamma$. The intensity ratio $I_{\text{short-wave}}/I_{\text{long-wave}}$ of the doublet groups is dependent on pressure and current density, especially so in the case of H_α; *e.g.*, at $p=0{\cdot}13$ and current density 0·039 the ratio is 1·05, whilst at $p=0{\cdot}015$ and current density 0·047 the ratio is 1·29. The separation $\Delta\nu$ is 0·317/cm. The results are discussed theoretically.

R. A. M.

Theory of the Fine Structure of H and He$^+$ Lines. L. B. HAM (*Physical Rev.*, 1924, [ii], **23**, 107).—Application of Glitscher's method (*Ann. Physik*, 1917, [iv], **52**, 608) gave a value for the hydrogen doublet of the Balmer series twice that given by relativity. Similarly, results for the *L*-doublets of the *X*-ray spectra were incompatible with experimental values; Kunz's electromagnetic emission theory (*Physical Rev.*, 1914, [ii], **3**, 464) gives the same results as relativity. The mass variation of the electron in jumping from orbit to orbit is considered.

A. A. E.

Recent Results in the Investigation of Fine Structure. E. GEHRCKE (*Physikal. Z.*, 1925, **26**, 675—677; cf. A., 1921, ii, 565; 1922, ii, 3, 726; *Ann. Physik*, 1924, [iv], **74**, 575).—The fine structure of the Balmer lines of hydrogen shows that the relative intensity of the component lines can vary. This variability is greatest for H_α and decreases with higher values for the series-term. In a tube 3 cm. wide at a pressure less than 0·1 mm., H_{α_1} is weaker than H_{α_2}, whilst in a tube 1·5 mm. wide at a few mm. pressure H_{α_2} is weaker than H_{α_1}. By decreasing the pressure and somewhat narrowing the tube, the intensities of H_{α_1} and H_{α_2} can be made approximately equal. The relative intensity of the two components can therefore be altered at will without profoundly influencing line breadths in the entire system. The experimental separation of H_{α_1} and H_{α_2} is $\Delta\lambda=0{\cdot}128$ Å. ($\Delta\nu=0{\cdot}296$/cm.).

An investigation of the fine structure of helium lines, especially the 4686 line, has been compared with Sommerfeld's theoretical classification. The three strongest components of the permitted lines show a separation in agreement with the theoretical predictions. The intensities of the other lines cannot, however, be reconciled with theory. Setting on one side the selection principle, the separation of the strongest lines leads to a lower value of $\Delta\nu$. Deviations of the same type from the requirements of theory have been observed by Bowen and Millikan for the doublet separation of Mg II, Al III, and S VI (this vol., ii, 252, 342). Therefore the lower value of $\Delta\nu$ for helium is not without strong evidence. The experimental results are compared with earlier work by Paschen. The work is discussed with special reference to the 4686 line of helium, by Paschen, Joos, Sommerfeld, Smekal, and the author.

R. A. M.

Spectrum of "Nebulium." H. B. LEMON (*Physical Rev.*, 1924, [ii], **23**, 766—767).—A study of 35 lines, of unknown origin, included in the spectra of the nebulæ. A. A. E.

New Combination Series in the Helium Spectrum. J. S. FOSTER (*Physical Rev.*, 1924, [ii], **23**, 293).—Direct measurements of wave-lengths of lines of the series $1P-mP$, $1P-mF$, $1P-mG$, $1P-mH$, etc. for $m=4$ to 6 differ in only one case by more than 0·2 Å. from the calculated values. With higher fields, lines belonging to the series $1S-mD$, $1S-mF$, $1S-mG$, etc. have been recognised. A. A. E.

Low-voltage Arc in Oxygen. L. L. LOCKROW (*Physical Rev.*, 1924, [ii], **23**, 553).—The critical potential for an ionisation process is 16·1 volts. The spectrum at 22 volts shows the negative bands, lines of the triplet system, and the one line 4368 Å., $1S-3P$, of the singlet system. A. A. E.

Absorption in Excited Gases. K. W. MEISSNER (*Physikal. Z.*, 1925, **26**, 687—689).—In a mixture of neon and helium some strong lines suffer little or no absorption, whilst other equally intense lines are very strongly absorbed. For neon, lines requiring $1s_3$ and $1s_5$ terms are strongly absorbed and the $1s_2$ and $1s_4$ states are only weakly absorbed. The $1s_3$ and $1s_5$ states must therefore exhibit relatively long life-periods. The results are in good agreement with the term-scheme of neon. The work has been extended to argon. Similar differences in absorption are observed, but the series classification is as yet too defective to allow of rigorous conclusions. The work on neon has been extended in an ingenious manner, whereby the life-period of the S_5 state has been calculated on the basis of the lines 6402, 6143 Å., and the value 0·0038 sec. obtained. The life-period of the S_3 state is markedly shorter and more difficult to estimate. R. A. M.

Red Neon Lines. K. BURNS (*J. Opt. Soc. Amer.*, 1925, **11**, 301—310).—The results from sixty-eight plates measured at the Allegheny Observatory indicated no appreciable change in the relative values of the mean wave-lengths of the red neon lines given by the Bureau of Standards. From their agreement amongst themselves and with the results of other observers, it is concluded that the Bureau of Standards values are sufficiently accurate to warrant the expressing of their means to 0·0001. Under the observational conditions, the lines examined showed no complexities which interfered with the accuracy of measurement with orders of intensity up to 100,000. A. E. M.

Distribution of Energy over the Lines of the Main Series of Neon in a Column Discharge. H. B. DORGELO (*Physica*, 1925, **5**, 90—100).—In a neon column (7 mm. pressure) with 350 volts and 50 milliamp., the energy is radiated practically entirely as $2p-2s$ and $2s-1s$ light. Values of the effective candle power are obtained by multiplication of the intensity of each line with the eye sensitivity factor for its wave-length. In the circumstances a

total 1·23 spheric candles per watt was calculated; direct measurement with a flicker photometer gave 1·66 spheric candles/watt. The average intensities of the multiplet components agreed with the intensity rules previously given; the energy distribution was, however, materially different from that in an excitation tube.

CHEMICAL ABSTRACTS.

Spectrum of Singly Ionised Silicon. M. SAHA (*Nature*, 1925, **116**, 644).—Certain lines, ascribed by Fowler to singly ionised silicon, but not included in his scheme of classification, can be arranged in a group of quadruplets. A. A. E.

Chlorine Spectrum in the Extreme Ultra-violet. J. J. HOPFIELD (*Physical Rev.*, 1924, [ii], **23**, 766).—Many new strong lines have been observed, as well as lines corresponding with those occurring in the vacuum spark spectrum. A new group of bands of aluminium chloride was observed at 2620 Å. A. A. E.

Arc Spectrum of Titanium from 7496 to 2273 Å. K. BEHNER (*Z. wiss. Phot.*, 1925, **23**, 325—341).—Using titanium sulphate in the arc between copper electrodes, about 1330 lines between wave-lengths 7496 and 2273 were measured. Wave-lengths are given to 0·001 Å., the maximum mean error being seldom more than 0·002 Å. Data of intensities of lines and of regular groups of multiplets are given. Nearly all the lines described by earlier workers were found, and in the ultra-violet a number of arc lines were measured which previously were considered to be spark lines. The new are compared with older measurements, with the view of reducing the Rowland values to the international system. From a comparison of Rowland's original values with his own, the author presents a new "error" curve, in which the correction curves of Kayser and Hartmann are also included for comparison. Marked deviations from both correction curves are found, although in some regions the agreement with either the Kayser or the Hartmann curve is good, so that for titanium neither can be considered the better. Individual lines show a marked deviation, and in general these are the lines for which Rowland found extreme values. Although a conversion from the Rowland to the international system is possible on the average, it is not so for individual lines. The author's results are compared with those of other workers, in particular with those of Crew (*Astrophys. J.*, 1924, **60**, 108—121). Crew's method of graphical interpolation for measuring his plates does not give the highest degree of accuracy. W. C.

Vacuum Spark Spectrum of Zinc in the Region 2100—4000 Å. R. A. SAWYER and E. J. MARTIN (*Physical Rev.*, 1924, [ii], **23**, 766).—In addition to 250 new lines, all the spark lines given by Exner and Haschek appeared, but of the arc spectrum only the subordinate triplets $2p$—$3s$, $2p$—$3d$, and $2p$—$4d$ appeared with considerable intensities. The new lines are grouped to some extent in the regions 2400—2700 Å. and 3500—4000 Å. A. A. E.

Infra-red Line Spectrum of Zinc and Cadmium. H. M. RANDALL and W. N. ST. PETER (*Physical Rev.*, 1924, [ii], **23**, 766).—The spectra of zinc and cadmium were examined in the region 1—5 μ. A. A. E.

Change of Wave-lengths for certain Lines of Zinc, Cadmium, and Mercury in a Condensed Discharge. M. FUKUDA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 183—192).—When a condensed discharge was passed between metal poles in a fused silica Geissler tube, certain spectral lines were shifted. The shifts increased with the distance of a spark gap inserted in series with the discharge tube. Many spark lines appeared in the spectrum of the condensed discharge, increasing in number and intensity as the spark gap was widened. The appearance of these lines was accompanied by augmented displacements of some lines. The shifted lines generally belonged to the sharp series and the displacements were of the order of 1 Å. towards the red. Under comparable conditions for lines having the same notation, the magnitude of the shift was in the order: cadmium (highest), mercury, zinc. In most cases, the lines of the diffuse series were displaced towards the red, but a few, *e.g.*, the yellow lines of mercury, were shifted in the reverse direction. It was concluded that the shift was due to the intermolecular electric field arising from close packing of ions and electrons in the capillary. R. A. M.

Series Relations in the Spectra of Doubly Ionised Gallium and Indium. J. A. CARROLL (*Physical Rev.*, 1924, [ii], **24**, 205).—The hot spark spectra of gallium, indium, thallium, and mercury have been examined from 500 Å. upwards. The principal pairs of the doublet systems of Ga III and In III are at 1495·2—1534·6 ($\delta\nu$=1720) and 1625·3—1748·8 ($\delta\nu$=4350), respectively, the outer electron being assigned a 4-quantum and a 5-quantum orbit. The line 1414·57 Å. is probably $1S$—$2P$ in Ga II. A. A. E.

Structure of the $K\alpha$ Lines of Molybdenum. F. K. RICHTMYER and R. C. SPENCER (*Physical Rev.*, 1924, [ii], **23**, 550—551).—Energy-wave-length diagrams show that the line $K\alpha_2$ is broader than $K\alpha_1$; the width of the latter is probably not greater than 0·0003 Å. The distribution of energy over the focal spot is not uniform. A. A. E.

Arc Spectrum Regularities for Ruthenium. W. F. MEGGERS and O. LAPORTE (*Science*, 1925, **61**, 635—636).—The condensed spark under water shows 85 distinct absorption lines between 2255 and 4709 Å. The lowest term of ruthenium is 5-fold with the separations 392·2, 621·7, 900·9, 1190·8 cm.$^{-1}$ and inner quantum numbers 0, 1, 2, 3, 4; it is regarded as a quintuplet D-term. The D-term combines with 46 or more higher levels, accounting for the majority of the strong lines in the ruthenium arc spectrum. In agreement with a general rule that the most sensitive lines of a spectrum always involve a quantum jump with ΔK=1, the "raies ultimes," 3436·74 and 3498·95 Å., occur also in a ^5D—^5F combination. A. A. E.

Width of the K_{β} Absorption Discontinuity in Silver. F. K. RICHTMYER and R. C. SPENCER (*Physical Rev.*, 1924, [ii], **23**, 760—761).—An experimental verification of the conclusion that with a perfect crystal, a target of uniform energy distribution, and a slit system of angular width α, then if the absorber has a perfectly sharp discontinuity showing no structure, (i) the width of the observed discontinuity should be α, and (ii) the shape of the energy curve through the discontinuity should be made up of two parabolas. A. A. E.

Line Spectra of Tungsten and Nickel in the Afterglow of a Discharge through a Mixture of Nitrogen and Argon. A. G. WORTHING and R. RUDY (*Physical Rev.*, 1924, [ii], **23**, 767).—With tungsten electrodes, two afterglows were obtained in a discharge through a mixture of argon (99·8%) and nitrogen (0·2%) at 300 mm.; the spectrum of the orange glow showed strongly the first and second groups of positive nitrogen bands, and that of the blue glow showed the tungsten lines superposed on a faint background consisting of a continuous spectrum and nitrogen bands. In the conditions favouring the latter, a dark deposit, probably tungsten nitride, is formed. With nickel electrodes, the blue glow gave place to a green one showing strong nickel lines. Glows obtained in pure nitrogen were much feebler. No argon lines were observed during the discharge or in the afterglow. A. A. E.

Excitation Function of the Mercury Spectrum. J. A. ELDRIDGE (*Physical Rev.*, 1924, [ii], **23**, 294).—For low pressures and currents, ionisation plays an unimportant rôle in spectrum excitation. Lines which originate in electrons falling from an S, D, or d_2 orbit become stronger, and those from an s, d_1, or d_3 orbit weaker with increasing energy of the primary electrons. A. A. E.

Behaviour of Mercury Arc Lines after Removal of the Exciting Potential. L. J. HAYNER (*Physical Rev.*, 1924, [ii], **23**, 294).—The line 2537 Å. was particularly strong in the after-spectrum, and exhibited also a second type of persistence between 40° and 200°. Its rate of decay appeared to determine the interval between the extinction of the arc lines and their reappearance. Principal series lines were not found in this after-spectrum. The extinction of the arc lines immediately after removal of the potential is probably due to absorption by excited atoms in the $2p$ state (Kurth, *ibid.*, 1923, **22**, 202). A. A. E.

Excited Atoms in the Striated Glow Discharge in Mercury Vapour. W. H. MCCURDY, L. A. TURNER, and K. T. COMPTON (*Physical Rev.*, 1924, [ii], **23**, 776).—It is suggested that ionisation in the striations is cumulative, depending on the existence of $2p_{1,2,3}$ excited atoms; the action of slight impurities, only in presence of which striations are possible, is to reduce the concentration of these excited atoms and prevent their diffusion into the dark spaces. The metastable states $2p_{1,2}$ are relatively most prominent; absorption involving inter-system transitions is less probable than that in one system. A. A. E.

Completion of the Series in the Arc Spectrum of Lead. H. GIESELER and W. GROTRIAN (*Z. Physik*, 1925, **34**, 374—388).—The spectrum was excited by a stream of electrons from a glowing filament in a long silica tube containing lead and surrounded by an electric furnace. Many new lines were found and measured. Several new series were found, of which two are the diffuse and sharp series with a P_0 term, and two others are described as combinations *pf* and yield a calculation of a Bergmann series.

E. B. L.

***X*-Ray Absorption Coefficients in the Neighbourhood of *K*-Limits.** F. W. WARBURTON and F. K. RICHTMYER (*Physical Rev.*, 1924, [ii], **23**, 291—292).—Atomic absorption coefficients on both sides of the respective *K*-limits have been determined for molybdenum, silver, tin, tungsten, gold, and lead. Values of $kN^4\lambda^3$ in $\mu_a=kN^4\lambda^3+\sigma_a$ are proportional to $N^4/(N-b)^6$ when in the expression $\sqrt{\mu} \propto (N-b)$, $b=7$; the change in the values on passing the *K*-limit decreases as *N* becomes large. For elements of higher atomic number, a smaller proportion of the absorbed energy is radiated as *K* fluorescence radiation. A. A. E.

***X*-Ray Spectra from a Ruled Reflection Grating.** A. H. COMPTON and R. L. DOAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 598—601).—Spectra of ordinary *X*-rays have been obtained by reflection at very small glancing angles from a grating of space 2×10^{-3} cm., ruled on speculum metal. Measurements made with this grating gave as the wave-length of the molybdenum $K\alpha_1$ line $0{\cdot}707\pm0{\cdot}003$, which is in good agreement with the value $0{\cdot}7078\pm0{\cdot}0002$ Å. obtained by crystal measurement. Measurement with a copper target gave wave-lengths of 1·4—1·5 Å. or values intermediate between the α and β lines of copper. A. E. M.

Zeeman Effect on the Helium Bands. W. E. CURTIS and W. JEVONS (*Nature*, 1925, **116**, 746—747).—The band near 4650 Å. has been studied, using magnetic fields up to 20,000 gauss; many other band lines also appear on the plates. The band lines exhibit no Zeeman effect of a "normal" order of magnitude, except in the case of the first member of each of the three branches, *i.e.*, $Q(1)$, $R'(1)$, and $P(2)$, which are broadened, but not resolved into components. In $Q(1)$ and $P(2)$, the component corresponding with vibrations parallel to the field is much broader than the "perpendicular" component, the reverse being the case for $R'(1)$ and for series lines. The effect is greatest in $Q(1)$, of which the extreme width in a field of about 20,000 gauss corresponds with a separation of about 0·27 Å. The effect of the magnetic field on the molecule is largely determined by the state of rotation of the latter, being relatively small for the higher speeds of rotation. A. A. E.

Fine Structures of Spectrum Lines. A. E. RUARK and R. L. CHENAULT (*Phil. Mag.*, 1925, [vi], **50**, 937—956).—The fine structure of spectral lines arising from complex levels, *i.e.*, levels with several components all characterised by the same total, azimuthal, and

inner quantum numbers, is discussed. An analysis is made of nearly all the available data on fine structures. It is shown that the fine structures examined cannot be due to isotopy. They are due probably to slight quantised variations in the configuration of loosely bound underlying electron shells. In the case of thallium, a fine quantum number f may be introduced, with a selection principle to govern its changes, but for other elements no selection principle has been discovered. Fine structures have proved to be an aid in classifying spectral lines. A. B. M.

Primed Terms in the Spectra of the Lighter Elements. O. LAPORTE (*J. Washington Acad. Sci.*, 1925, **15**, 409—413).—A theoretical paper in which the work of Millikan and Bowen (this vol., ii, 916) is criticised. These authors consider that if the atom of aluminium is in its normal state, two of its electrons are in $3s$, one in $3p$ orbits obtaining the $2P'$ state when one electron is in $3s$ and two are in $3p$. It is in contradiction with the alternation law to have several electrons in the same s or p orbit and moving in the same doublet-energy diagram. A new explanation is put forward in which the arc spectrum is built up from the spectrum of the ionised atom. Further considerations clarify the position with regard to the fact that pp' groups follow the irregular doublet law. R. A. M.

Summation Rules for the Intensities of Spectral Lines. R. H. FOWLER (*Phil. Mag.*, 1925, [vi], **50**, 1079—1083).—A theoretical discussion of the summation rules of Ornstein, Burger, and Dorgelo for the intensities of the components of complex lines (A., 1924, ii, 282, 361, and 433). It is shown that if the intensities are reckoned in numbers of quanta per second, then the summation rules ought to be fulfilled to the degree of accuracy with which the Fourier coefficients of the original electronic system are left unaltered by the superposed perturbation which splits the radiation up into the associated group of lines. A. B. M.

Explanation of Complex Spectra. II. F. HUND (*Z. Physik*, 1925, **34**, 296—308; cf. this vol., ii, 912).—The elements in the fourth and fifth groups of the periodic system are chiefly considered, and a scheme is developed indicating to which series limit the single terms of the multiplets correspond by transition to higher orbit numbers. The spectrum of neon is also discussed and the bearing of the Zeeman effect. E. B. L.

Minimum Velocity of Impact to Produce Secondary Electrons from Tungsten. O. STUHLMAN, jun. (*Physical Rev.*, 1924, [ii], **23**, 296—297).—The minimum potential for tungsten is 3·72 volts. A. A. E.

Post-arc Conductivity and Metastable Helium. C. ECKART (*Physical Rev.*, 1925, [ii], **26**, 454—464).—The abnormal conductivity observed by Kannenstine to persist for 0·007 sec. after the extinction of an arc in helium is not due to metastable excited helium atoms, but to positive ions and accompanying electrons. The only

evidence in favour of a very long life (10^{-2} to 10^{-3} sec.) of metastable helium atoms is therefore inadmissible, although the metastable states in helium have a longer life than other excited states. A. A. E.

Mechanics of Electrons and Light Quanta. K. Schaposchnikov and W. S. Fedorov (*Z. Physik*, 1925, **34**, 402—405).—Theoretical. E. B. L.

Chemical Statics of Electronic Phenomena. L. Rolla and G. Piccardi (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 173—177).—It follows from the principle of mobile equilibrium, since it has been shown that the potential of ionisation of elements is independent of temperature, that the logarithm of the electronic equilibrium constant, at constant temperatures, should be a linear function of the heat of ionisation. This latter, further, is proportional to the ionising potential. This linear relation is shown to hold for a number of elements for which the values of the ionising equilibrium constant and the ionisation potential were known. The slope of the line obtained by plotting log K against the ionisation potential indicates that only those elements the ionising potentials of which are below 8 volts may be expected to show ionisation in a Bunsen flame. The above relationship is used to calculate the ionising potentials of barium, strontium, copper, and molybdenum from observations of their flame spectra. The calculated values are in accord with those determined by other methods. F. G. T.

Predicted Ionisation Potentials of Niton [Radon] and Hydrofluoric Acid. G. Glockler (*Phil. Mag.*, 1925, [vi], **50**, 997—1001).—By extrapolation of the ionisation potential–atomic number curve for the rare gases, the ionisation potential for radon is found to be 10 volts. From Eve's rule, that the product of ionisation potential and atomic radius is constant, and from the value for the atomic radius ($2{\cdot}80 \pm 0{\cdot}25$ Å.) calculated from the diffusion coefficient in air, the ionisation potential is again calculated to be 10 volts. The ionisation potential of hydrogen fluoride, estimated by a method based on thermochemical considerations, is 15 volts. Both values differ from those obtained by Turner (A., 1924, ii, 797) on the basis of a linear relation between quantum defect and atomic number. A. B. M.

Structure of the Hydrogen Molecule Ion. H. C. Urey (*Proc. Nat. Acad. Sci.*, 1925, **11**, 618—621).—When the condition of dynamic stability is ignored, the steady state of lowest energy of the ionised hydrogen molecule is that in which the electron vibrates in a straight line perpendicular to the line joining the nuclei at its mid point. The energy of this state has been calculated and a formula obtained by means of which values for the ionisation potential of the molecule and critical potentials of the hydrogen atom have been calculated. These are in agreement with the determinations of Olson and Glockler (A., 1923, ii, 455), whose results are explained. The heat of dissociation of the hydrogen molecule and its moment of inertia calculated from this model are

in agreement with the results of other investigators. It is predicted that there should be an ultra-violet spectrum of the ionised hydrogen molecule, free from that of the neutral molecule, in the region 850—714 Å. A. E. M.

Probability of Ionisation of Gas Molecules by Electron Impacts. K. T. COMPTON and C. C. VAN VOORHIS (*Physical Rev.*, 1925, [ii], **26**, 436—453).—Values as follows are tabulated for N, the number of ions per cm. path produced by an electron moving through a gas at 1 mm. pressure, V_a, the maximum accelerating potential, and P, the corresponding probability that a collision will result in ionisation of the hit molecule :—hydrogen, 3·55, 145, 0·29; helium, 1·65, 210, 0·209; neon, 3·2, 340, 0·254; argon, 10·33, 140, 0·466; nitrogen, 9·96, 175, 0·423; mercury, 19·44, 135, 0·239; hydrogen chloride, 17·3, 130, 0·558. The weak ionisation observed in nitrogen at 10 volts was possibly associated with the presence of active nitrogen. A. A. E.

Impact Ionisation by Low-speed Positive Ions. M. A. TUVE (*Physical Rev.*, 1924, [ii], **23**, 111).—Positive ions produced by electronic collision in mercury vapour were caused to collide with mercury atoms, and the electron current in the ionisation chamber was measured. The current was again measured when positive ions or δ-rays were prevented from entering the chamber. The ratio of the difference to the total current was measured, giving definite upper limits of the amount of impact ionisation.
A. A. E.

Spectroscopic Evidence of Impact Ionisation by Positive Ions in Mercury Vapour. J. T. TATE (*Physical Rev.*, 1924, [ii], **23**, 293—294).—When positive sodium ions are accelerated at more than 40 volts into an ionisation chamber containing mercury vapour, both sodium and mercury arc lines appear. The ionising potential was not necessarily critical for positive ions, but impact ionisation by positive ions is indicated. When positive mercury ions were accelerated into the chamber at above 70 volts, mercury arc lines appeared. A. A. E.

Impact Experiments in Compound Gases. Ammonia. (MISS) A. T. WALDIE (*J. Franklin Inst.*, 1925, **200**, 507—518).—Ammonia has been shown to possess a critical ionisation potential at about 11 volts. The result was obtained both with photo-electrons and with thermions. With photo-electrons, the results indicate that the dissociation through ultra-violet light is slow, and that of the dissociation products hydrogen is more or less effectively removed by the nickel which was used as the electron source. In the thermionic experiments, the critical points determined in the direct region of the filament were principally those of hydrogen, indicating that, in that region, the ammonia is almost completely dissociated. Only when arrangements were made so that the electron impacts occurred at some distance from the filament could the above value for the ionisation potential be obtained. A. E. M.

Theory of Electrodeless Discharge in Gases. P. LASAREV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, [6], 127—132; from *Chem. Zentr.*, 1925, ii, 519).—The author derives formulæ for the ionisation and fluorescence of gases in electrodeless discharge, on the assumption that the number of ionised atoms is proportional to the total number of atoms and the strength of the field, and that the formation of molecules from ions (molisation) is a unimolecular reaction. G. W. R.

Mobility of Argon and Hydrogen Ions in Air. H. A. ERIKSON (*Physical Rev.*, 1925, [ii], **26**, 465—468).—Two positive ions and one negative ion were found in both cases, and in that of air. In the case of hydrogen, and probably also with argon, the initial positive ion becomes transformed into the second. Initial positive and negative ions of argon, air, and carbon dioxide, and the initial positive ion of hydrogen, have the same mobility in air at normal pressure; negative hydrogen ions possess an unexpectedly larger mobility. A. A. E.

Photo-electric Action of Total Radiation of a Solid Body. A. BECKER (*Ann. Physik*, 1925, [iv], **78**, 83—111).—The photo-electric action of light from an incandescent tungsten ribbon on an aluminium plate was investigated. The number of electrons emitted is related to the absolute temperature of the source of radiation by the formula $n=\text{const.}\times\theta^{x}e^{-c_2/\lambda_e\theta}$; x is greater than 2, and probably between 3 and 4. The distribution of velocities in the photo-electrons is identical with that of electrons emitted by hot bodies. The most probable velocity of escape is proportional to the absolute temperature of the radiator and of the same order of magnitude as for thermionic emission. The optical properties of the metal (absorption) do not affect the distribution of velocities, and the absolute value of the velocities only slightly. E. B. L.

Magnetism and the Structure of Atoms and Molecules. B. CABRERA (*J. Phys. Radium*, 1925, [vi], **6**, 241—258).—It is possible on the basis of a formula due to Larmor to calculate the mean radius of the electronic orbits of an atom from its magnetic susceptibility. By adopting the Bohr scheme of stable atomic levels, true atomic radii can be calculated which apply even to the "surface" of the atom. The magnetic susceptibility and certain derived constants exhibit the Mendeléev periodicity exceedingly well. From the values of χ_A (atomic susceptibility) found by Pascal (A., 1914, ii, 618, 764) and Hector (A., 1924, ii, 854) the following atomic radii have been calculated: $r_A\times10^8$, helium 0·57, neon 0·54, argon 0·85, krypton 1·03, xenon 1·44; for ions of the argon type, the following values are deduced: phosphorus (P^{---}) 1·37, 1·11; sulphur (S^{--}) 1·13, 1·01; chlorine (Cl^{-}) 0·98, 0·92; argon 0·85; potassium (K^{+}) 0·76, 0·80; calcium (Ca^{++}) 0·69, 0·74. The results are in good agreement with those obtained by Fajans, Grimm, and Herzfeld by a different procedure (A., 1921, ii, 168, 174). The values for the atomic radii of the rare gases obtained

by Jeans on the basis of the kinetic theory are about twice those obtained by the author. The results of Bragg (A., 1920, ii, 537) are not in agreement. By employing Sommerfeld's model for the hydrogen molecule, the author deduces from χ_A its moment of inertia and the value $1{\cdot}6\times10^{-40}$ is of the right order.

Dia- and para-magnetism are discussed in the light of modern atomic theory, and special consideration is given to Sommerfeld's interpretation of the Gerlach–Stern experiments. The author affirms that (*a*) The Bohr magneton is the natural unit of the magnetic moment of a free electronic orbit. (*b*) The Weiss magneton is the highest common factor of the magnetic moments of all electronic orbits and is therefore the unit applicable to cations and paramagnetic atoms. The two magnetons are probably related, the Bohr magneton being nearly five times the Weiss magneton. (*c*) Free atoms orient themselves under the action of an external field according to the principle of space-quantisation. Free orientation cannot occur in solutions or in solids. The data lead to the rejection of interpretations of the paramagnetism of cations based on the Bohr magneton and on the form of quantisation suggested by Pauli and Sommerfeld. The real existence of the Weiss magneton is confirmed. The orientation should be regarded as that of the magnetic axis rather than the atoms themselves. The real explanation is probably similar to that of Ehrenfest, which involves a reversal of the direction of movement of an electron in its orbit, and a distribution of the two movements governed by the Boltzmann probability law. This idea of reversal should be replaced by that of the constancy of the magnetic moment. The electronic orbits will then be distributed so that the resultant magnetic moment will always be a definite multiple of the Weiss magneton. To explain the effect of temperature on paramagnetism it is suggested that the orientation of the magnetic axis follows from the reorganisation of superficial electronic levels after collisions. R. A. M.

Separation of Chlorine into Isotopes (Isotopic Elements) and the Whole Number Rule. W. D. Harkins (*Proc. Nat. Acad. Sci.*, 1925, **11**, 624—628).—Evidence in support of the whole number rule for the atomic weights of isotopes (Harkins and Wilson, A., 1915, ii, 543) has been obtained by the separation by diffusion of hydrogen chloride to give a lighter fraction in which the atomic weight of the chlorine was 35·4177, or 0·04 unit lighter than ordinary chlorine. The separation thus obtained amounts to 60% of that indicated by the theory. A. E. M.

Isotopic Composition of the Element Chlorine: The Atomic Weight of Meteoric and Terrestrial Chlorine. W. D. Harkins and S. B. Stone (*Proc. Nat. Acad. Sci.*, 1925, **11**, 643—645).—Determinations of the atomic weight of chlorine obtained from a meteorite, and from rocks of non-marine origin such as wernerite, apatite, and sodalite, gave the same results as ordinary chlorine found on the earth. It is concluded that the chlorine from the three sources has the same isotopic composition. It is

suggested that this result in conjunction with that of Baxter for nickel indicates that elements had originally the same isotopic composition as they have at present, or that the composition has changed at the same rate in all localities. A. E. M.

Isotopic Composition and Atomic Weight of Chlorine in Meteorites. A. W. C. MENZIES (*Nature*, 1925, **116**, 643—644).—The atomic weight of chlorine from the "shale balls" associated with the Canyon Diabolo, Arizona, meteorite, is identical with that of "ordinary" chlorine to within 1 part in 2000 parts, which is within the estimated experimental error. The extra-terrestrial nature of this chlorine and of that examined by Harkins and Stone (cf. preceding abstract) remains in doubt. A. A. E.

Isotopes of Lead. H. BRENNEN (*Ann. Chim.*, 1925, [x], **4**, 127—155).—A fuller account is given of earlier work (this vol., ii, 174) with a review of the literature. The author has repeated the work of Dillon, Clarke, and Hinchy (A., 1922, ii, 710) and of Atkinson (A., 1923, ii, 689) which claimed to make a partial separation of the isotopes of ordinary lead, and has found that with an experimental error of 0·01 in the determination of atomic weight these methods do not lead to any separation of isotopes. The values 206·19 and 206·14 have been obtained for the atomic weight of two samples of lead extracted from pitchblende from Belgian Congo. R. A. M.

Radioactivity of Potassium, Rubidium, and other Elements. W. D. HARKINS and W. G. GUY (*Proc. Nat. Acad. Sci.*, 1925, **11**, 628—630).—By balancing the natural leak of the ionisation chamber against that due to β- and γ-rays from uranium oxide, the absence of β-ray activity greater than $3{\cdot}3\times10^{-6}$ that of uranium was proved for the salts of fifteen elements and ten single elements. The measured activity of various potassium salts was found to be directly proportional to the amount of potassium present. The radiation from rubidium salts is not homogeneous. Rubidium is 1·39 times as radioactive as potassium, but the radiation from rubidium is ten to fifteen times less penetrating than that from potassium. The results indicate that the activities of rubidium and potassium salts cannot be traced to a common source such as the presence of radioactive impurities. The source of the radioactivity of potassium salts is discussed. A. E. M.

Scattering of α-Particles by Atomic Nuclei and the Law of Force. (SIR) E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1925, [vi], **50**, 889—913).—The scattering of α-particles by a number of elements has been observed. The angle of scattering was kept constant at 135°, and the velocity of the incident α-particles was varied by the interposition of suitable mica screens. The number of particles scattered and the distribution of velocity in the scattered beam were observed. Within the accuracy of experiment, the results for gold, platinum, silver, and copper showed no deviation from the simple laws of scattering, which assume that the particles can be regarded as point charges and that the inverse

square law of force holds. The light elements, magnesium and aluminium, however, showed a marked departure from these laws. The scattering decreased as the energy of the incident α-particles was diminished, falling to a minimum for particles of range about 5 cm. in air, increasing again, and approaching the theoretical value for particles of small range. The scattering by uranium was compared with that of gold, but showed no indication of a departure from the usual laws, although a fast α-particle would be expected to penetrate deeply into the nuclear structure of the uranium atom. The scattering by gold, determined by Chadwick's method (A., 1921, ii, 7), over wide ranges of scattering angle and energy of incident α-particles, was shown to be normal to within about 2%. The gold nucleus behaves as a point charge and the law of force is the inverse square for distances of approach between $3{\cdot}2\times10^{-12}$ and 10^{-11} cm. The α-particles scattered by aluminium are accompanied by protons liberated by disintegration of the aluminium nucleus. The evidence is at present insufficient to decide the fate of an α-particle which succeeds in ejecting a proton from the nucleus. From experiments on the absorption of ejected protons, it is estimated that they acquire a minimum critical speed of about $2{\cdot}4\times10^{9}$ cm. per sec. in escaping from the nucleus. The scattering curves for aluminium and magnesium showed the same type of deviation from normal with a scattering angle of 90° as with one of 135°. Neither the assumption that the scattering may be governed by quantum conditions nor Bieler's assumption (*Proc. Roy. Soc.*, 1924, **A**, **105**, 434) of an inverse fourth power law of attraction superimposed on the ordinary repulsion forces appears adequate to account for the deviations observed. A tentative explanation of the experimental results is made, based on the assumption that the aluminium nucleus consists of a central charged core surrounded by a satellite distribution of positive and negative charges. A. B. M.

Penetrating Radiations Observed at Sea-level. G. Hoffmann (*Physikal. Z.*, 1925, **26**, 669—672).—An apparatus has been devised employing very thick lead screens for registering the intensity of the penetrating radiations akin to γ-radiation. The results seem to prove that there is nothing mysterious about the penetrating character of these radiations at the sea-level and that the rays can be explained entirely as coming from known radioactive elements. A more detailed account is promised. R. A. M.

Measurements of Radioactivity. C. Matignon and (Mlle.) G. Marchal (*Chim. et Ind.*, 1925, **14**, 503—510).—An account of the methods used for the determination of radioactive material. The methods outlined depend on (1) α-ray activity, (2) activity of radium emanation, and (3) γ-ray activity. The use of the gold-leaf electroscope, the chemical methods of opening up radioactive minerals, and the three types of apparatus used by Curie (*J. Physique*, 1912, [v], 2, 813) for γ-activity, are described and illustrated. L. S. T.

Half-value Period of Radium-*E*. G. Fournier (*Compt. rend.*, 1925, **181**, 502—504).—Bastings (this vol., ii, 9) found the period of

decay of radium-*E* to be 4·98 days instead of 4·85 days as found by Thaller (*Sitzungsber. Akad. Wiss. Wien*, 1912, **121**, 1611). Lead containing radium-*D* + -*E* has been used. The separation of radium-*E* from this is described. The period of decay was measured by employing a piezo-electrometer, and for sources prepared in different ways the values 4·86, 4·86, and 4·84 days were obtained, confirming Thaller's value. R. A. M.

Behaviour of Lead Containing Radium-Ω in the Formation of Formaldehyde by Thunberg's Method. A. Stolfi (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 195—197).—By using lead carbonate, prepared from the radioactive mineral cotunnite, it has been found that the presence of radium-Ω is without influence on the preparation of formaldehyde by Thunberg's method (A., 1923, i, 1271). F. G. T.

Photographic Action of H-Particles from Paraffin and Aluminium. M. Blau (*Z. Physik*, 1925, **34**, 285—295).—The impact of α-particles on a paraffin film ejects hydrogen nuclei with high velocity. With polonium as the source of α-particles of 4 cm. range, the H-particles produced an effect on a photographic plate similar to that of the α-particles. When lamp-black was substituted for paraffin, little or no effect was obtained, which is to be expected, as there is no hydrogen present, and the disintegration of the carbon nucleus takes place to a very small extent only, if at all. With radium-*C* as source of α-particles, the other radiations fogged the plates in spite of precautions taken to avoid this. E. B. L.

Transmutation of Mercury to Gold. H. Nagaoka (*J. Phys. Radium*, 1925, [vi], **6**, 209—216; cf. this vol., ii, 835). —When a high-tension condensed discharge of 600,000 volts is passed between electrodes of mercury and tungsten wire, both of which are immersed in hydrocarbon oils, the very intense field causes artificial disintegration with production of a small quantity of gold. The mercury used was redistilled two or three times in a vacuum at temperatures below 200°, and control tests indicated the absence of gold from the product. After the discharge had been passed for several hours, the viscous black mass of carbon, oil, mercury, etc. was examined in various ways. Reliance was placed on the formation of ruby glass as a test for gold. Positive results were obtained. The gold appeared to be largely colloidal and adsorbed on the carbon. When the discharge is passed across drops of mercury falling between iron electrodes immersed in oil, both gold and a complex white metal (largely silver) are formed. The simultaneous production of gold and silver is significant because gold is usually found with silver rather than with mercury in terrestrial minerals. It is pointed out that if the isotopes of mercury are arranged in order of ascending mass number and 80 is subtracted from each number, the mass numbers of the isotopes of tin are found, so that the mercury nucleus may be regarded as compounded of krypton and tin nuclei. Krypton was not detected in the experiments. R. A. M.

Structure of Cadmium. H. COLLINS (*Chem. News*, 1925, **131**, 290—294).—Speculative; the structure of cadmium is deduced to be Na_2Zn. A. R. P.

Force of Attraction and Repulsion in Atoms. A. KORN (*Atti R. Accad. Sci. Torino*, 1925, **60**, 41—45).—A suggestion is made, based on the author's mechanical theory of gravitation, that, in addition to protons and electrons, atoms contain "gravitational" particles. These three constituents are of identical composition, and differ from one another only in dimensions and in their inherent type of vibration. To explain the stability of systems built up from these units, it is necessary to assume that the usual force laws of Newton and Coulomb become invalid for very small distances, and that a modified force law operates. This force is assumed to originate in the vibration of the particles in the atom. These vibrations are similar to, but different in magnitude from, those to which the author attributes the ordinary gravitational and electrical forces. The mutual reactions of these three types of unit are discussed, and the conditions are formulated for stability in a system composed of them. It is a corollary of these conditions that the size of the gravitational particles must be greater than that of either the electron or proton. Structures are suggested for the atoms up to chlorine. F. G. T.

Estimation of Maximum Coefficients of Absorption. R. C. TOLMAN (*Physical Rev.*, 1925, [ii], **26**, 431—432).—On the basis of the correspondence principle, Einstein's coefficient of absorption may be estimated from the equation $B_{na}=2\pi^3e^2Q^2/3h^2$, where e is the charge and Q the amplitude of the virtual oscillator which corresponds with the transition by absorption from state S_n to state S_a. Values of $(B_{na})_{max.}$ are in agreement with those previously calculated. A. A. E.

Whittaker's Atomic Model. J. A. ELDRIDGE (*Proc. Roy. Soc. Edin.*, 1925, **45**, 245—248).—Whittaker has suggested an atomic model designed to absorb and emit radiation by quanta (A., 1922, ii, 632). It is pointed out that a mechanism involving the existence of unipolar magnets has been employed. The assistance of the ether must be invoked in order to retain conservation of momentum. The criticism is regarded by Whittaker (in a note) as due to the confusion of bar-magnets with the new concept of "magnetic current." The idea that momentum can be stored by the ether is regarded as proved. Allen (in a note) suggests that the criticism is only valid for a particular case and proposes a way out of the difficulty. R. A. M.

Treatment of Radiation-pressure and Gas-pressure as due to Intermolecular Forces. J. Q. STEWART (*Physical Rev.*, 1925, [ii], **26**, 491—494).—Calculation of the average repulsive force between two gas molecules associated respectively with the emission and absorption of radiation affords a justification of Eddington, in his theory of stellar constitution, regarding the total pressure as the sum of the gas- and radiation-pressures. The fiction ascribing gas-

pressure to the effect of statistical repulsive forces between the molecules is examined mathematically. A. A. E.

Soft *X*-Ray Levels and the Bohr Scheme of Atomic Structure. F. L. MOHLER (*Physical Rev.*, 1924, [ii], **23**, 765).—A survey of data on critical radiation potentials of solids and gases yields results consistent with the conclusions of Bohr and Coster regarding the probable course of soft *X*-ray levels on the Moseley diagram. A. A. E.

Fulcher Lines in the Hydrogen Spectrum. C. R. BURY (*Phil. Mag.*, 1925, [vi], **50**, 1139—1143).—It is suggested that the 10 triplets in the many-lined spectrum of hydrogen, which were arranged by Fulcher in two bands, are each the three brightest lines of ten different bands. These bands are arranged in two series and each band consists of two branches. A number of the lines in the spectrum have been classified on this basis. A. B. M.

Measurement of Negative Oxygen Bands in the Visible Spectrum Region. F. HOLLAND (*Z. wiss. Phot.*, 1925, **23**, 342—363).—Results of measurements of three groups of negative oxygen bands are given. For group I, from 6226 to 5807 Å., 403 lines are given; for group II, from 5644 to 5509, 274 lines; and for group III, from 5295 to 5196, 225 lines. Mean errors of measurements are given and discussed, together with the intensities and the wave-lengths in air and after reduction to vacuum. W. C.

Relations between the Band Spectra of Zinc, Cadmium, and Mercury and their Atomic Spectra. E. HULTHÈN (*Nature*, 1925, **116**, 642).—It is concluded that the metal atoms remain in their metastable $2p_i$ states during the molisation act with the hydrogen atom, the other hydrogen atom carrying away the energy not to be quantised by the molecule. The electron transition is located in the metal atom, the hydrogen atom being optically inactive. A. A. E.

Resonance Radiation from Cadmium Vapour. A. D. POWER (*Physical Rev.*, 1924, [ii], **23**, 293).—If cadmium vapour in an evacuated silica tube is illuminated by a spark discharge, the wave-lengths 3262 Å. ($1S—2p_2$) and 2289 Å. ($1S—2P$) are radiated strongly by the freshly-formed vapour. The presence of thallium as an impurity was revealed in this radiation, but not by the spark. A. A. E.

Terms of the Mercury Hydride Bands. H. LUDLOV (*Z. Physik*, 1925, **34**, 485—495).—The terms of the mercury bands are represented by Kratzer's formula (*ibid.*, 1923, **13**, 82) and the structure of the mercury hydride molecule is discussed. The moment of inertia is not greatly affected by the orbit of the radiating electron, nor does this electron greatly influence the combination of the nuclei; it revolves about the mercury hydride ion at a relatively great distance. The spectrum is also produced by the passage of active hydrogen over mercury. In common with the hydrides of cadmium and zinc, the states of lower energy have the

greater moments of inertia; the nearer the radiating electron approaches the nuclei the feebler becomes their mutual attraction. E. B. L.

Structure and Distribution of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1925, **181**, 410—412; cf. this vol., ii, 930, 1023).—For the substances of simple composition hitherto examined the position of the principal absorption bands is given by sub-multiples of the universal constant, d_1, 1062·5, and is simply related to the number and size of the constituent atoms. For eleven spectra in the infra-red and twenty-nine in the visible and ultra-violet, the most intense band has a frequency which is a multiple of d_1. The same law applies to the strongest lines in the spectra of the atoms. It is suggested that 1062·5 is a fundamental frequency, related on the one hand to Planck's quantum of action and on the other to the unknown law for the mutual action of electric charges on atoms and molecules at very small distances apart. E. B. L.

Energy Levels in Band Spectra. O. S. DUFFENDACK (*Astrophys. J.*, 1925, **61**, 209—222).—A study of the relation between the radiating potentials of the molecule and its band spectrum. There are, in addition to a change in its translational motion, three ways in which a molecule may absorb energy (instead of only one, as for the atom) associated with changes in (*a*) the electronic configuration of the molecule, (*b*) the configuration of the nuclei of the constituent atoms, and (*c*) the rotational state of the molecule, the amount of energy gained or lost decreasing in that order. The rotational and vibrational spectra are in the infra-red, but spectra due to electronic shifts may be in the visible spectrum or the ultra-violet. The normal state of the molecule is that of the zero electronic and vibrational states, coupled with some rotational state m. The first band system should therefore consist of a single set of bands with frequencies related in a second Deslandres progression, but succeeding systems should consist of groups of bands. The extent of a band system is limited by the overlapping of energy levels, and by the stability and the ionisation of the molecule. The minimum radiating potential of a system is the potential of the zero vibrational level. A. A. E.

Use of Half-quantum Numbers in Interpretation of Hydrogen Chloride Absorption Bands. W. F. COLBY (*Physical Rev.*, 1924, [ii], **23**, 295).—Assignment to the electronic momentum of a value $\frac{1}{2}h/2\pi$ accounts for the missing centres of the well-known bands and for the lines of a new faint combination band observed for hydrogen chloride at 300°. A. A. E.

Effect of Pressure on the Infra-red Absorption of Hydrogen Chloride. G. BECKER (*Z. Physik*, 1925, **34**, 255—272).—The observations were made on the rotation–oscillation band at 3·4 μ, by comparing the effect of compression of the hydrogen chloride with the effect of addition of air, the product of length of column by density being kept constant. The increase in absorption is due to

broadening of the lines composing the band; the breadth does not depend solely on the number of molecular collisions. E. B. L.

Emission and Absorption Bands of Carbon Dioxide in the Infra-red. J. W. ELLIS (*Physical Rev.*, 1925, [ii], **26**, 469—474).—A new weak absorption band of carbon dioxide was observed, using a self-registering infra-red quartz prism spectrograph of an auto-collimation type, at 2·02 μ, forming a linear, although not harmonic, frequency series with known bands at 2·73 μ and 4·25 μ; it was identified with a band at 1·99 μ in the Bunsen flame emission spectrum. The emission region at 2·7 μ was resolved into equally intense components at 2·58 μ and 2·76 μ. The temperature of the Bunsen flame is computed to be about 2000° Abs. A. A. E.

Vibration of the Carbonate Group. P. A. TAYLOR (*Phil. Mag.*, 1925, [vi], **50**, 1158—1160; cf. Chapman and Ludlam, this vol., ii, 1025).—Kornfeld's treatment of the problem of the infra-red vibrations of the carbonate group in crystals is modified by the introduction of terms for the force between the oxygen atoms. The discrepancy between theory and observation is thereby made worse, emphasising the difficulty, pointed out by Chapman and Ludlam, of explaining the observed infra-red vibrations of the carbonate group by a simple theory. A. B. M.

Optical Researches on Sulphurous Acid and its Alkali Salts, Especially Potassium and Ammonium Pyrosulphites. R. DIETZEL and S. GALANOS (*Z. Elektrochem.*, 1925, **31**, 466—473).—The absorption spectra of aqueous solutions of sulphur dioxide show that these contain chiefly molecules of unchanged sulphur dioxide and of its hydrate, and only small amounts of sulphurous acid and its ions. Alcoholic solutions absorb much more strongly than aqueous solutions, from which it follows that a new substance, possibly an alcoholate with the formula $O_2HS{\cdot}OC_2H_5$, is formed. Aqueous alkali hydrogen sulphite solutions show similar results to sulphur dioxide solutions. Aqueous and alcoholic solutions of potassium and ammonium pyrosulphites show no spectrum characteristic of the ion $S_2O_5^{--}$. It is concluded that the equilibrium in these cases also is similar to that in aqueous sulphur dioxide solutions. On being exposed to light or warmed, solutions of hydrogen sulphites and pyrosulphites show after some time an alteration in the absorption, which is increased and displaced in the direction of longer wavelength. This effect is due to a photo-oxidation of the HSO_3^- ions which results in formation of the normal sulphate, sulphurous acid, and the hydrate of sulphur dioxide. Schafer's assumption of an isomerisation of the HSO_3^- ions to explain this phenomenon is unnecessary. N. H. H.

Behaviour of Benzene in Aqueous Solutions. Ultra-violet Absorption as a Function of p_H. F. VLÈS and (MLLE.) M. GEX (*Compt. rend.*, 1925, **181**, 506—509).—Benzene in the proportion of 0·5 c.c. per litre was added to various solutions of hydrochloric acid or sodium hydroxide. The resulting solutions were kept for different periods in completely filled closed flasks. On opening, the

absorption spectra were photographed, and the p_H values measured, as quickly as possible. The results are expressed by plotting φ (ratio of absorptive powers at 260 and 254 $\mu\mu$) against p_H values (cf. this vol., ii, 472). The curve exhibits well-defined maxima at p_H values 1·2, 5, 9·5, 13, which occur whether the solutions were examined 7 or 24 hrs. after preparation; in the latter case, however, the values of φ are uniformly lower. The results are considered to prove that the benzene molecule is not inert towards hydrogen ions or towards electrolytic equilibria into which they enter.

R. A. M.

Absorption Spectra of Some Ketones. S. L. LANGEDIJK (*Rec. trav. chim.*, 1925, **44**, 931—934; cf. this vol., i, 408).—A reply to Plotnikov (this vol., ii, 837). G. M. B.

Hæmatoporphyrin. R. FABRE (*Compt. rend.*, 1925, **181**, 623—625; cf. Dhéré, Schneider, and van der Bom, A., 1924, ii, 643). —The curve of spectral distribution of fluorescence of hæmatoporphyrin has a maximum at 6350 Å., is best defined at a dilution of 1 in 8000, is more characteristic than the absorption spectrum of hæmatoporphyrin, and disappears after 12 hrs.' irradiation by a mercury vapour lamp. The absorption curve loses its characteristics after irradiation for 8 hrs. L. F. H.

Fluorescence Radiation of Nitrogen. O. OLDENBERG (*Proc. Nat. Acad. Sci.*, 1925, **11**, 595—597).—When a condensed spark occurs in nitrogen which is at a pressure of a few tenths of a mm. and special arrangements are made to prevent glow discharges, it is possible to observe the fluorescence radiation excited by the spark. The fluorescence spectrum is different from that of the spark and contains the bands: 3755, 3805, 3894, 3914, 3943, 3998, 4059, 4142, 4201, 4239, 4281, 4344, 4416, 4489, 4574, 4653, and 4709 Å. From the work of Wien (A., 1923, ii, 349), it is certain that the bands 4709, 4281, 4239, 3914, and probably some others, are due to the ionised nitrogen molecule, whilst the others originate in the neutral molecule. It is suggested from analogy with the alkaline earths that two-electron jumps occur within the molecule and that the absorption of a wave-length beyond the limit of a series would ionise the atoms and at the same time excite the ion. A. E. M.

New Experiments with Crookes' Tube. A. DAUVILLIER (*Compt. rend.*, 1925, **181**, 601—603).—The hypothesis that the appearance of bubbles in the walls of Crookes' tubes after prolonged use is connected with the disappearance of gas from the tube has been shown to be erroneous by exposing pieces of glass cut from tubes which had shown this effect, to a homogeneous beam of cathode rays, under conditions in which negative luminescence and ionic discharge were absent. The green fluorescence of these test-pieces disappeared after ½ hr. exposure, and the glass became violet-brown in colour. Thin sections, showing no visible fluorescence, showed the same coloration, which was deep-seated and unaffected by aqua-regia. It disappeared easily on heating, without triboluminescence, but with the formation of bubbles. Fusion of the

coloured test-pieces by cathode ray bombardment gave the same result. It is suggested that the coloration is due to the liberation of atoms of alkali metals by the destruction of negative ions, the freed electrons passing to adjacent positive ions. The formation of gas bubbles is due to the decomposition of the glass by the alkali metal, and is independent of the absorption of gas, and of fluorescence. The disappearance of gas is attributed to polymerisation in the negative luminescence. The author's theory of the origin of the Crookes' dark space (" La Technique des Rayons-*X*," p. 14) is supported by the production of a positive stream in a secondary dark space in a tube containing neon. F. G. T.

Polarised Fluorescence of Dyes. VI. W. L. LEVSCHIN (*Z. Physik*, 1925, **34**, 330—336; cf. this vol., ii, 13, 629).—By comparing the polarised fluorescence from dyes in viscous solutions and in colloidal solutions, the conclusion is reached that the total polarisation in the latter is the sum of the polarisation in the single phases. E. B. L.

Luminous Efficiency of Chemi-luminescence Reactions. E. Q. ADAMS (*Physical Rev.*, 1924, [ii], **23**, 771).—The ratio of light production to energy input in the case of phosphorus (nitrogen saturated with phosphorus vapour being brought into contact with air) is slightly above 1 lumen per kilowatt at either 25° or 40°. A. A. E.

Decay and Regeneration of Radio-luminescence. C. H. VIOL, G. D. KAMMER, and A. L. MILLER (*Science*, 1925, **61**, 489).—The decrease in the glow of niton (radon) in glass tubes and in the luminescence of phosphorescent zinc sulphide is believed to be due to the masking of the radiation luminosity by the colour which the material acquires, due to the action of the radiation. When the colour is discharged by just sufficient heating the luminescence returns. A. A. E.

Oscillation Phenomena in Diffraction Spectra. E. BUCHWALD (*Physikal. Z.*, 1925, **26**, 672—675).—The blue colour of the sky owes its existence to fluctuations in the density of the diffracting molecules of air. Opalescence has a similar cause. The continuous ground in *X*-ray diffraction images is affected by thermal motion of the crystal particles. The paper is theoretical and consists of an attempt to clarify the mathematics of the oscillation phenomena entering into those enumerated. R. A. M.

Effect of Light on the Thermal Conductivity of Selenium. R. E. MARTIN (*Physical Rev.*, 1925, [ii], **26**, 475—485).—A selenium cell which was not sensitive electrically was also not sensitive thermally. The red end of the spectrum is more effective than the shorter wave-lengths. The results furnish additional evidence that thermal and electrical conductivities in metals largely depend on the same factors. A. A. E.

Method for Determining the Dielectric Constants of Electrolytes which Conduct Well. H. HELLMANN and H. ZAHN (*Physikal. Z.*, 1925, **26**, 680—682).—The method, based on

high-frequency oscillations, leads to accurate values for small differences in the constant and has been tested by a determination of the influence of the addition of small volumes of acetone to solutions of sodium and potassium chlorides. R. A. M.

Dielectric Constants of Ethane, Ethylene, Acetylene, and Butylene, and the Symmetry of Unsaturated Bonds. C. P. SMITH and C. T. ZAHN (*J. Amer. Chem. Soc.*, 1925, 47, 2501—2506).—The method of Zahn (A., 1924, ii, 809) was employed and the values obtained are in accord with Debye's theory of dielectrics as applied to gases. The molecules of the gases studied have no electric moment except α-butylene, which has a small moment. The electronic structure of an unsaturated linking is symmetrical, but with a stronger field of force around it than that around a saturated linking, so that if the unsaturated linking is unsymmetrically located in the molecule, the induced electronic shifts will give a moment to the molecule as a whole. W. T.

Electric Moment of Gaseous Hydrogen Chloride and Hydrogen Bromide Molecules. K. T. COMPTON and C. T. ZAHN (*Physical Rev.*, 1924, [ii], **23**, 781—782).—Measurements were made of the dielectric constant of gaseous hydrogen chloride and hydrogen bromide throughout a temperature range of 400° beginning just above the liquefaction point. The data accurately obey Debye's equation based on the existence of fixed moments in the molecule. For hydrogen chloride the moment is $1{\cdot}03 \times 10^{-18}$ c.g.s.u., and for hydrogen bromide, $0{\cdot}7881 \times 10^{-18}$ c.g.s.u. A. A. E.

Dielectric Fatigue in Rochelle Salt. J. VALASEK (*Physical Rev.*, 1924, [ii], **23**, 114).—Rochelle salt behaves as though it contained conducting elements insulated from one another. Anomalous effects have been observed only between −20° and +25°, the range in which the crystal is piezo-electrically active. There is a corresponding piezo-electric fatigue due to the same causes. A. A. E.

Colour-vision Spectrometer. W. PEDDIE (*Proc. Roy. Soc. Edin.*, 1925, **45**, 302—307).—A new design is described for a spectrometer which can be employed both for the three-standard and the two-standard colour methods of determining colour sensation curves. R. A. M.

Scattering of Light in Mixtures of Air and Carbon Dioxide. D. BANERJI (*Physical Rev.*, 1925, [ii], **26**, 495—499).—The intensity of the light scattered transversely by a mixture of the two gases varied linearly with the percentage of carbon dioxide. The ratio of the intensities of the components polarised horizontally and vertically varies in accordance with Raman's theory. A. A. E.

Dispersion Constants and Critical Electron Velocities of Molecular Hydrogen. H. SCHÜLER and K. L. WOLF (*Z. Physik*, 1925, **34**, 343—346).—The experimental values for the index of refraction of hydrogen are represented by a dispersion formula containing two terms which are discussed in connexion with the critical velocities found for the impact of electrons on the hydrogen

molecule. It is suggested that these terms are the frequencies at the centres of gravity of two regions of continuous absorption, of which the long wave-length limits correspond with 13 and 16 volts, respectively. E. B. L.

Dispersion of Potassium Chloride and Sodium Chloride. K. F. HERZFELD and K. L. WOLF (*Ann. Physik*, 1925, [iv], **78**, 35—56).—In these simplest heteropolar crystals, the metal will have lost an electron and the halogen will have gained one; both will then possess an outer electron shell containing eight electrons and will thus resemble the noble gases. Sodium chloride will give ions resembling neon and argon, but the sodium ion will hold its electrons more firmly than neon on account of its positive charge and the chlorine less firmly than argon because of its negative charge. From these considerations, dispersion formulæ are developed which consist of three members, one for the cation and two for the anion. The two positions taken for the absorption of the chlorine ion are the resonance line and the centre of gravity of the continuous absorption in the far ultra-violet, resulting from the complete loss of an electron. This requires, in addition to the work done against the electron affinity, the work done against the attraction exerted by the other points in the lattice. In this way, the desired wave-lengths can be calculated. Conversely, from the wave-lengths for the cation, the ionisation potentials of the potassium and sodium ions can be calculated. E. B. L.

Molecular Dissymmetry and Optical Activity. E. DARMOIS (*J. Phys. Radium*, 1925, [vi], **6**, 232—240).—The inadequacy of Drude's electromagnetic theory has led to various new theories of rotatory power (A., 1918, ii, 283; *Ann. Physik*, 1915, [iv], **48**, 1—56; *Phil. Mag.*, 1920, [vi], **40**, 713). The theory of de Malleman (*Ann. Physique*, 1924, [x], **2**, 5—239) is discussed at some length. On this theory, optical anisotropy of liquids is due to elliptical vibrations resulting from the superposition of effects due to rotatory power and birefringence. The molecular rotatory power is a mean effect varying with changes in the orientation of the molecules. Evidence supporting this has been obtained by de Malleman for orientation in an electric field and by Longchambon for the rotatory power of active crystals. Gouy's relation $\delta^2=\varphi+4\omega^2$ (φ the birefringence, ω the rotatory polarisation) is found to hold when the birefringence is feeble. It is claimed for de Malleman's theory that it correlates birefringence, rotatory power, concentration, and temperature effects. The author considers that the purely physical theories cannot, however, explain the large variations of rotatory power with dilution and temperature changes. Physico-chemical mechanisms must be employed such as association of active molecules with each other (*e.g.*, tartaric acid) or with the solvent. In other cases, definite evidence of chemical reaction between the active substance and the solvent (*e.g.*, malic acid and molybdates) must enter into the mechanisms put forward. The author considers the Kerr and Cotton–Mouton effects. The relations between

chemical constitution and the existence of circular dichroism are also discussed. R. A. M.

Rotation-Dispersion of Optically Active Compounds. Dimethoxysuccinates and Pyridine. T. S. PATTERSON and J. D. FULTON (*J. Chem. Soc.*, 1925, **127**, 2435—2444).—With the object of determining whether the rotation values on both sides of a maximum or minimum in the temperature–rotation curve for an optically active substance and its derivatives fall on a single characteristic diagram, the temperature–rotation curves between 0° and 100°, for six different wave-lengths, have been examined for benzyl *d*-dimethoxysuccinate in the homogeneous state and in solution, as well as for *d*-dimethoxysuccinic acid and its methyl ester, and benzyl tartrate in solution. The dispersion ratios calculated from the rational zero give values approximating to that of ethyl tartrate (T., 1913, **103**, 145). As little variation of the temperature–rotation curve is shown, and no definite maximum or minimum, nicotine has also been examined. Rotations on either side of the zero of rotation have been obtained, but no suitable solvent could be found to bring the region of anomalous dispersion under observation. The dispersion ratios for nicotine, whether in the homogeneous condition, in an inert solvent, or as a salt, show good agreement. M. S. B.

Optical Activity and the Polarity of Substituent Groups. II. Menthyl Esters of Substituted Acetic Acids. H. G. RULE and J. SMITH (*J. Chem. Soc.*, 1925, **127**, 2188—2194).—The rotatory powers of menthyl esters of the acids $CH_2X{\cdot}CO_2H$, where X=CN, CO_2H, OH, OMe, and OEt, have been determined at temperatures between 20° and 95° and for light of four different wave-lengths. Where possible, the compounds have been examined in the homogeneous state. In all cases, the observed rotations may be expressed within the limits of experimental accuracy, by a Drude equation of one term. Temperature has little effect on the results. The values of λ_0^2 vary between 0·0238 and 0·0316 for homogeneous esters. Observations made with menthyl cyanoacetate, glycollate, and hydrogen malonate in benzene and chloroform solution show that, in these cases also, dispersion is apparently simple in character. By comparison with molecular rotations for menthyl esters of other monosubstituted acetic acids, as determined by earlier investigations, the relative effect of substituents on optical activity appears to be as follows :

$$CN > Cl > Br > OH > OMe > OEt > Me > CO_2H > H.$$

This corresponds very closely with the general polar effect of the groups as shown by their influence on molecular inductive capacity (Rule and Paterson, this vol., i, 29) and the dissociation constants of the acids (Betti, A., 1923, ii, 674). There is no indication of positive groups affecting the rotatory power in an opposite sense to negative groups as illustrated by the behaviour of the benzoates. M. S. B.

Varying Valency of Platinum with Respect to Mercaptanic Radicals. II. (SIR) P. C. RÂY and K. C. B. RAY (*J. Indian Chem. Soc.*, 1925, **2**, 178—190).—Further evidence is brought forward in support of the view that in compounds with certain mercaptanic radicals platinum behaves as a bi-, ter-, quinque-, sexa-, and octa-valent element, respectively (cf. Rây, T., 1923, **123**, 133). The determination of the mol. wt. of the compound Et_2S_2PtCl obtained by the interaction of ethyl disulphide and platinic chloride (Rây, *loc. cit.*) shows that the molecular formula is treble the empirical formula, the compound having a ring structure in which the platinum is ter- or quinque-valent. By the interaction of sodium dithioethylene glycol and platinic chloride in acetone, the compounds $C_2H_4<\overset{S}{\underset{S}{>}}Pt<\overset{S}{\underset{S}{>}}C_2H_4$ and $[(C_2H_4S_2)_2{:}Pt{\cdot}S{\cdot}CH_2{\cdot}]_2$, in which the metal is respectively quadri- and quinque-valent, are obtained. By the interaction of ethyl sulphide and platinic chloride, the following products, in which platinum varies from ter- to octa-valent, have been isolated, those to which no reference is given being new *compounds*: (1) Et_2SPtCl, not melting below 250°, (2) $(Et_2S)_2PtCl_2$, which has been isolated in six isomeric modifications, the products obtained depending on the temperature of the reaction and the active mass of the reactants, α, golden-yellow needles, m. p. 108° (cf. Tschugaev and Malzschewsky, A., 1924, i, 934); β, white, m. p. 108°; γ, greenish-yellow, m. p. 110° (cf. Tschugaev and Malzschewsky, *loc. cit.*); δ, colourless, m. p. 104°; ε, m. p. 96°; the sixth isomeride, m. p. 77°, was obtained by Rây (*loc. cit.*); (3) $(Et_2S)_2PtCl_3$, orange-red, m. p. 109°, which is a molecular compound of (2) and (4) [cf. Tschugaev and Benevolenski, A., 1913, i, 1149; Loir, *Ann. Chim. Phys.*, 1853, **39**, 441, who, by crystallisation from boiling alcohol, evidently decomposed the compound into its two components and isolated (4) only]; (4) $(Et_2S)_2PtCl_4$, yellow needles, m. p. 198° (cf. Rây, *loc. cit.*); (5) $(Et_2S)_2PtCl_5{,}2H_2O$, orange needles, m. p. 90°. The constitution of these compounds on Werner's co-ordination theory is discussed. Crystallographic data for the compounds (2) ε and (4) are given. J. W. B.

Colour and Molecular Geometry. IV. Explanation of the Colours of Cyanine Dyes. J. MOIR (*J. Chem. Soc.*, 1925, **127**, 2338—2343; cf. this vol., ii, 634).—The inactive portions of a dye molecule lying outside the two positive colour centres produce a "loading" effect on the colour, raising the position of the absorption bands by an amount varying between 0·5% and 10%. The colour bands of diquinolylmethane may be deduced from those of dipyridylmethane by multiplying by the square of the colour factor 1·105, thus showing that the effect of "loading" with a portion of a benzene ring is the same as in the ordinary naphthol-phenol dicyclic family of dyes. There is only a minute difference between the colours of pseudo*iso*cyanine and of activated di-2-quinolylmethane, the methyl colour factor being apparently 1·005. The azocyanine family is abnormal in that the unmethylated member does not become activated with acid. Thus the effect of the methyl

groups is large, the factor being 1·06 instead of 1·005. All the cyanines have two bands close together, and the ratio of the absorption centre wave-lengths for the two bands of each substance is practically always 1·065. By a coincidence, the bands of the cyanines are calculated from those of the *iso*cyanines, and the bands of the latter from those of the pseudocyanines, by multiplying by 1·065 also, the same factor holding good for the carbocyanine series. The bands of activated dipyridylmethane are explained on the author's spatial theory of colour. M. S. B.

Atoms and Isomorphism. A. N. WINCHELL (*Science*, 1925, **61**, 553—557).—A discussion of isomorphism in relation to valency and atomic domain. Although substances which are chemically closely similar are often isomorphous, the miscibility of substances in crystals is determined by the relative sizes of the atoms, and not by their valency. A. A. E.

Law of Periodicity and the Theory of Cyclic Unsaturated Compounds. P. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1925, [ii], **111**, 23—35).—A survey of published data on the mutual influences of various portions of an organic molecule leads to the generalisation that the approximation and accumulation of one and the same substituent causes a diminution or even a reversal of the usual influence of the particular group on the character of the molecule. Examples are afforded by the unexpectedly low ionisation constant of trichloroacetic acid as compared with that of the monochloro derivative, where the strongly acidic influence of the substituting chlorine is depressed by its accumulation, and by the low basicity of hydrazobenzene as compared with benzidine, where the basic character of each nitrogen atom is depressed by its proximity to the other. A similar explanation applies to dibasic acids, diketones, and ketonic acids, containing the grouping $-CO\cdot[CH_2]_n\cdot CO-$, where instability increases with decreasing value of n down to $n=1$, whilst when the two carbonyl groups are adjacent the compounds are perfectly stable. This explanation removes the anomaly of the strong dissociation of the second carboxyl group of oxalic acid, which is contrary to Ostwald's rule that the dissociation of the second carboxyl group in dibasic acids is less the nearer the two carboxyl groups approach one another. Similar, quantitative data are quoted for the influence of $-Cl$, $-CO_2H$, $-OH$, and $-C_6H_5$ groups in analogous series. Thus, whilst the dissociation constant of phenylacetic acid is 3 times that of acetic acid, that of benzoic acid is only 0·2 of that of formic acid, owing to the close proximity, in benzoic acid, of the phenyl group to the carboxyl group. Similar regularities are observed amongst diamines, of which hydrazine can be considered as an extreme case. The increase in acidity produced by the etherification of an α-hydroxy group in carboxylic acids is explained analogously, and the explanation is extended to include the increase in acidity of boric acid in presence of glycerol, and the acidity relationships of polybasic mineral acids, where the anhydro-acid is stronger than the simple compound (cf. Hantzsch, A., 1923, ii, 475). The "accumulation influence" can be considered

similarly to explain the inactivity of conjugated unsaturated systems, and an analogy is drawn in this sense between the groupings –C:C·C:C– and –C:CX– (X=halogen), both of which exhibit unexpected passivity. Analogy is drawn between the activity relationships of the series CH_2:CH·CH_2X, CH_2:CHX, CH_2:CX_2, in which the middle term represents the least reactive compound, and those observed by Vorländer (A., 1901, i, 444) amongst carboxylic acids, and this analogy is extended to the three unsaturated, conjugated ring systems in *cyclo*octatetraene, benzene, and *cyclo*butadiene, where increasing proximity of active groups (unsaturated linkings) first depresses the total activity and then, reversing the effect, enhances it. A form of periodicity is thus set up, and can be experimentally demonstrated by a study of reactivities in suitable series (cf. this vol., ii, 802), although in many cases it may be impossible to discover the full " wave " of the periodicity curve. Similar considerations can be applied to condensed and heterocyclic ring systems. F. G. W.

Born's Dipole Theory of Anisotropic Liquids. G. Szivessy (*Z. Physik*, 1925, **34**, 474—484).—According to Born's theory, an anisotropic liquid should exhibit an electric charge at its boundary when its molecules are subjected to an external force which would cause them to be parallel to each other. This should be the case when a magnetic field is applied, but no such effect was observed, although one-millionth of the predicted effect could have been detected. E. B. L.

Magnetochemistry of Closed Chains. P. Pascal (*Compt. rend.*, 1925, **181**, 656—658; cf. this vol., ii, 371, 634).—The magnetic properties of three-, four-, and five-membered ring compounds were investigated. The diamagnetism decreases with progressive unsaturation. *cyclo*Pentanes behave magnetically, like the corresponding chain compounds; the same holds when one or two carbon atoms are substituted by nitrogen atoms, or when an unsaturated linking is introduced. The magnetic susceptibilities of the compounds investigated vary in proportion to the angular strains predicted from Baeyer's theory. S. K. T.

Structure and Molecular Dimensions of Non-metallic Hydrides. H. G. Grimm (*Z. Elektrochem.*, 1925, **31**, 474—480).—The principle is put forward that atoms preceding the inert gases in the periodic classification by one to four places alter their properties by taking up a hydrogen atoms, where a is one to four, in such a way that the resulting complexes behave as pseudo-atoms having similar properties to the atoms a groups to the right of the original atoms. The work involved in the dissociation of oxygen and nitrogen is calculated from measurements of ionisation by collision, and from these figures the work of dissociation of non-polar molecules is determined. The true diameter of simple non-metallic hydrides is calculated. With the aid of these and other data, models of simple organic molecules are described which seek to elucidate their dimensions and physical properties. N. H. H.

Average Cross-sectional Areas of Molecules by Gaseous Diffusion Methods. E. MACK, jun. (*J. Amer. Chem. Soc.*, 1925, **47**, 2468—2482).—A simple method for the determination of the diffusion coefficients of volatile substance is described, and the average cross-sectional areas of the molecules of iodine, benzene, naphthalene, anthracene, toluene, diphenyl, aniline, and benzidine are calculated by the equation of Stefan, Maxwell, and Jeans. The results obtained agree with those proposed by Bragg from *X*-ray analysis. They do not agree so well with values determined from Huggins' models. The carbon atoms in the chain of the *n*-octane molecule are probably arranged in a zigzag manner. The diffusion method confirms the conclusion, based on chemical evidence, that diphenyl and benzidine have a " collapsed " structure. W. T.

Search for the Element 93. I. Examination of Crude Manganese Compounds and Isolation of Element of Atomic Number 75. J. G. F. DRUCE (*Chem. News*, 1925, **131**, 273—277).—From theoretical considerations it seems possible that an element related to manganese, and of atomic number 93, may exist in quantity sufficient to make it readily accessible to chemical analysis. An investigation of the impurities in 100 g. of crude manganese sulphate has therefore been made. From the solution which could not be precipitated by hydrogen sulphide 75 mg. of a light brown oxide, soluble in acids but not in sodium hydroxide, has been obtained. Examination in an *X*-ray spectrograph indicated, in addition to well-known elements, the presence in appreciable quantity of an element with the characteristic radiations 1·43 Å. and 1·233 Å., corresponding with lines in the characteristic *L* radiation of the element rhenium (atomic number 75), recently discovered (cf. Noddack, Tacke, and Berg, this vol., ii, 939). No trace was found of any line corresponding with the characteristic radiations to be expected from an element 93. M. S. B.

Eka-cæsium. F. H. LORING and J. G. F. DRUCE (*Chem. News*, 1925, **131**, 289).—*X*-Ray examination of a specimen of crude rhenium oxide disclosed a faint line corresponding with the $L\alpha$ line of element 87 (eka-cæsium). A. R. P.

Eka-cæsium and Eka-iodine. F. H. LORING and J. G. F. DRUCE (*Chem. News*, 1925, **131**, 305).—A preparation of crude rhenium oxide from pyrolusite gave an *X*-ray spectrum containing lines of wave-length 1·040 and 0·895, corresponding with the $L\alpha$ lines of elements 85 (eka-cæsium) and 87 (eka-iodine), respectively. A. R. P.

Allotropy of Manganese. A. J. BRADLEY (*Phil. Mag.*, 1925, [vi], **50**, 1018—1030; cf. Westgren and Phragmén, this vol., ii, 1035).—A number of specimens of manganese have been examined by the method of the *X*-ray powder photograph. The varying types of photograph obtained have been shown to be due to the existence of three allotropic forms of the element. Two of these, β and γ, are present normally in commercial manganese. The β-form is stable in the range 150—850°, and the γ-form from

650° upwards. Within the region 650—850°, both forms are stable, and the element appears to show the phenomenon of isodynamic allotropy, an equilibrium mixture of the two allotropes corresponding with each temperature. The pure γ-form is easily obtained by raising the temperature above 850° in a vacuum, and suddenly quenching. It does not appear easy to obtain pure β-manganese by heat treatment alone, but it is formed from the γ-form by sublimation in a vacuum at 1105°. The third allotrope, α, has only been obtained electrolytically. *X*-Ray measurements show that the α-form can be regarded either as a face-centred tetragonal structure with axial ratio $a:c=1:0{\cdot}9445$, or as a body-centred tetragonal structure with axial ratio $1{\cdot}34:1$. It is apparently stable only at low temperatures. On heat treatment, α-manganese is converted into the β- and γ-forms, but the change does not appear to be reversible. A. B. M.

Amorphous Carbon and Graphite. O. Ruff, G. Schmidt, and W. Olbrich (*Z. anorg. Chem.*, 1925, **148**, 313—331).—The conclusion of Debye and Scherrer (A., 1917, ii, 437) and of Kohlschütter (A., 1919, ii, 151, 152) that amorphous carbon is merely a finely divided form of graphite is shown to be probably incorrect. Amorphous carbon is a true modification which at 1100° begins to pass into a "paracrystalline" form, the properties of which approach those of graphite. The numerous forms of amorphous carbon are to be attributed to the presence of varying proportions of graphite, amorphous carbon, and the "paracrystalline" form. Only true amorphous carbon can be activated, activation being associated with the property of adsorption from solution. The authors' conclusions are supported by examination of the röntgenograms of various carbons and of the röntgenograms, resistivity towards oxidising agents, and electrical conductivity of graphites prepared by heating lamp-black at 1600—2600°, either with or without catalysts (*e.g.*, metals). The conversion proceeds stepwise; the nature of the atmosphere in the furnace probably has some influence. The conditions governing the effect of the catalysts are also considered. S. K. T.

***X*-Ray Investigation of Palladium–Silver Alloys containing Hydrogen.** F. Kruger and A. Sacklovsky (*Ann. Physik*, 1925, [iv], **78**, 72—82).—Hydrogen forms a solid solution in palladium up to a certain saturation accompanied by expansion of the lattice. Addition of silver also expands the lattice, and if this expansion has not reached the limit given by hydrogen alone in palladium, then the alloy will absorb hydrogen. With 70% of silver, this point has been reached and palladium with 70% of silver will not absorb hydrogen. E. B. L.

***X*-Ray Analysis of the Crystal Structure of Lead Dioxide.** A. Ferrari (*Atti R. Accad. Lincei*, 1925, [vi], 2, 186—191).—An examination, by the Debye method, indicates a tetragonal structure of the rutile type. The dimensions of the elementary cell, which contains the molecule PbO_2, are $a=4{\cdot}98$, $c=3{\cdot}40$ Å. The value,

c/a=0·682, of the axial ratio differs slightly from that determined crystallographically. The density, calculated from the dimensions of the unit cell, is 9·42, and agrees excellently with that determined directly. In preparing lead dioxide by different methods, no evidence was obtained of the hexagonal modification reported by Geuther and Lüdecke. F. G. T.

X-Ray Examination of Maleic and Fumaric Acids. K. YARDLEY (*J. Chem. Soc.*, 1925, **127**, 2207—2219).—Examination of monoclinic maleic acid crystals by the *X*-ray spectrometer shows that the unit cell contains four asymmetric molecules, so that the planosymmetry usually ascribed to maleic acid from chemical considerations has no existence in the crystalline state. The dimensions of the cell are a=7·49, b=10·14, and c=7·12 Å., β=117° 7′. Perfect cleavage is obtained parallel to the (001) plane, and imperfect cleavage parallel to (010), and the crystals can be bent and twisted in certain directions without fracture. Twinning takes place with great facility, and almost invariably on the (100) plane. The crystals belong to the space group C_{2h}^5 and a probable structure is suggested. The unit cell of fumaric acid is triclinic, a=7·56, b=15·00, and c=6·20 Å., whilst α=90° 40′, β=88° 30′, and γ=89° 48′. The cell appears to contain either six simple molecules, forming a single asymmetric unit if the crystals are pedial, or, if they are pinakoidal, the six molecules are arranged in two groups of three, each group being asymmetric in itself but centro-symmetric with respect to the other. The significance of this structure with reference to the physical properties of fumaric acid is discussed. Very complex twinning takes place. *X*-Ray examination of derivatives of maleic and fumaric acids does not indicate association in the solid state in any other case (cf. this vol., ii, 1033). M. S. B.

X-Ray Diffraction Measurements on the Pyroxenes. R. W. G. WYCKOFF, H. E. MERWIN, and H. S. WASHINGTON (*Amer. J. Sci.*, 1925, [v], **10**, 383—397).—*X*-Ray diffraction photographs have been made of the different types of minerals (in powder form) usually classed as pyroxenes, thus dividing them into groups with related *X*-ray patterns, *i.e.*, showing the same type of crystal structure, namely, diopside, enstatite, wollastonite, and rhodonite. The exceptions are clino-enstatite, babingtonite, spodumene, pyroxmangite, alamosite, and sobralite, each of which has a diffraction pattern unlike any other. In spite of varied composition, the spacings of diopside-like minerals, with the exception of jadeite, which is probably formed under conditions of very high pressure, show remarkable similarity. This indicates that (1) atoms of magnesium and ferrous iron have practically the same effective volumes in this structure, (2) the volume of manganese atoms is somewhat larger, and (3) that of calcium atoms is considerably larger. Measurements on the diopside group also indicate that there is no apparent connexion between the excess of aluminium and ferric oxides present and the sizes of the unit cells. Density calculations, combined with the *X*-ray spacing measurements, prove

that these oxides cannot be present in the molecules in addition to the diopside-like metasilicate molecule. It is not possible, however, to distinguish between the possibility of some kind of isomorphous replacement and the formation of intimate mechanical mixtures with the excess oxides in forms of similar density to that of the diopside-like constituents. M. S. B.

X-Ray Study of Cyanite and Andalusite. J. T. Norton (*J. Amer. Ceram. Soc.*, 1925, **8**, 636—639).—Natural, raw cyanite and andalusite have different atomic structures, both the positions and the relative intensities of the lines in the diffraction patterns showing distinct variations. After having been heated to about 1450° and about 1600°, respectively, the two compounds exhibit the diffraction pattern of artificial sillimanite. F. S.

Differentiation between Mullite and Sillimanite by their X-Ray Diffraction Patterns. L. Navias and W. P. Davey (*J. Amer. Ceram. Soc.*, 1925, **8**, 640—647).—*X*-Ray diffraction patterns were obtained for natural sillimanite, mullite (prepared by fusing alumina and silica), and calcined china clays and ball clays. The patterns of two substances were taken, one above the other, on the same film, the lower one in each case being that of mullite, so that direct comparison was possible. In the patterns for sillimanite and mullite, distinct differences in the positions of lines in the region of 2·12—1·70 Å. were apparent. The specimens were prepared by the powder method. Sillimanite and mullite showed entirely different characteristics when ground to give a maximum particle size of 0·06 mm.; the lines of the sillimanite pattern were smooth, whereas those of the mullite were scratchy in appearance, indicating that the mullite fragments had "packed" to form lumps. The negative results obtained by other investigators are accounted for by this packing tendency. Mullite ground to an average particle size of 0·002 mm. and annealed for 2 hrs. at 900—1000° gave lines as smooth as those of sillimanite. Re-examination of the diffraction patterns previously obtained for calcined china clays and ball clays confirmed the conclusion that the crystalline phase of fired clays is mullite. [Cf. *B.*, 1925, 546.] F. S.

Method of Following the Course of certain Chemical Reactions by Means of X-Rays. Oxidation of Unsaturated Fatty Acids. J. J. Trillat (*Compt. rend.*, 1925, **181**, 504—506).—Very small quantities of saturated fatty acids deposited on a plane piece of metal yield intense *X*-ray spectra by the rotating crystal method (this vol., ii, 752). The work has been extended by attacking lead with thin films of oleic, linoleic, and linolenic acids containing one, two, and three double linkings, respectively. The lead salts catalyse oxidation by air. In oleic acid, the first effect is shown by the appearance of an intense spectrum with a reticular distance of d=29·8 Å. After a few hrs., a new spectrum d=37·5 Å. appears, and after about 40 hrs. the preparation shows no spectrum. The first spectrum is attributed to lead oleate and the second to its oxidation product and the subsequent absence of structure to

non-oriented polymerides. For linoleic acid, the first spectrum d_1 = 37·1 Å. appears at once, followed after 2—3 hrs. by d_2=49·2 Å., with subsequent disappearance of structure. Thus oxidation of both double linkings in the lead salt occurs simultaneously, since no intermediate stage is observed. Linolenic acid shows three stages, d_1=21·2, d_2=28, d_3=34·4 Å. (ill-defined) on the way to random distribution in the fully "dried" oil. The oxidation of this acid is very rapid and d_1 is regarded as due to the first product. Thus in all three acids oxidation of a double linking is accompanied by a molecular lengthening of 6—7 Å. Unstable products are formed by the fixation of oxygen, and polymerisation follows. R. A. M.

Reality of the Compton Effect. J. A. Becker, E. C. Watson, W. R. Smythe, R. B. Brode, and L. M. Mott-Smith (*Physical Rev.*, 1924, [ii], **23**, 763).—Unambiguous evidence is adduced in support of the reality of the Compton effect. A. A. E.

Theory of Impulse-radiation and Compton's Scattered Radiation. G. Mie (*Physikal. Z.*, 1925, **26**, 665—669; cf. this vol., ii, 844).—The inert period between energy-jumps postulated by the older quantum theory is replaced in the newer theory of Bohr, Kramers, and Slater by the time occupied in the actual radiation process, without any change in the atom itself occurring during the emission. The more recent treatment of the theory has been extremely fruitful in the direction of reconciling interference and polarisation with quantum mechanisms, but impulse-radiation and Compton's scattered radiation have so far not been explained by Bohr and his colleagues. The author advances a theory which is at variance with the newer quantum theory. Collision between an electron and a light quantum occupies a finite period of time, and the electron can either gain mechanical energy without radiating, or it can be excited, whereupon it may radiate energy. Similarly, absorption inside the atoms can occur in two ways resulting respectively in the Compton effect and the photo-effect. In opposition to Bohr, Kramers, and Slater, the radiation from a single excited electron must be strictly monochromatic. The views advanced by the author are discussed by Smekal, Sommerfeld, and Bothe.

R. A. M.

Theory of the Number of β-Rays Associated with Scattered X-Rays. G. E. M. Jauncey and O. K. De Foe (*Physical Rev.*, 1925, [ii], **26**, 433—435).—By the application of a correction factor to the ratio σ/τ, better agreement for long wave-lengths is obtained for the equality of this ratio with that of the number of recoil electron tracks to that of photo-electron tracks (cf. Compton and Simon, this vol., ii, 347). A. A. E.

Wave-length of Molybdenum $K\alpha$ Rays Scattered by Light Elements. A. H. Compton and Y. H. Woo (*Physical Rev.*, 1924, [ii], **23**, 763).—Radiators of lithium, boron, graphite, and water were employed; the spectra observed in each case showed a faint line identical with the primary $K\alpha$ line and a stronger line of wave-

length greater by 0·039 Å., in agreement with the quantum theory of scattering. The relative intensities of the modified and unmodified lines do not depend on whether the radiator is crystalline or amorphous. A. A. E.

X-Ray Diffraction Effects from Solid Fatty Acids. R. W. G. Wyckoff, F. L. Hunt, and H. E. Merwin (*Science*, 1925, **61**, 613—614).—Microscopical examination shows that films of palmitic acid, obtained by solidification from a single point outwards, exhibit large areas having a common optical orientation; *X*-ray examination shows the characteristic several orders of large spacing. Even more definite results were obtained with large plates from solution in acetone or 1-chloronaphthalene. Films obtained by solidification at many points yield lines typical of a powder photograph. Thus the acid appears to be truly crystalline, and not in a smectic or other sub-crystalline state. The symmetry of palmitic acid is either monoclinic or triclinic; the long carbon chains are inclined at an angle to the reflecting face, so that the increase in spacing with the number of carbon atoms is not a simple and direct measure of carbon-to-carbon distances. A. A. E.

Relative Number of *K* and *L* Electrons Expelled by *X*-Rays. F. K. Richtmyer (*Physical Rev.*, 1924, [ii], **23**, 292).—With certain assumptions, the part of the $(L+M)$ absorption which is due to the L electrons only may be computed. The ratio of K to L absorption is then almost equal to that of the respective ionisation potentials, whence the ratio of the probabilities of ejection of K and L electrons is independent of the relative numbers of those electrons, and is inversely proportional to the ionisation potentials, a result at variance with Compton's theory of scattering. A. A. E.

Crystal Structure and Chemical Constitution. I. Transformation Properties of Matter. K. Weissenberg (*Z. Physik*, 1925, **34**, 406—419).—A theoretical discussion of the principles underlying the present conception of the properties of matter. Matter being regarded as a discontinuum in space and time, it is shown that physical as well as geometrical properties of matter may be finally referred to the invariance of the properties of an object under change of the system of co-ordinates by which it is described. W. A. C.

Crystal Structure and Chemical Constitution. II. Structural Theory of Crystals. K. Weissenberg (*Z. Physik*, 1925, **34**, 420—432).—A complete geometrical theory of crystal structure can only be based on the transformation properties of matter. The 230 space-groups of Schoenflies' system may thus be derived; but this system is conceived rather with a view to the practical investigation of crystals. A much larger number of different space-groups is possible. Exhaustive examination of crystal symmetry must lead to a definite number of space-groups of about 10,000. W. A. C.

Crystal Structure and Chemical Constitution. III. Analysis of Crystal Structure. K. WEISSENBERG (*Z. Physik*, 1925, **34**, 433—452).—Crystals are built up of "islands" consisting of a definitely grouped number of atoms such that the "island" repeats itself subject to the symmetry of the crystal. The simplest "island" has a finite number of atoms and a finite volume, but others are possible in which an infinite number of atoms forms a chain, a flat network, or a space-lattice. A second form of atomic grouping is called a "dynad," the characteristic of which is that its constituents are held together by atomic forces, whereas the "island" is a purely geometrical grouping. All "dynads" are "islands," but not *vice versa*. Both kinds of groups must be arranged, in a crystal, in one or other of the extended series of space-groups based on transformation properties. W. A. C.

Crystal Structure of Some Simple Inorganic Substances (Condensed Gases, Sulphates, etc.). H. MARK (*Z. Elektrochem.*, 1925, **31**, 523).—*X*-Ray examination of solid carbon dioxide and solid ammonia by the powder method indicates four molecules to the cell in both cases. Barium, strontium, and lead sulphates, potassium permanganate and perchlorate are found to crystallise in the space-group Q_h^{16}, anhydrous calcium sulphate in Q_h^{17}. The arrangement of the atoms is such that any metal atom is not surrounded by equidistant anion groups, but that one of the latter stands in an exceptional position towards the former. W. A. C.

Crystal Structure of Copper–Manganese Alloys. R. A. PATTERSON (*Physical Rev.*, 1924, [ii], **23**, 552).—In the formation of solid solutions by the addition of manganese (up to 30%) to copper, copper atoms in the face-centred cubic lattice are replaced by manganese atoms, with an increase in the side of the cube from 3·60 to 3·70 Å. Further addition of manganese causes the formation of a new lattice. The minimum m. p. at 30—35% Mn is in accord with Rosenhain's view that the straining of a lattice by the substitution of new atoms lowers the m. p. A. A. E.

Crystal Structure of Potassium Dihydrogen Phosphate and its Isomorphs. O. HASSEL (*Z. Elektrochem.*, 1925, **31**, 523—529).—Crystals of potassium and ammonium dihydrogen phosphates (tetragonal–scalenohedral) have been examined by the rotating-crystal method with *X*-rays. There are four molecules to the cell, with spacings for the potassium salt $a=7·42$, $c=6·97$ Å., for the ammonium salt $a=7·48$, $c=7·56$ Å. The halvings indicate a body-centred cell of the space-group D_{2d}^{12}. An arrangement of atoms in the cell is proposed, in which the free oxygen atoms are equivalent and grouped tetrahedrally about the phosphorus atom. From the identity of the *a*-spacings in the two salts, it follows that the potassium or ammonium points in the lattice lie in line with the phosphorus points along the *c*-axis. This result had been previously inferred by Groth from the goniometric data. W. A. C.

Theories on the Constitution of Natural Silicates. G. N. RIDLEY (*Chem. News*, 1925, **131**, 305—308).—A review of modern

theories of the constitution of natural silicates and aluminosilicates with especial reference to the hexite–pentite theory of W. and D. Asch. A. R. P.

Structure of Quartz. (Sir) W. H. Bragg (*J. Soc. Glass. Tech.*, 1925, **9**, 272—282).—It has already been shown that the quartz crystal consists of a set of similar and similarly placed spirals with three SiO_2 molecules to each turn of the spiral, but four parameters still remained to be determined to fix completely the separate atoms. The solution now suggested is based on the change of α- to β-quartz which occurs at 575°, for the former has a trigonal structure, the latter hexagonal. Proof of the difference is obtained by the study of crystal symmetry, from pyro- and piezo-electrical properties, from *X*-ray Laue photographs, and from elasticity determinations on crystal sections. The structure of β-quartz is more easily elucidated, since the four parameters then reduce to one, the silicon atom being fixed and the oxygen atoms lying on certain straight lines. Intensity measurements then serve to determine the position of the oxygen atoms. The most probable value so obtained gives a structure in which the silicon atom is at the centre of a regular tetrahedron, the corners of which are occupied by oxygen atoms. Evidence favours the assumption that the α-form only differs from β-quartz in the relative positions of the atoms in the unit cell. This change, probably only involving a twist of individual units through 8°, would readily account for the various twinnings of α-quartz. A. Cousen.

Cristobalite. L. Longchambon (*Compt. rend.*, 1925, **181**, 614—616).—It has been observed that in the crystallisation of tridymite from a solution in which cristobalite is dissolving, between 870° and 1470°, the crystals of tridymite form in oriented positions on the dissolving cristobalite crystals. The transformation appears to be gradual, the tridymite crystal having the same direction of extinction, and preserving the skeleton of the cristobalite. This arranging of the cristobalite molecules according to the tridymite lattice in a continuous manner exemplifies an indirect oriented polymorphism. The quasi-identity of the crystal lattices of cristobalite and tridymite is supported by the fact that the densities of these substances are almost identical near 1000°. In the crystallisation of quartz between 870° and 1470°, it has been found that, if the quartz is powdered and sieved so as to eliminate very fine powder, tridymite is obtained, but that from unsieved powdered quartz cristobalite is produced, owing to the supersaturation induced by the rapid solution of the impalpable dust. The statement of Weil (this vol., ii, 757) that the transformation of cristobalite in the neighbourhood of 200° occurs at a constant temperature for each crystal or part of a crystal is not confirmed. The transformation appears to be subject to fortuitous retardations dependent on the previous treatment of the crystal. F. G. T.

Structure of Ultramarine. M. Dominikiewicz (*Rocz. Chem.*, 1925, **5**, 308—339; cf. this vol., ii, 1036).—The structural formulæ of various forms of ultramarine are derived from that of kaolin,

the sulphur being attached at the eight internal additive points of the molecule, namely, two points each on each side of the aluminosilicate radical. For ultramarines of low sulphur content, a variety of points of attachment is thus available, leading to the existence of numerous isomerides. In all ultramarines, the sulphur is bound to both aluminium and silicon atoms, the colour depending on the existence of polysulphide bindings, ·Al·S·S·Al·, together with sulphides of the type ·Si·O·SNa. In colourless ultramarines, the sulphur exists only as ·Al·SNa and ·Si·O·SNa. The large inner aluminate radicals have no influence on the coloration of ultramarine, since ultramarines of the highest sulphur content can be divided, by elimination of these aluminate radicals, into two halves, each of which still fulfils all the necessary conditions for the possession of colour, and represents a variety of ultramarine of high silica content, called natrolite ultramarine. In the preparation of this, by fusing silica, kaolin, and sodium hydroxide, the kaolin molecule breaks down into two natrolite molecules, whilst the aluminate radical thus liberated combines with two silicic acid molecules to form a third molecule of natrolite. The colour of ultramarine is explicable by the same theory as for organic dyes, the aluminosilicate radicals playing the part of chromogens, the polysulphide bindings that of chromophores, and the sulphide groups that of auxochromes. R. T.

Determination of Crystal-orientation in Conglomerates. G. TAMMANN (*Z. anorg. Chem.*, 1925, **148**, 293—296).—Careful inspection of the geometry of the etched figures produced when metallic surfaces are treated with ammonium persulphate solution and determination of the relative numbers of certain well-defined types of structures furnish trustworthy information regarding the orientation. J. S. C.

Isotropic Ions, Building of Molecules and the Crystal Lattice. F. HUND (*Physikal. Z.*, 1925, **26**, 682—685).—The shape of a molecule and the type of lattice in which a substance crystallises follow in principle from the conception of isotropic ions, which considers three properties only, their charge Ze, the mutual attractions or repulsions given by b/r^n, and their polarisability by an electric field (Born and Heisenberg, A., 1924, ii, 434), the strength of which is denoted by a. Z, b, n, and a define the properties of an isotropic ion. The conception is admittedly crude, but it serves to prove that a structure for ions cannot be deduced from the shapes of either molecules or crystals. It is not claimed that the reasoning is adequate for all molecular or crystalline forms; crystals made up of neutral atoms are specifically excluded. R. A. M.

Change of State of Aggregation and Polymorphism. V. K. SCHAUM [with W. NAUMANN, K. UNGER, and H. HOFFARTH] (*Z. anorg. Chem.*, 1925, **148**, 217—224).—Investigations on undercooled vapours, supercooled liquids, and supersaturated solutions support the authors' assumption of the existence of space-lattice fragments in "fresh" solutions and fused masses (A., 1922, ii, 264). J. S. C.

Isomorphism of the Molybdates of the Rare Earths with those of Calcium, Strontium, Barium, and Lead. F. ZAMBONINI and R. G. LEVI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 149—152).—In pairs of isomorphous salts, in which the substituent atoms have the same valency, the difference of molecular volume of the compounds, expressed as a percentage of the smaller molecular volume, has values between 40 and 50. For isomorphous pairs in which the substituent atoms have different valencies, the corresponding figure is about 150. The latter, however, give normal values if the volumes of equivalent weights of the compounds, instead of molecular volumes, are used in the calculation. The rule has been shown to apply also to mixed crystals. Extended to crystal structure, the rule implies that the unit cells of isomorphous pairs and of mixed crystals contain equivalent volumes of the component. An *X*-ray investigation of the crystal structure of the molybdates of calcium, strontium, barium, lead, lanthanum, praseodymium, neodymium, samarium, and of tervalent cerium has been made to establish this rule. F. G. T.

Isomorphism of Quadrivalent Uranium and Zirconium Compounds. L. FERNANDES (*Atti R. Accad. Lincei*, 1925, [vi], 2, 182—186; cf. this vol., ii, 748).—The compounds $Zr(SO_4)_2,4H_2O$ and $U(SO_4)_2,4H_2O$ are isomorphous, and form mixed crystals over the range 99·14—10·3% $Zr(SO_4)_2$. They are isomorphous also with the corresponding compounds of cerium and thorium. F. G. T.

Magnetic Quality in Crystals. J. FORREST (*Phil. Mag.*, 1925, [vi], **50**, 1009—1018).—The theory of the magnetic quality of crystals has been developed from the point of view of the magnetic potential energy in a homogeneous assemblage of equal magnetic doublets, and has been experimentally tested for about twenty different crystalline substances. The results are here summarised, the full theoretical discussion and experimental details being published later. The longitudinal and transverse components of the intensity of magnetisation produced by an external field of varying orientation, in circular plates cut in chosen planes from selected crystals, were measured. By comparison with the theoretical variations of internal field appropriate to the various possible lattices, the lattice arrangement of the centres of the doublets, *i.e.*, the magnetic lattice, was determined. In many cases, the solution is unique, but in others more than one lattice gives the actual relative positions of maxima and minima. For magnetite, iron crystals, the cubic alums, calcite, and some others, there is agreement between the magnetic lattice and the atomic lattice found by *X*-ray analysis. In other cases, *e.g.*, iron pyrites, cobaltite, fluorspar, etc., these do not correspond, unless the magnetic maxima and minima are interchanged. For potassium sulphate and ammonium sulphate more than one magnetic lattice gives the correct relative intensities, but that corresponding with the *X*-ray lattice best explains the behaviour of the crystal in the field. Possible explanations are suggested for the interchange of positions

of maxima and minima occurring in some cases, and for a constant effect found in the parallel component in all cases and not accounted for by the theory. The results of a theoretical investigation of the stability of the types of magnetic lattice met with are briefly summarised. A. B. M.

Constitution of Magnetic Iron. F. Gross (*Bol. Assoc. Brasil. Pharm.*, 1924, **5**, 216—223; from *Chem. Zentr.*, 1925, ii, 708).—Since ferroso-ferric oxide is the only magnetic oxide of iron, it is suggested that it contains the nucleus $\begin{matrix}Fe\\ ||\\ Fe\end{matrix}>Fe$. Magnetic properties are attributed to the presence in the molecule of atoms of differing valency, according to Ampère's cross-current theory of magnetism. G. W. R.

Recrystallisation Phenomena as Functions of the Crystal Growth after Hot Deformation. H. Hanemann (*Z. Metallk.*, 1925, **17**, 316—319).—For copper and steel, the curves showing the relation between the grain size and degree of deformation and between the temperature at which recrystallisation takes place and the deformation are in each case hyperbolas. The parameter of the grain size hyperbola for steel is a linear function of the recrystallisation temperature, whilst the curve of this relation for copper is a segment of a circle. If r is the radius of this circle, v the degree of deformation, φ^2 the grain size, and t the temperature of recrystallisation, then $2v\phi^2=(b\pm\sqrt{r^2-(t-c)^2})^2$ for copper and $2v\phi^2=a^2(t-t_R)^2$ for steel, where t_R is the minimum temperature at which recrystallisation takes place, and a, b, and c are constants. For steel t_R is 620° and for copper 235°. [Cf. *B.*, 1925, 925.] A. R. P.

Molecular Physics. I. Relationship between Elastic Limit and Atomic Concentration. P. Lasarev (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 1005—1006; from *Chem. Zentr.*, 1925, ii, 514).—The elastic limit of a metal is proportional to $N^{5/3}$, where N is the number of atoms per c.c. This relationship holds approximately for silver, gold, platinum, palladium, and iron, but is inapplicable to lead and copper. It has a theoretical basis if it be assumed that intermolecular force is proportional to atomic concentration, and a certain power, the same for all metals, of intermolecular distance. G. W. R.

Changes in the Conductivity of Coloured Films on Bleaching. N. Schtschodro (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 727—746; from *Chem. Zentr.*, 1925, ii, 521—522).—A platinum film deposited on a quartz plate was so treated as to leave two comb-shaped electrodes with teeth interlacing. A colouring matter was then fixed on the plate, by means of a collodion film. The colouring matters used were cyanine, pinaverdol, and pinachrome. A current was then passed between the electrodes and a condenser arranged in series, the potential of the condenser being measured by a quadrant electrometer. The rate of increase of potential of the condenser served as a measure of the conductivity of the film. Conductivity increased when the film was bleached

through being submitted to illumination. The effect ceased when bleaching was complete. Independently of the light effect the strength of current increased with the time on account (*a*) of polarisation, which gradually sinks to zero when the current is interrupted, (*b*) of irreversible changes produced in the film by the current. The light effect was independent of the potential used. The conductivity of the film increased with the duration of illumination according to a curve which was concave to the time axis. When the illumination was interrupted, the conductivity decreased according to a curve which is convex to the time axis. The increase in conductivity, L, under illumination could be represented by the equation $L=L_0+a(1-e^{-bJ})$, where L_0 is the conductivity in darkness, J the intensity of illumination, and a and b are constants. The effect on conductivity was greatest for that wave-length which is most absorbed by the dye used. The increase in conductivity was almost directly proportional to the absorption of light energy. G. W. R.

Plant for Liquefaction of Helium. Some Measurements made with the Aid of Liquid Helium. W. MEISSNER (*Physikal. Z.*, 1925, **26**, 689—694).—The paper contains a description of the liquefying apparatus, a discussion of certain physical properties of helium, and measurements of supra-conductivity at the temperature of liquid helium. The fraction total helium/liquid helium is denoted by ε. The value of ε calculated from Nernst's equation is negative and from the law of corresponding states is 0·06; the observed value is 0·2. Hence helium shows a very strong deviation from the law due to quantisation of translational energy. The author has examined the conductivity of various metals in order at a later date to decide whether supra-conductivity is a property of all metals in the pure state at a sufficiently low temperature. If $r=R_T/R_0$, where R_T is the resistance at $T°$ and R_0 that at 0°, for constantan wire r is 0·9569 at 4·21° Abs. and 0·9552 at 2·62° Abs.; for lead wire the value is already $< 1\times10^{-8}$ at 4·21° Abs.; for tin wire it is $7·89\times10^{-4}$ at 4·20° and $< 2\times10^{-8}$ at 3·61° Abs. A long series of measurements has been made on gold. The highest conductivity obtained corresponded with a value of $r=0·39\times10^{-3}$. Gold wire was altered by heating for 3½ hrs. at 350°. The treated wire showed a resistance one-tenth as great at the temperature of liquid helium as the original wire. A series of single crystal wires was also examined, with the result that a polycrystalline wire after being subjected to heat treatment exhibited the same values of r as the single crystal wires. This means that gap-resistance in the treated wire cannot occur between the single crystals in the polycrystalline mass. R. A. M.

Thermo-electric Power and the Hall Coefficient. C. W. HEAPS (*Phil. Mag.*, 1925, [vi], **50**, 1001—1009).—The effect of a magnetic field on the thermo-electric power of bismuth, antimony, graphite, and carbon has been measured and compared with the Hall coefficient for the same substances. The specimen to be

investigated was soldered across two parallel brass tubes, and placed between the poles of an electromagnet. Steam was passed through one tube and cold water through the other. The thermo-electric power was measured for different values of the magnetic field. The Hall coefficients for the same specimens of bismuth and graphite had previously been determined (*Physical Rev.*, 1918, [ii], **12**, 340). For the other substances, it was measured in the usual way by connecting the potentiometer to side arms on the specimen and sending a current through the latter, using the brass tubes as terminals. Theory requires a linear relation between $E_H - E_0$, the change in thermo-electric effect, and $\log R_H$, where R_H is the Hall coefficient. This relation is satisfied by the results for bismuth, and the slight deviation in the case of graphite can be attributed to experimental error. The change in thermo-electric power was different for transverse and longitudinal magnetic fields. The effects for antimony are very small, but the changes are in the right direction. For carbon no change in thermo-electric power was observed with the strongest field used, and R_H was constant within the limits of experimental error. The relation for ferromagnetic elements appears to be more complicated.

A. B. M.

Thermo-electric Effect in Single Crystal Zinc Wires. E. G. Linder (*Physical Rev.*, 1925, [ii], **26**, 486—490).—The ratio of thermo-*E.M.F.* to the temperature difference between the ends of the crystal is not linear, but increases more rapidly with the latter. For wires with the angle of orientation (between the vertical axis of the crystal and the axis of the wire) $\theta = 14°$ and $\theta = 86{\cdot}5°$ the *E.M.F.* (directed at the hot junction from the latter to the former) with $t = 250°$ is $6{\cdot}50 \times 10^{-4}$ volt.

A. A. E.

Thermal Conductivity and Thermo-electric Force of Single Metal Crystals. P. W. Bridgman (*Proc. Nat. Acad. Sci.*, 1925, **11**, 608—612).—The thermal conductivity at the ordinary temperature and the thermo-*E.M.F.* over the range from the ordinary temperature to 100° have been measured as a function of the orientation for single crystal rods of bismuth, zinc, cadmium, and tin. Within wide limits of experimental error, the thermal conductivities of the four metals have rotational symmetry about the axis and also the electrical resistance is an inverse linear function of the thermal conductivity. These results are in agreement with the deductions of Voigt. The generalised Wiedemann–Franz law does not hold for all directions in the crystals. In the thermo-*E.M.F.* the Thomson effect is directly proportional to the resistance, whilst, except with cadmium, no such relationship exists for the Peltier effect. The Thomson effect shows rotational symmetry, whilst the Peltier effect does not. Considerations of the internal Peltier effect lead to the assumption that an electron functions as a dipole and that when moving in different directions in the non-isotropic force-field of a crystal it assumes different orientations.

A. E. M.

Measurements on Small Tungsten Arcs. W. DE GROOT (*Physica*, 1925, **5**, 121—129).—Determination of the temperature (by radiation pyrometry) of the small spherical electrodes in a tungsten arc, combined with voltage and current measurement, permits verification of some theoretical considerations on the energy balance of the electrodes. The anode receives an amount of heat $U_a \geqq i\phi$; the cathode $U_k \leqq -i\phi + ne(V_i + fV)$; where i is the current, ϕ Richardson's constant, n the number of positive ions reaching the cathode, V_i ionisation potential, f a factor varying from $\frac{1}{2}$ to 1 and depending on the cathodic field concentration. Besides the obvious condition (if $V < 2V_i$) that $ne \leqq \frac{1}{2}i$, it can be expected that $ne < (U_k + i\phi)/(V_i + \frac{1}{2}V)$. In neon these relations were completely confirmed by the results; at low current values (high potential) the fraction mentioned approaches $\frac{1}{2}i$; in argon and mercury the ion current is slightly higher. The arc voltage, which converges to V_i at high current values in neon and in argon, approaches 15·2 V in mercury, far above V_i. Thomson's condition for an arc: voluntary electron emission of cathode $i - ne = i_R$, the thermionic electron stream, is satisfactorily borne out for neon and mercury; for argon the values of i_R are a little too low.

CHEMICAL ABSTRACTS.

Refractive Index of Air in the Visible Spectrum between 0° and 100°. A. PÉRARD (*J. Phys. Radium*, 1925, [vi], **6**, 217—227).—The index of refraction of air has been obtained by the observation of interference fringes in a vacuum and then in dry air free from carbon dioxide for five lines in the spectra of cadmium and mercury at temperatures varying between 0° and 100°. The refraction $(N-1)$ is nearly proportional to the pressure at 600 and 760 mm. The variation of the refractive index with temperature is given by $N_0 - 1/(1+\alpha\theta) = N_\theta - 1$, where N_0 and N_θ are the indices at 0° and θ°, respectively, and α is a constant, which does not appear to depend on the wave-length. The average value for α is 0·003716 ± 0·000007. The following are the most probable values:

λ in μ.	0·4358	0·5461	0·5780	0·5086	0·6438
$(N_0 - 1) \cdot 10^6$	296·68	293·34	292·73	294·21	291·77

The following general formula is valid for pressures up to 1 atm., temperatures 0—100°, and wave-lengths in the visible $(N-1) \cdot 10^6 = (288{\cdot}02 + 1{\cdot}478/\lambda^2 + 0{\cdot}0316/\lambda^4)h(1 + \beta h)/760(1 + 760\beta) \cdot 1/(1 + 0{\cdot}003716\,\theta)$, where λ is the wave-length in μ, h is the pressure in mm. The value of β is small and may be neglected. A list of previous determinations and numerical results is given. R. A. M.

Optical Properties of Ethylenic Isomerides. J. ERRERA and V. HENRI (*Compt. rend.*, 1925, **181**, 548—550; cf. A., 1913, ii, 815).—The ultra-violet absorptive power of *trans* isomerides is greater than that shown by the *cis* forms. Similarly the refraction for the sodium *D*-line is higher for the more strongly absorbing isomeride. The differences in extinction coefficient increase with decreasing wave-length. The data include molecular refractions

for *cis*- and *trans*-dichloroethylenes (20·25, 20·56), bromoethylethylenes (27·8, 27·9), bromomethylethylenes (27·8, 27·85), chloroiodoethylenes (28·6, 29·5), maleic and fumaric esters (42·23, 42·9), methyl citraconate and mesaconate (37·2, 38), *iso*crotono- and crotono-nitriles (20·5, 20·7), *iso*crotonic, m. p. 15·5°, and crotonic, m. p. 72°, acids (21·4, 22·85). The absorption spectra for the first four pairs of isomerides are recorded and generally the ratio $\epsilon_{trans}/\epsilon_{cis}$ is 1·0—1·5. The work enables the solid crotonic acid and its corresponding nitrile to be classified as *trans* isomerides.

R. A. M.

Metastability of Matter and Physical Constants. E. COHEN (*Z. Elektrochem.*, 1925, **31**, 539).—Attention is directed to the desirability of taking possibilities of monotropic or enantiotropic diversity into account in laying down the physical constants of solids.

W. A. C.

Specific Heat of an Elastic Gyroscopic Model of the Hydrogen Molecule. J. H. VAN VLECK (*Physical Rev.*, 1924, [ii], **23**, 308).—Even when the vibrational degree of freedom is considered, the specific heats of the Born model and the author's non-gyroscopic model of the hydrogen molecule are almost identical if in each case the probability is taken proportional to the total angular momentum. The Born model is in agreement with specific heat observations up to 2000° Abs., provided the moment of inertia and vibrational frequency are $1{\cdot}98\times10^{-41}$ g.cm.^{2} and $1{\cdot}46\times10^{-14}$ per sec., respectively.

A. A. E.

Specific Heat of Liquids according to the Theory of Corresponding States. E. FOA (*Atti R. Accad. Sci. Torino*, 1925, **60**, 160—166).—Theoretical. By combining thermodynamic relationships with the principle of corresponding states it is deduced that, at the same reduced temperature, the difference between the molar heat capacity, C_l, of a substance as a liquid and its molar heat capacity at constant pressure, C_p, when in the condition of a perfect gas, is the same for all substances which conform to the principle of corresponding states. This relationship has been tested for water, ammonia, carbon dioxide, and sulphur dioxide at a series of reduced temperatures between $\theta=0{\cdot}5$ and $\theta=0{\cdot}95$, and is found to be approximately valid. The value of C_l-C_p rises from 9·7 at $\theta=0{\cdot}5$ to about 23·0 at $\theta=0{\cdot}95$. For the reduced temperature $\theta=0{\cdot}6$, the relation is satisfied by chloroform, ethyl ether, acetone, and benzene, the value of C_l-C_p averaging 11·9.

F. G. T.

Theory of the Specific Heats of Electrolytes. F. ZWICKY (*Physikal. Z.*, 1925, **26**, 664—665).—A solution of n mols. of a non-electrolyte such as sugar in n_0 mols. of water (specific heat c_0) shows a specific heat given by $C=n_0c_0+nc$, where c is the specific heat of 1 mol. of the non-electrolyte in the solid state. Thus C is always greater than n_0C_0, in contradistinction to the view that for electrolytes C is generally less than n_0c_0. The electric charges exert a two-fold influence. The electric work A_e given by $e^2(D-1)/2aD$ (D is dielectric constant of water, a ionic radius) is

necessary to annul electric polarisation of water. The work A_x, equal to the negative work of compression, is required to counteract the pressure effect of the charges. The free energy f of 1 mol. of electrolyte solution will then be given by $f=f_0-A_e-A_x$, where f_0 is the value for a non-electrolyte. The energy of the electrolyte solution is then $U=f-T\delta f/\delta T$ and $C_v=(\delta U/\delta T)_v$. The smallness of the specific heat of an electrolytic solution is due much more to the A_x than to the A_e factor.

The foregoing may be tested by using the dipolar moment of water as an unknown constant, and the relation $\delta C_p/\delta T=-T\delta^2 v/\delta T^2$ for calculating the specific heat of water at increased pressures from measurements of specific volume at high pressures. Good agreement with experiment is obtained; the data, however, are not given in this preliminary paper. The reasoning may be extended to other physical properties of electrolytes with the proviso that the Debye–Hückel theory must be introduced as occasion requires.

R. A. M.

Errors Introduced in certain Thermochemical Data and the Correction Coefficients of these Data. W. Swientoslawski (*J. Chim. physique*, 1925, **22**, 391—394).—Mainly introductory to following papers. The systematic errors which occur in determinations of heats of combustion are tabulated. The majority of previous investigations contain a systematic error arising from the acceptance of the specific heat of water given by Regnault (error +0·13%) and neglect of the correction of the thermometer to the hydrogen scale (0·30% error). The chief of other errors lies in the determination of the constant for the calorimetric bomb. Berthelot's method is discussed. The correction coefficient for given data is evaluated by comparing the heats of combustion, A_1, A_2, etc., of several substances as found with freshly determined values A_1', A_2', etc. (benzoic acid, 6324 Cal. at 15° for 1 g. in air is taken as standard). The mean value of the ratios $A_1':A_1$, $A_2':A_2$, etc. is the correction coefficient to be applied. L. S. T.

Correction of the Thermochemical Data of P. Lemoult. W. Swientoslawski and M. Popov (*J. Chim. physique*, 1925, **22**, 395—398; cf. preceding abstract).—The correction coefficient for the data on heats of combustion by Lemoult has been evaluated from a redetermination of the figures for naphthalene, *p*-aminoazobenzene, and β-naphthylamine. The mean of three ratios gives 0·99489±0·01%. A table of uncorrected and corrected data for all substances investigated by Lemoult is given. L. S. T.

Correction of the Thermochemical Data of A. Valeur. W. Swientoslawski and (Mlle.) H. Starczevska (*J. Chim. physique*, 1925, **22**, 399—401; cf. preceding abstracts).—The coefficient of correction for the data of Valeur (A., 1901, i, 154) evaluated from the redetermined values of the heats of combustion of benzoquinone, β-naphthol, and anthraquinone, is 0·9974±0·01%. Corrected and uncorrected values of all substances examined are again given. L. S. T.

Simple Method for the Indirect Determination of Molecular Heats of Vaporisation. J. NARBUTT (*Z. Elektrochem.*, 1925, **31**, 511—512).—An apparatus for determining the molecular heat of vaporisation from the equation $\lambda=RT^2/p \cdot dp/dT$ is described. A water manometer is recommended as being as accurate as a mercury instrument and more easily made. The error in the values obtained by this method is less than 0·2%. N. H. H.

Latent Heat of Fusion of Camphor. N. N. EFREMOV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 765—776; from *Chem. Zentr.*, 1925, ii, 524).—The latent heat of fusion of camphor calculated from the freezing-point depression with different compounds is 8·39 cal./g. G. W. R.

Heat of Dissociation of Calcium Carbonate and the Entropy of Carbon Dioxide. H. L. J. BÄCKSTRÖM (*J. Amer. Chem. Soc.*, 1925, **47**, 2443—2449).—The heat of dissociation of calcite at 25° has been obtained from the heat of solution of calcite in hydrochloric acid and the heat of solution of calcium oxide in the acid; the value obtained is 42,600±200 cal./mol. On the basis of this value a free energy equation for the reaction $CaCO_3=CaO+CO_2$ has been derived, which represents the dissociation pressure measurements within limits of error. The entropy of carbon dioxide was found to be 50·85 units, which is in good agreement with values obtained from other sources. W. T.

Thermochemical Researches on the Oximes. IV. Acetaldoxime. (MLLE.) A. DORABIALSKA (*Rocz. Chem.*, 1925, **5**, 386—394; cf. A., 1922, ii, 548; 1924, i, 646).—The heats of neutralisation by sodium hydroxide of various preparations of acetaldoxime fall into two series, one varying about 4·6 cal., the other about 3·6 cal. It is hence deduced that ordinary preparations of acetaldoxime are mixtures of two unstable stereoisomerides of varying composition. The heat of transformation of the α- into the β-isomeride is about −2 cal. R. T.

White and Black Diamonds and their Relation to [other Forms of] Carbon. W. A. ROTH and W. NAESER (*Z. Elektrochem.*, 1925, **31**, 461—466).—The heats of combustion of different forms of carbon have been measured, with the following results: β-graphite, 7856±1; α-graphite, 7832±1; white diamond, 7873±4; black diamond (carbonado), 7884±2 cal./g. The results of Berthelot and Petit (*Ann. Chim. Phys.*, 1889, **18**, 80), which showed a lower heat of combustion (and therefore a greater stability) for white diamond at the ordinary temperature than for graphite, are thus refuted. Several different forms of natural and artificial graphite were measured. The α-form is that stable at higher pressures. The high value for carbonado is explained by the assumption that it consists of normal crystals of white diamond permeated with amorphous carbon, the heat of combustion of which is about 8060. This is in general agreement with the *X*-ray work of Gerlach (A., 1924, ii, 753). N. H. H.

Density and Temperature. V. W. HERZ (*Z. Elektrochem.*, 1925, **31**, 512—514; cf. A., 1924, ii, 524).—From the consideration of a large number of substances cited, it is shown that the temperature, expressed as a fraction of the critical temperature (both in absolute units), at which the density in the liquid state bears any given relation to that of the saturated vapour, is very nearly the same for all substances. Other temperature–density relationships connected with the above are demonstrated. N. H. H.

Density of Beryllium Halides. C. MESSERKNECHT and W. BILTZ (*Z. anorg. Chem.*, 1925, **148**, 152—156).—The following data are recorded: beryllium chloride, d_4^{25} 1·901; bromide, d_4^{25} 3·465; iodide, d_4^{25} 4·325. The density of the chloride is in agreement with the value obtained by Hönigschmid and Birckenbach (A., 1922, ii, 214). J. S. C.

Additivity of Boiling Points. J. J. VAN LAAR (*Physica*, 1925, **5**, 130—134).—Objection is raised to the use of $\sqrt{a}$ values calculated from measurements of the b. p. (cf. van Arkel and de Boer, this vol., ii, 734, 758) instead of the critical point; the b. p. is not a "corresponding" temperature and may give untrustworthy $\sqrt{a}$ values. The use of methane and carbon tetrachloride values happens to be rather unfortunate, since these substances show large discrepancies from the rules originally given.

CHEMICAL ABSTRACTS.

Additive Properties of Boiling Points. II. A. E. VAN ARKEL and J. H. DE BOER (*Physica*, 1925, **5**, 134—141; cf. this vol., ii, 734, 758, and preceding abstract).—For many organic halogen compounds, particularly methyl halides, it is a sufficient condition for the additivity of the b. p. that $\sqrt{a_x}/b_x$ has the same value for every halogen; this leads to a b. p. formula $T_s=K(\Sigma V-V_c)^2/\Sigma V=K_2(\Sigma\sqrt{a_x})^2/\Sigma V$ (V is the Kopp molecular volume). If this equation is applied to ethane compounds, K is found to have a lower value; this may be due to a mutual screening effect of the halogen atoms (X), with a consequent decrease of $\sqrt{a}$. The authors express this effect in an empirical screening coefficient to be subtracted from $\sqrt{a}$. Values of the b. p. of the pure halogens and of iodine monochloride and monobromide calculated in this manner agree well with the facts. CHEMICAL ABSTRACTS.

Value of $\sqrt{a}$ Calculated from the Vapour Tensions of Alkali Metals and Halides in Relation to the Additive Nature of this Quantity. J. J. VAN LAAR (*Z. anorg. Chem.*, 1925, **148**, 235—255; cf. this vol., ii, 950).—From existing data, the vapour-pressure equations of the type, $\log p=-A/T-B\log T+C$, are derived for the alkali metals and halides, the value of B being practically zero in the case of the salts. From the values of A, the magnitude of the quantity a_0 in the author's equation of state is calculable. The value of $\sqrt{a_0}$ for the halides is approximately

the sum of the corresponding values for the metal and halogen concerned. J. S. C.

Vapour Pressure of Sodium. W. H. RODEBUSH and T. DE VRIES (*J. Amer. Chem. Soc.*, 1925, **47**, 2488—2493).—The vapour pressure has been found from the weight of vapour passing through a small opening in a definite time at constant temperature, and has been determined over the range 181·8—597°. The following equation holds for the vapour pressure from 180° to the b. p.: $\log p = -5922/T - 1{\cdot}6184 \log T + 12{\cdot}9605$. The entropy of sodium vapour at 298° Abs. and 1 atm. is calculated to be $35{\cdot}7 \pm 0{\cdot}5$ units. W. T.

Kinetic Theory of Vaporisation. II. S. C. BRADFORD (*Phil. Mag.*, 1925, [vi], **50**, 1147—1158; cf. this vol., ii, 26).—The equilibrium between liquid and vapour is considered on the basis of the kinetic theory, and the following expression for the vapour pressure is deduced: $p = 81{\cdot}84 T\lambda e^{-9{\cdot}656 S v A^{2/3}/T\delta'\lambda^3}/A\Phi$, where λ is the ratio of the average velocity of the molecules in the liquid to that in the vapour, A is the factor giving the state of aggregation of the liquid, Φ the co-volume of the liquid, S the surface tension, v the volume of a mole of the liquid, and $\delta' \times 10^{-8}$ the nearest distance of approach of the centres of the molecules in the liquid; λ is calculated from data for a few almost unassociated liquids and shown to be a function of density and temperature only. The formula is applied to a number of liquids at different temperatures and gives good agreement between calculated and observed values. A. B. M.

Existence of Liquid Racemates. F. D. AGUIRRECHE (*Anal. Fis. Quim.*, 1925, **23**, 409—418).—The existence of racemic compounds in the liquid state implies molecular association, and may therefore be best studied by means of those properties which are affected by association. The principal physical properties of ethyl *d*-tartrate and ethyl *r*-tartrate are compared. The viscosity of the latter is less than that of the former. The differences in density, refractive index, and surface tension are insignificant. G. W. R.

Theory of State of Matter. II. Internal Pressure, Co-volume, and Association. F. SCHUSTER (*Ber.*, 1925, **58**, [*B*], 2183—2186; cf. this vol., ii, 951).—Expressions are deduced for the internal pressure and molecular co-volume of substances and the constants are calculated for an extended series of inorganic and organic compounds. The factor of association at the b. p. under normal pressure is calculated for many substances, the results being in agreement with the data obtained by other methods. H. W.

Determination of Surface Tension from Photographic Records of the Formation of Drops. T. MOLODYI and F. PAVLOV (*Bull. Acad. Sci. St. Pétersbourg*, 1920, **13**, 241—258; from *Chem. Zentr.*, 1925, ii, 750).—The formation of drops of a liquid

in an atmosphere of its own vapour was followed kinematographically. From the records the critical value for the diameter of the "neck" of a forming drop at the point of destruction of equilibrium was obtained and the surface tension was calculated from Tate's formula $\pi d\gamma = P$, where d is the critical diameter, γ the surface tension, and P the weight of the drop. The following values were obtained: water at 14·9°, 7·24—7·46; at 16·5°, 7·29—7·38; aniline at 16·1°, 4·31—4·42; *m*-xylene at 14·7°, 2·76—2·89; benzene at 14·7°, 2·97—3·05; ethyl alcohol at 15°, 2·39—2·47. G. W. R.

Viscosity of Liquids under Pressure. P. W. Bridgman (*Proc. Nat. Acad. Sci.*, 1925, **11**, 603—606).—The relative viscosities of forty-three liquids, including water, have been measured at 30° and 75° under pressures from atmospheric to 12,000 kg. per sq. cm. The values for water have been determined also at 0° and 10·3°. At low temperatures and pressures, the viscosity of water decreases with increasing pressure, passing through a pressure minimum, and then increases. With increasing temperature this minimum flattens and disappears finally at about 25°, above which temperature the viscosity increases continuously with increasing pressure. The viscosity of the other liquids increases uniformly with increasing pressure. The increase under a pressure of 12,000 kg. per sq. cm. varies from 10-fold for methyl alcohol to at least 10^7-fold for eugenol. The temperature coefficient of viscosity increases with increasing pressure. The results are not in accord with the theories of Phillips (*ibid.*, 1921, **7**, 172) and Brillouin (*J. Phys. Radium*, 1922, [vi], **3**, 326, 362), and since the pressure effects are greatest with substances with more complicated molecules, it is suggested that there is an interlocking of these which the theories neglect.

A. E. M.

Diffusion of Helium through Different Glasses. C. C. Van Voorhis (*Physical Rev.*, 1924, [ii], **23**, 557).—Measurements were made between 200° and 500°. Increase of silica and boron trioxide increases the permeability; increase of basic oxides decreases the permeability, but oxides only slightly acidic or basic, *e.g.*, lead oxide and alumina, have scarcely any effect. A. A. E.

General Theory of Solvent Systems. A. F. O. Germann (*J. Amer. Chem. Soc.*, 1925, **47**, 2461—2468).—Based on a study of the analogy between reactions in water and in carbonyl chloride solutions, a general theory of acids, bases, and salts in their relation to a parent solvent has been outlined, and its application to sulphuryl chloride, selenium oxychloride, and thionyl chloride as solvents is discussed. W. T.

Vapour Pressures and Miscibilities of Binary Liquid Mixtures. K. F. Herzfeld (*Z. Elektrochem.*, 1925, **31**, 536—539).—By a simplification of van der Waals' method of treating liquid mixtures, the following expression for the energy of a mixture is arrived at: $U = -\lambda_A \cdot x - \lambda_B(1-x) + \lambda_{AB}x(1-x)$, where λ_A and λ_B are the latent heats of the components and $\lambda_{AB}x(1-x)$ is the heat

of mixing at the molecular concentration x. It would follow that the same heat is evolved when little of component A is dissolved in much of component B as *vice versa*. A formula for the ratio of partial pressures in the vapour phase is developed, according to which the vapour-pressure curve is convex or concave upwards, according as the heat of mixing is negative or positive. All pairs of liquids have an azeotropic mixture below the temperature given by $T=\lambda/R \log_e p_A/p_B$, where λ is the heat of mixing; the temperature range in which azeotropy can no longer exist may, however, be out of practical bounds. The upper critical temperature of miscibility may be expressed by the formula $T_K=-\lambda(2R)$, from which the molecular ratio of components should always be 1 : 1 at the critical point; this is approximately confirmed by the available data. W. A. C.

Selective Solvent Action. IV. Cryoscopy in Mixed Solvents. R. WRIGHT (*J. Chem. Soc.*, 1925, **127**, 2234—2238; cf. T., 1922, **121**, 2252; 1923, **123**, 2493; A., 1924, ii, 838; 1898, ii, 17).—The addition to the mixed solvents nicotine–water, alcohol–benzene, acetone–benzene, and alcohol–ethylene dibromide of a substance soluble only in one constituent raises the freezing point of the other constituent. It appears that a semi-solute forms solvates with the constituent in which it is soluble, and thus raises the freezing point and vapour pressure of the one in which it is insoluble. When the added substance is also soluble to a slight extent in the second constituent, the freezing point of this constituent is first raised and then lowered as the concentration of the solute is increased. If the solute is completely miscible with each constituent of a 50% mixture, then the effect on the freezing point indicates which constituent has the greater attraction for it. Thus the lower members of the aliphatic alcohol series show a greater attraction for ethyl alcohol than for benzene, whereas the higher alcohols and aromatic compounds have a greater attraction for benzene. A. G.

Theory of [Solid] Solutions. P. LASAREV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 207—214; from *Chem. Zentr.*, 1925, ii, 515).—The author calculates the force exerted on a molecule lying on the interface between two phases by the molecules of each phase. The force acting between any two molecules is an unknown but constant function of the distance between them, and consists of two terms, of which one is proportional to, and the other independent of, the dielectric constant of the medium. Since a solid substance attracts its superficial molecules with a force proportional to its atomic concentration, and as the latter is proportional to the hardness, the solubility must vary inversely with hardness. G. W. R.

Nature and Constitution of Glass. W. E. S. TURNER (*J. Soc. Glass Tech.*, 1925, **9**, 147—166).—Investigation of the constitution of glass in the light of published physical and chemical data gives indeterminate results. Molecular association is suggested by surface-

tension determinations and by the analogy of certain properties with those of other liquids. On the other hand, relationships between percentage oxide composition, various physical properties, and chemical durability suggest a state of dissociation. Silica probably enters into loose combination with the silicates present and it may form a sponge or network soaked in silicates or their products of dissociation. [Cf. *B.*, 1925, 920.] A. COUSEN.

Constitution of Glass. F. ECKERT (*J. Soc. Glass Tech.*, 1925, **9**, 267—272).—The constitution of the final product is dependent on the previous heat treatment of the glass, that is, on the initial state and on the time which the material has had to adjust itself to the temperature range, since the velocity of internal reactions (molecular interaction, dissociation, etc.) is a function of the temperature. Recent determinations of optical constants and density of glasses have indicated variations of properties determined by the past history of the glass. Similar changes are shown in the viscosity and in hardening phenomena observed with rapidly cooled glass. A. COUSEN.

Constitution and Density of Glass. A. Q. TOOL and E. E. HILL (*J. Soc. Glass Tech.*, 1925, **9**, 185—207).—The hypothesis is advanced that when glass is cooled under proper conditions, certain practically reversible processes occur, involving some or all of the molecules and so preventing other possible processes often associated with cooling, such as segregation, crystallisation, etc. The character and rate of the processes are determined by the temperature of the glass, and when the latter is maintained at any given value the reactions proceed until equilibrium is attained. In proof of the theory, samples of flint and of pyrex glass when heated to various temperatures in the range 360—750° and maintained at these temperatures until equilibrium is attained, were found on cooling in air to have varying densities according to the temperature of treatment, although strain was absent in each case. Preliminary tests have shown that the change in the refractive index of the flint glass is approximately proportional to that of the density. [Cf. *B.*, 1925, 920.] A. COUSEN.

Glasses as Supercooled Liquids. G. TAMMANN (*J. Soc. Glass Tech.*, 1925, **9**, 166—185).—Conditions governing the supercooling of liquids are (1) the number of crystallisation centres in unit volume, which, with easily fusible substances, generally reach a maximum at about 100° supercooling, and (2) the rate of crystallisation, which, when not exceeding 3—4 mm. per min., generally reaches a maximum at about 30° supercooling. The formation of crystal centres is subject to the laws of probability. Liquids are mobile for about 90° supercooling, then become viscous, and at 20° lower brittle and hard. At normal pressures glasses are unstable, but the growth of crystal centres is so slow as to be practically negligible. The temperature of maximum crystallisation centre formation is influenced little by impurities, but the actual number

of centres formed is greatly affected. Supercooling conditions for mixed salts and for glasses are considered. [Cf. *B.*, 1925, 920.]

A. COUSEN.

Viscosity of Glass. V. H. STOTT (*J. Soc. Glass Tech.*, 1925, **9**, 207—225).—The log. viscosity–temperature curve of a soft laboratory glass gave a point of inflexion at about 500°. The heating curve indicated heat absorption beginning at 535°. Application of the Michelson load–displacement formula also indicated a state of discontinuity between 486° and 529°. All these phenomena are probably caused by the same change of constitution. The extended form of the Le Chatelier viscosity–temperature equation for glass, namely, $\log . \log \eta/\eta_0 = Mt + P$, is not capable of general application. [Cf. *B.*, 1925, 921.] A. COUSEN.

X-Ray Diffraction Measurements on Some Soda–Lime–Silica Glasses. R. W. G. WYCKOFF and G. W. MOREY (*J. Soc. Glass Tech.*, 1925, **9**, 256—257).—Glasses crystallising with greatest difficulty give broad *X*-ray powder bands; easily crystallisable glasses give lines when the glasses contain a considerable proportion of readily crystallisable components. [Cf. *B.*, 1925, 921.]

A. COUSEN.

Cause of Inverse Segregation [in Alloys]. G. MASING (*Z. Metallk.*, 1925, **17**, 251—257).—The conditions for the occurrence of inverse segregation in an alloy are that there must be a tendency for the primary crystals to grow in a dendritic form, a tendency for the formation of mixed crystals having zones of differing composition, and a considerable difference in the composition of the crystals first formed and the remaining liquid (cf. Bauer and Arndt, *ibid.*, 1921, **13**, 497). Iokibe (*B.*, 1924, 297) has shown that inverse segregation occurs in zinc–copper alloys in which zinc predominates, and that such alloys expand on solidification. This work has been confirmed, and similar observations on certain copper–tin and aluminium–copper alloys show that expansion on solidification is the primary cause of inverse segregation, whilst a tendency to supercooling is a secondary cause. Simple contraction on cooling is shown mathematically to have no influence on inverse segregation. [Cf. *B.*, Dec. 24th.] A. R. P.

Chemical Resistance of Metals and Alloys, especially Those Containing Molybdenum. W. GUERTLER and T. LIEPUS (*Z. Metallk.*, 1925, **17**, 310—315).—The resistance of more than one hundred alloys containing two or more of the metals cobalt, nickel, iron, chromium, manganese, tungsten, molybdenum, copper, silicon, tin, and aluminium, against attack by acid, alkaline, and neutral salt solutions has been examined. Whilst a considerable number of the alloys, especially those containing nickel, cobalt, and molybdenum or iron, are very resistant to alkaline reagents, it is found that only certain alloys of the nickel, chromium, and cobalt or molybdenum series resist nitric acid. The most resistant alloys to hydrochloric acid consist of nickel with silicon and molybdenum,

nickel–cobalt–molybdenum, and cobalt–manganese–molybdenum. Nickel containing small amounts of molybdenum with or without aluminium and chromium is the only metal that is not corroded by mercuric chloride solutions. [Cf. *B.*, 1925, 925.] A. R. P.

Solubilities of the Phosphates of Zirconium and Hafnium. G. HEVESY and K. KIMURA (*J. Amer. Chem. Soc.*, 1925, **47**, 2540—2544).—The composition of zirconium and hafnium phosphate precipitated from 6*N*-hydrochloric acid corresponds with $MO(H_2PO_4)_2$. On ignition, the precipitates lose 2 mols. of water. The solubility of the zirconium phosphate in 6*N*-hydrochloric acid is 0·00012 and that of the hafnium phosphate 0·00009 mol. per litre. In 10*N*-hydrochloric acid the values are 0·00023 and 0·00012. The importance of the phosphate precipitation for the detection and determination of the two elements is discussed. W. T.

Solubility of Ammonium Salts in Presence of Ammonia. E. WEITZ (*Z. Elektrochem.*, 1925, **31**, 546—549).—Ammonium salts of monobasic acids are in general more soluble in ammonia than in water alone; those of polybasic acids are less soluble, and may be salted out of solution by passing in ammonia gas. The difference is attributed to the formation of soluble ammonia additive compounds by monobasic salts, but not by polybasic salts. Fluoride, iodate, periodate, and borate behave as if the acids were polybasic, probably owing to polymerisation. On the other hand, the persulphate and the dithionate show the same effect as monobasic salts, possibly because the substituted hydrogen atoms are on two distinct branches of the structural molecule. Ammonium *iso*phthalate and benzene-*m*-disulphonate also stand out as exceptions, although their *o*- and *p*-isomerides follow the polybasic rule. W. A. C.

Influence of Electrolytes on the Solubilities of Some Organic Acids. N. A. YAJNIK, M. P. JAIN, and D. NATH (*J. Indian Chem. Soc.*, 1925, **2**, 115—128).—The influence of several electrolytes and of their respective anions and cations on the solubility of *o*-, *m*-, and *p*-nitrobenzoic, *p*-amino- and *p*-hydroxybenzenesulphonic acids in water, at varying concentrations and temperatures, has been studied. The results obtained for the sulphates, nitrates, and chlorides of ammonium, sodium, potassium, calcium, strontium, and barium at 25°, 35°, and 45° in the case of the nitrobenzoic acids, and 20°, 30°, and 40° in the case of the sulphonic acids, are tabulated and discussed. With increase in the concentration of the electrolyte, the solubility of the *o*- and *p*-acids first increases, reaches a maximum (that of the *para* isomeride being greater than that of the *ortho*), and then decreases again, whilst in the case of the *m*-acids an initial rapid decrease in the solubility is followed by a more slow and regular decrease. With rise of temperature, the influence of the nitrates and chlorides of the alkali metals decreases, whilst that of the corresponding salts of the alkaline-earth metals increases. The influence of the cations increases in the order given above, whilst the influence of the anions

varies in the order $NO_3' > Cl' > SO_4''$. The nature of the acid also affects the results, the solubility of the stronger acids being influenced to a greater extent than that of the weaker, the nitro-acids more than the amino-acids, which in turn are more influenced than the hydroxy-acids. J. W. B.

Cause of Surface Tension. E. H. KENNARD (*Nature*, 1925, **116**, 643).—Polemical. A. A. E.

Variation in the Surface Tension of Solutions as a Function of the Concentration. J. SCHECHTMANN (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 657—662; from *Chem. Zentr.*, 1925, ii, 530—531).—The surface tension of solutions of naphthalene in benzene, as determined by capillary rise is represented by $\gamma = 28{\cdot}65 + 1{\cdot}1079c$ where γ is the surface tension at 20° and c the molar concentration. The temperature coefficient $1/\gamma \cdot d\gamma/dt$ at 20° is 0·00453. Density and concentration are connected by the relationship $d = 0{\cdot}8787 + c/51{\cdot}654$ at 20°. G. W. R.

Orientation of Molecules in the Surfaces of Liquids. W. D. HARKINS (*2nd Colloid Symposium Monograph*, 1925, 141—173).—A consideration of the development of the concept of interfacial orientation, the wedge theory of emulsions, molecular orientation as exhibited by the relations between the energy of surface formation and that of vaporisation, energy of thermal emission, adsorption and distribution of substances between different phases, relations at surfaces and interfaces, and adsorption at interfaces.
CHEMICAL ABSTRACTS.

Unimolecular Soap Films in Emulsions. W. RIEMAN 3RD and P. A. VAN DER MEULEN (*J. Amer. Chem. Soc.*, 1925, **47**, 2507—2514).—Emulsions of the oil-in-water type, containing a solution of phenol in toluene as the internal phase and sodium oleate as the emulsifying agent, have been studied (cf. A., 1924, ii, 389). The average area of interface covered per mol. of soap depends primarily on the concentration of soap in the external phase of the dilute emulsion. Most of the phenol passes from the toluene to the water layer and may partly displace the soap in the interface. The results are in agreement with the hypothesis that the protective film is composed of a single layer of oriented molecules. With soap concentrations up to 0·01*M*, an average area of 17 Å.^{2} per soap mol. was found, and it is suggested that this may be the average cross-sectional area of the hydrocarbon chain of oleic acid. Soaps of stearic acid are not sufficiently soluble to give satisfactory emulsions. W. T.

Multimolecular and Unimolecular Films. W. D. HARKINS and J. W. MORGAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 637—643).—Measurements of the variations of compressibility with change in area have been made for a number of surface films on water and on aqueous salt solutions, principally calcium chloride. The results are discussed in connexion with the preceding work (A., 1923, ii,

127). In general, multimolecular films are much weaker than unimolecular ones. Mixtures of two substances, each of which gives a unimblecular film when alone, give rise to unimolecular films. When mixed films composed of two substances one of which is normally unimolecular and the other multimolecular are compressed, the substance giving the multimolecular film slides over the other, leaving a unimolecular film of the latter beneath it.

A. E. M.

Adsorption Forces and their Electrical Nature. II. The Electrical Moment of the Adsorbed Molecule and the Superficial Energy of the Adsorbent. B. Ilin (*Phil. Mag.*, 1925, [vi], **50**, 1144—1146; cf. A., 1924, ii, 663).—The electrical theory of adsorption leads to a relation between heat of adsorption and the electrical moment of the adsorbed molecules (τ), permitting calculation of the absolute value of the latter. This calculation is applied to Titov's results for the adsorption of gases by charcoal (τ varies from $4{\cdot}1\times10^{-19}$ for hydrogen to $20{\cdot}5\times10^{-19}$ for ethylene), and Langmuir's results for mica (τ varies from $3{\cdot}0\times10^{-19}$ for hydrogen to $15{\cdot}0\times10^{-19}$ for ethylene). These results are of the same order of magnitude as given by other methods. The data are shown to lead also to an approximate value of the surface energy of the solid adsorbent, giving for charcoal 1000 ergs/cm.^{2}

A. B. M.

Absorptive Power of Lipoid Mixtures. A. Schäfer (*Biochem. Z.*, 1925, **159**, 250—256).—The distribution of ferric thiocyanate between water and a second medium consisting of ether, benzene, oil, an ether–benzene mixture, or an ether–oil mixture indicates that the solvent power of the ether is diminished by the presence of either benzene or oil.

P. W. C.

Adsorption of Iodine by Starch. E. Angelescu and J. Mircescu (*Soc. Romana Stiinte, Bul. Chim.*, 1924, **27**, 59—64).—The adsorption of iodine by starch is independent of the concentration of potassium iodide between 2% and 15%, the general adsorption equation holding good within these limits. The constants of the equation: $C_{\text{starch}}=kC_{\text{I}}^{p}$ are $p=0{\cdot}166$ and $k=0{\cdot}27$. The fact that a rise in the concentration of the iodide increases the solubility of iodine but does not increase the amount adsorbed by starch is evidence in favour of the formation of a definite starch–iodine compound.

A. R. P.

Nature of Hydrolytic Adsorption with Reference to the Adsorption of Electrolytes and of Water. I. General and Theoretical Introduction. J. N. Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 191—224).—A theoretical paper in which the author develops his view regarding the distribution of ions in the Helmholtz double layer (cf. A., 1922, ii, 689) to account for hydrolytic adsorption in systems where acids and alkalis are liberated by the interaction of solutions of salts having a neutral reaction and insoluble substances which give no acid or alkaline extract with

water. Four simple types of reactions, attributable to the preferential adsorption of one ion by the adsorbent, are discussed, and a brief summary of the experimental evidence (to be published in detail later) in support of each type is given. The four types are (1) interaction between a neutral electrolyte and adsorbed acids of which the anion is primarily adsorbed; (2) interaction between a neutral electrolyte and adsorbed alkali of which the cation is primarily adsorbed; (3) generation of acids or alkalis during the precipitation of barium sulphate from neutral salt solutions; (4) adsorption of water and its constituent ions in their relation to hydrolytic adsorption. It is shown that when well-washed barium sulphate and other precipitates are left in contact with potassium chloride solution, the liquid develops an acid reaction, the acidity depending on the conditions under which adsorption takes place. The acidity developed in contact with pure water is almost negligible. In the precipitation of barium sulphate, if the potassium sulphate is in excess, the medium becomes alkaline (p_H 11), whilst with an excess of barium chloride it becomes acid (p_H 5). Theoretically possible types of interaction between adsorbed water molecules, its constituent ions, and ions in solution, are illustrated by the primary adsorption of anions by hydrated silica, which shows, in contact with water, a marked negative charge which is decreased by the addition of acids and increased by alkalis. In reference to the dependence of adsorption on the degree of hydration of a substance, it is shown that whilst the primarily adsorbed layer is probably only one molecule thick, the adsorbed water molecules which hydrate the surface form a layer several molecules in depth.

J. W. B.

Theory of Permeability of Membranes for Electrolytes. L. MICHAELIS (*J. Gen. Physiol.*, 1925, **8**, 33—59).—Experiments are described on the diffusion of electrolytes across membranes, such as apple skin, parchment-paper membrane, and dry collodion, including the measurement of the *E.M.F.* developed. The velocity of the anions is much reduced as compared with that of the cations, and in the case of membranes of collodion and apple skin there is practically complete impermeability to anions. The theory of the diffusion process is worked out in detail for the case where the velocities of the two ions across the membrane are different but finite, and also where the membrane is permeable to anion but impermeable to cation. The theoretical results are compared with those of experiment, and for univalent cations it is found that the order of the ionic mobilities through a collodion membrane is the same as in aqueous solution, but that the differences are very much increased. For example, the hydrogen ion has a mobility approximately 900 times that of lithium ion, whereas in aqueous solution it is only ten times as great. Further, it appears that the mobility of bivalent cations is very small and indefinite, whereas that of tervalent cations is of the same order as that of univalent cations. The mobility of anions, even of hydroxyl, appears to be exceedingly small, if not zero.

W. O. K.

Electrical Properties and Ionic Permeability of Membranes. III. Potential Differences at Parchment Membranes. A. FUJITA (*Biochem. Z.*, 1925, **159**, 370—378).—If two solutions containing different concentrations of the same electrolyte are separated from each other by a parchment membrane, the potential difference is not the same as when the two solutions are directly in contact. The change is such as would be brought about if the mobility of the anions had been diminished to a larger extent than that of the cations. For the cations the effect diminishes in general with rise in valency, but is very small in the case of hydrogen ions. For the anions the effect increases with rise in valency. H. D. K.

Cryoscopy of Solutions of Gases in Various Solvents. F. GARELLI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 120—124).—Cryoscopic observations on solutions of gases have shown their tendency to enter the solid phase (Garelli and Falciola, A., 1904, ii, 312). In the present work, the apparatus used is of the usual Beckmann type, but it is shut off from the atmosphere and provided with a side tube by which the gas-stream passes into the solvent. In benzene and dimethylaniline, acetylene dissolves in the form of simple molecules, the saturated solutions containing 0·744 g. and 0·737 g. per 100 g. of the respective solvents. The following solubilities, in grams of acetylene per 100 g. of solvent, are also obtained: in aniline, 0·800 g.; in *cyclo*hexane, 0·3107 g.; in nitrobenzene, 0·5537 g. In most solvents, nitrogen, carbon monoxide, and helium first produce very slight elevations of m. p. On expelling these gases, however, this higher value of the m. p. generally persists and, on resaturation, the m. p. is often depressed. It is therefore thought that the elevation is due to the removal by the gas-stream of slight impurities of the solvent (cf. Falciola, A., 1908, ii, 1015). In benzene, nitrogen ultimately gives a depression of 0·005° and nitric oxide one of 0·04°; on the assumption of simple molecules of solute, the latter corresponds with a concentration of 0·235 g./100 g. of benzene. In bromoform, nitrogen and nitric oxide ultimately give depressions of 0·005° and 0·025°, respectively; nitrogen in nitrobenzene depresses the m. p. by 0·005° and nitric oxide gives a depression of 0·135°, whence the concentration is 0·058 g./100 g. In *cyclo*hexane the depression caused by nitrogen is 0·005°, whilst nitric oxide gives 0·225°, the concentration thus being 0·337 g./100 g. In no case is it certain that helium produces a depression. The ultimate depression caused by carbon monoxide in benzene is 0·03°; according to Just's absorption coefficient, the depression should be 0·032°. In nitrobenzene, the ultimate depression is 0·025°; Just's value is 0·022°. Considering the high constant of bromoform, the depression of 0·02° in this solvent shows that carbon monoxide is practically insoluble. W. E. E.

Hydration of Ions. J. BABOROVSKY (*Chem. Listy*, 1925, **19**, 297—300).—Starting from the assumption that the hydrogen ion is attached to 1 mol. of water, the author deduces from the results of various investigators that the chlorine ion is combined with 6,

the sodium ion with 22—25, the potassium ion with 10, and the lithium ion with 35 mols. of water. A. R. P.

Uric Acid. III. Nature of the Hydrotropic Supersaturated Solution of Uric Acid. R. STERN (*Biochem. Z.*, 1925, **159**, 192—198).—Hydrotropically dissolved uric acid (in presence of "atophan") causes a rise in the concentration of hydrogen ions, this acid being dissociated to about the same extent as when present in true solution. The hydrotropic effect is based on the formation of loosely combined, dissociating compounds between "atophane" and uric acid (cf. this vol., ii, 34, 196, 504). P. W. C.

Electrolytes in Solutions of Low Dielectric Constant. P. GROSS and O. HALPERN (*Physikal. Z.*, 1925, **26**, 636—642).—From Debye and Hückel's mathematical development of the theory of inter-ionic forces in solution (A., 1923, ii, 459, 724; this vol., ii, 171), it can be shown that, for solutions of salts in liquids of low dielectric constant at low temperatures, the influence of the ions on osmotic effects may be not only small but even negative. The solute will thus appear to be associated, the apparent association increasing with the electrical conductivity. From a consideration of the thermodynamic equilibrium conditions, it is shown that the activity may increase with decreasing salt concentration, to a limit not of 1, but of ∞. This rapid change of activity with concentration should result in an increase of ionisation with increasing concentration giving anomalous concentration–conductivity curves which display maxima and minima. This phenomenon is comparable with the increase of ionisation of a weak electrolyte in aqueous solution by the addition of ions. If solvents with successively decreasing dielectric constants are considered, the concentration at which the minimum appears ought to become lower. All these deductions, which depend solely on the electrical effect postulated between the ions, are in qualitative agreement with experimental facts. M. S. B.

Colloidal Oxide of Manganese. A. ANARGYROS (*Compt. rend.*, 1925, **181**, 419—421).—Potassium permanganate in the presence of sodium protalbinate was reduced by means of sodium arsenite at 65—70°, giving a brown, colloidal solution which could be kept for more than a month. The amount of chlorine liberated from hydrochloric acid corresponded with the formula Mn_2O_3, but this does not exclude the possibility of a mixture of other oxides. The colloidal solution rapidly liberates oxygen from hydrogen peroxide, acting more rapidly in alkaline than in neutral solution. E. B. L.

Colloidal Kaolin. I. Properties. W. J. POPE and T. M. HAINES (*Lancet*, 1925, I, 1123—1124).—Kaolin which remained in aqueous suspension for a week was flocculated on the addition of 0·3% of hydrochloric acid or 1·3% of sodium chloride. It is a negative colloid and adsorbs iodine and basic dyes. CHEMICAL ABSTRACTS.

Colour of Colloidal Silver and Mercury. R. FEICK (*Ann. Physik*, 1925, [iv], **77**, 573—596).—The author has recalculated the absorption curves for silver hydrosol according to the theory of Mie (cf. *Ann. Physik*, 1908, [iv], **25**, 377; Müller, *ibid.*, 1911, [iv], **35**, 500). He concludes that this theory in its simplest form is not in agreement with the experimental results (cf. Zsigmondy, A., 1906, ii, 679; Schaum and Lang, A., 1921, ii, 506; Schaum and Marx, A., 1922, ii, 696). However, so far as it concerns the diffuse radiation of the silver particles it is in agreement with experiment; the conclusion that the absorption colour should be complementary to the true colour of the particles is also satisfied in this case. The extension of Mie's theory proposed by Gans (A., 1912, ii, 508; 1920, ii, 256; *Ann. Physik*, 1925, [iv], **76**, 29) explains some of the difficulties met with in the application of the simple theory, although the complicated phenomena met with in the colours of the photohalides are still unexplained. In this connexion, Weigert has pointed out that the older Maxwell–Garnett theory has a certain range of validity (*Z. Physik*, 1921, **5**, 410). The radiation and absorption of colloidal mercury are calculated from the results of Meyer (*Ann. Physik*, 1910, [iv], **31**, 1017), in the same way as for colloidal silver. The results are in agreement with experiment so far as can be seen from the data available, which are, however, only qualitative. The spectrometric results and the determination of the dispersity of the sols is difficult owing to their instability, but this work is proceeding. The author discusses the reasons why complete concordance between the calculated and the experimental results should not be expected. D. C. J.

Chemical Properties of Colloidal Starch Derivatives. SAMEC (*Compt. rend.*, 1925, **181**, 477—479; cf. A., 1921, ii, 707).—By heating to 120° and fractional electro-dialysis, electrolyte-free sols have been obtained from starch; these differ in the colour produced with iodine (red to blue), in mol. wt. (90,000—156,000), and in protective-colloid function. The colour produced with iodine appears to be independent of the presence of electrolytes, of the degree of dispersion, and of the protective-colloid properties. L. F. H.

Sols with Non-spherical Particles. H. FREUNDLICH (*2nd Colloid Symposium Monograph*, 1925, 46—56).—Vanadium pentoxide sol shows the Majorana phenomenon (double refraction in a magnetic field) and streaks when stirred; this is due to "dityndallism," which is consequent on the elongated shape of the particles—probably rod-like crystals. Other similar phenomena are discussed. CHEMICAL ABSTRACTS.

Determination of the Distribution of Size of Particles in Emulsions. A. J. STAMM (*2nd Colloid Symposium Monograph*, 1925, 70—79).—The principle of the method is similar to that of Wiegner (*Landw. Versuchs-Stat.*, 1918, **91**, 41) and of Ostwald and Hahn (A., 1922, ii, 205), but so modified and improved that emulsions with a rising dispersed phase may be studied, *e.g.*, benzene in

soap solutions. The distribution curves showing particle sizes were obtained from the experimentally determined accumulation curves by Svedberg's method, and duplicate determinations check fairly well. Changes in concentration alter the maximum but slightly. Potassium oleate tends to give emulsions with larger drops than potassium palmitate, in harmony with the wedge theory. Homogenisation increased dispersity with soaps, but broke emulsions with gelatin or fatty acids as stabilisers. CHEMICAL ABSTRACTS.

Oriented Wedge Theory of Emulsions. W. D. HARKINS and N. BEEMAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 631—637).—A continuation of previous work by Harkins and others. The size distribution of oil particles in an emulsion is the same, within experimental error, whether sodium, potassium, or cæsium soaps are used as emulsifying agents. When water-in-oil emulsions are produced by soaps of bi- or ter-valent metals, the distribution of the water particles is the same as that of the oil particles in the former cases. These results are not in agreement with the oriented wedge theory of Langmuir, for, according to this, the size of the particles should decrease with increasing size of the positive radical in the soap. If soaps are regarded as completely ionised there is little ground for supposing that the shape of the emulsifying molecules should affect the size of the particles produced. A. E. M.

General Principles of Ion Effects on Colloids. L. MICHAELIS (*2nd Colloid Symposium Monograph*, 1924, 15 pp.).—The addition of ions to a sol may produce two effects: (*a*) electrostatic, due to its fixation by adsorption or combination, (*b*) hydrophilic or lyotropic, due to competition for water between micelles and dissolved ions. In the first case an electric double layer may be produced by (*a*) appositional adsorption, the ion most highly adsorbed determining the particle charge, (*b*) dissociation tendency in colloidal particles, and (*c*) orientation of polar water molecules at indifferent surfaces. Acidoids, *e.g.*, silicic acid, nucleic acid, resin acids, are insoluble, but tend to dissolve, and in the absence of easily adsorbable ions form a layer of hydrogen ions which may have diffusity, but need not be unimolecular; they tend to emit hydrogen ions and become negative. Gelatin, casein, etc. may be termed ampholytoids; cellulose, collodion, agar, gas bubbles, etc. form double layers without active participation of the colloidal phase. It is tentatively supposed that hydroxyl ions have a greater capillary activity than hydrogen ions, so that any aqueous interface will be charged negatively against the mass of water, unless forces come into play which disturb the distribution spontaneously aimed at. Orientation of water molecules at the interface might account for the charge. Although flocculation by electrolytes usually involves adsorption, hydrochloric acid coagulates mastic sol by suppressing its tendency to emit hydrogen ions; in most other cases "exchange adsorption" occurs. The hydrogen ion is exceptional in its power of reducing swelling, *e.g.*, of agar, its effect exceeding that of tervalent ions.
CHEMICAL ABSTRACTS.

Coagulation of a Colloidal Solution by Hydrogen Ions. A. B. WEIR (*J. Chem. Soc.*, 1925, **127**, 2245—2248).—Prussian-blue sols were precipitated by sulphuric, hydrochloric, citric, and acetic acids, and the p_H of the supernatant liquid was determined by means of a hydrogen electrode when precipitation was just complete. The values for the first three acids were nearly equal (1·80—1·91), but for acetic acid the p_H was higher (2·27). In the absence of the colloid the same concentrations of acid have slightly lower p_H values, indicating adsorption by the colloid. A more dilute Prussian-blue sol, prepared by grinding with water without the addition of acid, was precipitated by oxalic acid at p_H 0·8—0·9, compared with 2·6 for hydrochloric acid. A. G.

Precipitation of Colloidal Gold by Proteins. H. A. KREBS (*Biochem. Z.*, 1925, **159**, 311—324).—Colloidal gold may be precipitated either as a result of mutual precipitation of the two oppositely charged colloids or by the formation of a protein–gold complex as a result of adsorption of the gold by the protein. For the first type of precipitation, the acidity of the medium must be greater than that of the isoelectric point of the protein. Precipitation occurs only when the quantities of protein are small (0·002 mg. per 10 c.c. of gold solution), is mostly irreversible, and is indicated in all cases by colour changes of the gold and the formation of a small amount of blue precipitate. For the second type, the formation of the protein–gold complex takes place with any concentration of protein, is completely reversible on the addition of acid or alkali (so long as the p_H is outside the isoelectric zone), and is indicated by the appearance of cloudiness followed by precipitation of coarse, red particles. It is often possible to obtain both types simultaneously. The work is extended to a consideration of the effect of colloidal protein on colloidal solutions of gum mastic. P. W. C.

Influence of Some Stable Colloids on the Flocculation of Sols and Suspensions. A. BOUTARIC and (MLLE.) G. PERREAU (*Compt. rend.*, 1925, **181**, 511—513).—The action of varying amounts of gum arabic, gelatin, albumin, casein, and dextrin on negatively charged suspensions has been examined. In most cases addition of small amounts of the colloid renders sols more sensitive to the action of electrolytes. With larger quantities the increase in sensitivity falls gradually to zero and still larger quantities cause the appearance of a more or less definite protective action. Very large additions of colloid, however, cause flocculation of the sols even in the absence of electrolytes (cf. this vol., ii, 526). R. A. M.

Protective Action of Soaps and Further Evidence in Favour of the Chemical Theory of Adsorption. III. S. S. BHATNAGAR, M. PRASAD, and D. C. BAHL (*J. Indian. Chem. Soc.*, 1925, 2, 11—22; cf. this vol., ii, 293).—The protective action of soap on sols of arsenic, antimony, and cadmium sulphides has been examined for various concentrations of soap, the drop pipette method (cf. Donnan, A., 1900, ii, 201) being employed. The surface tension of soap solutions decreases with increasing concentration of the soap, but in the

case of the sulphide sols the colloidal particles produce no change in the surface tension of the dispersion medium. When the soap solution and the sol are mixed, the concentration of the soap as indicated by the drop number is greatly reduced, affording evidence of the adsorption of the soap molecules by the particles of the sulphide sols. Similar results were obtained with various solid absorbents. The ratio of the amount of soap adsorbed to the quantity of solid employed decreases as the concentration of the soap solution is decreased. The adsorbed soap, although shown by chemical tests to be present in the washed coagula after the colloidal solutions had been coagulated by a 0·1*N*-solution of barium chloride, loses its property of dissolving in, and lowering the surface tension of water, since the drop numbers for the aqueous extracts of the coagula are the same as for pure water. Experiments on the adsorption of dyes by fine precipitates gave similar results, the adsorbed dye losing its capacity to dissolve in water. These facts support the chemical theory of adsorption. J. W. B.

Hydrophilic Effect of Ions on Agar and Protoplasmic Components. D. T. MacDougal and B. L. Clarke (*Science*, 1925, **62**, 136—137).—Sodium, potassium, calcium, and magnesium chlorides, at 0·001—0·0001*M*, cause excessive hydration of sections of agar; the effects of the cations are distinctive, and differences are shown by the nitrate and sulphate ions. Excessive swelling was observed with 0·0001*N*-hydrochloric acid, in solutions containing weak hydroxides, glycine, histidine, phenylalanine, asparagine, or alanine over the range p_H 4·2—11. A. A. E.

Kino-ultramicroscope. E. O. Kraemer (*2nd Colloid Symposium Monograph*, 1925, 57—69).—Various colloid phenomena were studied with the kino-ultramicroscope. With gelatin the viscosity appears to increase gradually, although in the later stages the motion appears to be localised more than would correspond with a simple viscosity effect; with magnesium arsenate and dibenzoylcystine gel formation occurs comparatively suddenly following an induction period which probably corresponds with an initial state of supersaturation followed by condensation. In the last-named case, moving fibres were observed. Gelatin gel shows local preferential melting. An alkaline solution of bismuth tartrate is reduced by light, and a Carey Lea silver solution is coagulated by light. In the initial stages, the aggregation of particles seems to be spontaneously reversible, so that the union between particles in agglomerates must be loose and flexible. Chemical Abstracts.

Polar Emulsifying Agents. H. N. Holmes and H. A. Williams (*2nd Colloid Symposium Monograph*, 1925, 135—137).—In a clean bottle, 2 c.c. of methyl alcohol give an emulsion stable for at least a week with 10 c.c. of water and 10 c.c. of benzene, the methyl group being apparently oriented towards the benzene, and the hydroxyl group towards the water. Good results were also obtained with stearic, palmitic, oleic, linoleic, and linolenic acids, sodium β-naphthylaminesulphonate, benzonitrile, or rancid fats as

emulsifying agent, slight effects with phenol, butyl alcohol, resorcinol, sulphonic acids, or neutral fats, and negative results with higher alcohols, glycol, glycerol, sugars, naphthols, benzyl alcohol, ketones, nitro and amino compounds. Oleic acid lowers the surface tension benzene/water, but not benzene/air, and should accumulate as a film at the interface. Molecular association does not seem to be a factor. There is a great difference in the emulsifying powers of the soaps and the lower alcohols; certain substances in true solution form distinct emulsions. CHEMICAL ABSTRACTS.

Plasticity in Colloid Control. E. C. BINGHAM (*2nd Colloid Symposium Monograph*, 1925, 106—113).—The formula $V=\mu(F-f)r$, where μ is the mobility, *i.e.*, the reciprocal of the consistency, F the shearing stress, and r the distance between the shearing planes, is probably applicable over a wide range of shearing stresses. In suspensions the flow is a linear function of the shearing stress, and is independent of the dimensions of the instrument; for emulsoids this is not the case. The distinction is ascribed to two causes providing the internal friction: diffusional viscosity, resulting from inter-diffusion of molecules having different amounts of transitional energy, and collisional viscosity caused by actual spatial interference as the layers are sheared over each other. In suspensions a third cause is the rotation of the particles in the shearing process. In many cases m. p. is without scientific value.
CHEMICAL ABSTRACTS.

Mobility of the Particles in Gold Hydrosols. P. A. THIESSEN and J. HEUMANN (*Z. anorg. Chem.*, 1925, **148**, 382—390).—The mobility of the particles in gold hydrosols is about 3×10^{-4} cm./sec. under a potential gradient of 1 volt/cm., and is independent of their size and of the method of preparation of the sols. Prolonged dialysis and protective colloids (*e.g.*, gum arabic) are also without influence. Addition of sodium carbonate raises the mobility, probably because of the adsorption of hydroxyl ions; addition of electrolytes such as barium and strontium chlorides diminishes the mobility, coagulation setting in before the particles are completely discharged.
S. K. T.

Influence of Neutral Salts on the Combination of Gelatin with Acids. J. CSAPÓ (*Biochem. Z.*, 1925, **159**, 53—57).—The capacity of gelatin to combine with sulphuric, nitric, and hydrochloric acids is increased by $K^{\cdot}$, $Na^{\cdot}$, $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, in ascending order, and by Cl', NO_3', I', but is diminished by SO_4''. The amount of acid absorbed in 0·02—0·03*N*-sulphuric acid is less than in the same concentration of hydrochloric acid. E. C. S.

Effect of Temperature on the Hygroscopicity of Hydrogels of Aluminium Oxide, Ferric Oxide, and Silica. B. AARNIO (*Geol. Kommiss. Finland Geotekn. Meddel.*, 1920, No. 25, 1—12; from *Chem. Zentr.*, 1925, ii, 525).—Hydrated ferric oxide precipitated by ammonium hydroxide contains, after drying at 100°, 10% of water and has a hygroscopic coefficient of 34%. At 200°, the corresponding values are 1·5% and 42%; at 300°, 1% and 29·6%;

at 700°, it becomes anhydrous and completely loses its hygroscopicity. The hygroscopic coefficient of hydrated aluminium oxide is 24% at 100°, 45% at 400°, 44% at 800°, 17% at 1000°, and 0·53% at 1200°. At the last temperature, the water content is 0·2%. The hygroscopic coefficient of hydrated silica is 41% at 100°, 56% at 200°, 45% at 400°, 50% at 500°, 0·62% at 1000°, and 0·5% at 1100°.

G. W. R.

Electrodialysis of Agar. Preparation of the Free Agar Acid. W. F. HOFFMAN and R. A. GORTNER (*J. Biol. Chem.*, 1925, **65**, 371—379).—Electrodialysis of a suspension of agar for 18 hrs. resulted in almost complete removal from the latter of calcium, but there was no change in the sulphur or silicon. The resulting agar acid, in approximately 0·78% solution, had p_H 2·475 and was about 56% ionised. All the sulphur is in the form of sulphuric acid, and the formula is therefore probably $R{\cdot}O{\cdot}SO_2{\cdot}OH$, where R is a polysaccharide residue. Titration data and the percentage of alkaloid in the alkaloid compounds of the acid indicate that the mol. wt. of the latter is about 3000. Neutralisation of sols of the acid with inorganic or organic bases gives rise to rigid gels.

C. R. H.

Mechanism of the Liesegang Phenomenon. A. STEOPOE (*Bul. Soc. Romana Stiinte*, 1924, **27**, 51—58).—The mechanism of the formation of Liesegang rings in extremely thin gelatin layers containing potassium chromate on the addition of a drop of silver nitrate solution is discussed. Under the microscope, these rings are seen to consist of several bands separated by a very narrow band of clear gel and each ring is separated from the next by a wider band of clear gel. The origin of these phenomena is ascribed to three causes, viz., a diminution of the viscosity of the gel caused by a slight increase in temperature due to the heat of reaction, the diffusion of the water added with the silver nitrate, and the greater velocity of diffusion of the silver ion compared with the chromate ion. These factors contribute towards periodic denudation of the solution in chromate ions so that the silver chromate is deposited in rings surrounding the drop of silver nitrate solution. This explanation is in accord with the fact that the central bands of each ring are denser than the outside bands.

A. R. P.

Electro-ultrafiltration. H. BECHHOLD (*Z. Elektrochem.*, 1925, **31**, 496—497).—An apparatus for the accelerated removal of crystalloids from colloidal solutions is described, which involves a combination of ultrafiltration and electro-dialysis. A comparison between the results obtained by its use and those obtained by other methods is distinctly favourable to the former.

N. H. H.

Equilibrium of Carbon Dioxide with Carbon Monoxide and Oxygen in the Corona Discharge. G. L. WENDT and M. FARNSWORTH (*J. Amer. Chem. Soc.*, 1925, **47**, 2494—2500).—Carbon dioxide or a mixture of carbon monoxide and oxygen under the influence of the corona discharge reaches an equilibrium corresponding with the decomposition of 28·54% of the carbon dioxide;

thermodynamically this would correspond with a temperature of 2600°, whereas the temperature in the corona was not more than about 35°. W. T.

Dissociation Constants of Organic Complexes. H. Ley and R. Grau [and, in part, W. Emmerich] (*Ber.*, 1925, **58**, [*B*], 1765—1775; cf. Ley and Pfeiffer, A., 1921, i, 335).—The dissociation constants of additive compounds of amines with trinitrobenzene have been determined from measurements of the solubility of the latter in solutions of the amine in chloroform at 17·5°. The additive compounds of dimethylaniline and dimethyl-*p*-toluidine with trinitrobenzene are very extensively dissociated, so that the intense colour of the solutions is remarkable. Dimethyl-*o*-toluidine depresses the solubility of trinitrobenzene in chloroform; in this case, the solubility effect which reduces the concentration of the nitro derivative in the saturated solution and the complex formation effect (which is only very slight) are superposed. A similar solubility effect is observed with the dimethylxylidines in which at least one methyl group is contiguous to the dimethylamino group. The dissociation constants of the compounds of trinitrobenzene with dimethylaniline and dimethyl-*o*-toluidine have also been determined photometrically, the results being in fair agreement with those given by the previous method, but the procedure is not completely satisfactory for compounds which are so considerably dissociated. Determinations of the dissociation constants are also obtained from the apparent mol. wts. of the additive compounds in boiling chloroform. The results agree in order of magnitude with those of the photometric method, but are somewhat smaller than those of the solubility method. H. W.

Heterogeneous Equilibria between Tungsten and Oxygen, and Tungsten and Water Vapour at High Temperatures. H. Alterthum and F. Koref (*Z. Elektrochem.*, 1925, **31**, 508—511).—The calculations of Wöhler (A., 1917, ii, 455; 1921, ii, 633; 1923, ii, 471) for the equilibria between tungsten and oxygen and between tungsten and water vapour do not take into account the vaporisation of the oxides of tungsten at high temperatures. The heats of vaporisation of the oxides have been calculated from the modified Trouton's law. The disappearance of the oxide film from the tungsten filament in a lamp, and the appearance of the Tyndall effect in the gas space are used to estimate the b. p. The equilibrium constants are calculated from the heats of vaporisation by the Nernst heat theorem. They show that with rise of temperature the action of oxygen on tungsten decreases, whilst that of water vapour increases greatly. N. H. H.

Magnetic Transformation Points in the System Ferric Oxide–Magnesia. H. Forestier and G. Chaudron (*Compt. rend.*, 1925, **181**, 509—511; cf. this vol., ii, 534).—The variation with temperature of the magnetic transformation point (t. p.) of mixtures of ferric oxide and magnesia has been studied by the direct method of Curie and by a differential dilatometric method.

When the proportion of ferric oxide is between 2% and 50%, the t. p. remains constant at 310°, and the compound Fe_2O_3,MgO exists in the free state. Between 50% and 56% of ferric oxide the t. p. rises to 400° and a solid solution of the double compound in ferric oxide is formed. Between 56% and 100% of ferric oxide the t. p. of pure ferric oxide at 675° is always observed. Magnesium ferrite is stable below its m. p. (1700°). Magnetic ferrites of nickel, calcium, and cadmium have been prepared by the general method of adding sodium hydroxide to a mixture of chlorides and strongly heating the precipitate. Nickel ferrite shows a magnetic t. p. at 590° and is stable at high temperatures. Cadmium and calcium ferrites lose their magnetic properties irreversibly when heated at 400° and 700°, respectively. R. A. M.

Chemical Equilibrium between Lead Sulphide and its Roasting Products. III. R. Schenck (*Z. anorg. Chem.*, 1925, **148**, 351—368; cf. this vol., ii, 419).—The nine possible bivariant equilibria with lead sulphide in the gaseous phase are considered and the conditions necessary for the formation of various products are outlined. Some of the diagrams previously given are modified. [Cf. *B.*, Dec. 24th.] S. K. T.

Equilibria in Fused Salts (Reactions between Alloys of Alkali and Alkaline-earth Metals and their Chlorides). K. Jellinek (*Z. Elektrochem.*, 1925, **31**, 542—545).—When fused chlorides are electrolysed with cathodes of molten lead, tin, antimony, and bismuth or carbon anodes, equilibria are attained between the salt and the cathodic alloy of its base. A number of binary mixtures of chlorides have been thus examined. When alkalis alone or alkaline earths alone are concerned, quotients such as $(Ba)(CaCl_2)/(Ca)(BaCl_2)$ are found constant. With mixed alkalis and alkaline earths, however, the equilibrium constant takes the form $(Na_2)(BaCl_2)/(Ba)(Na_2Cl_2)$. Hence molten alkali metals and alkali chlorides appear to be associated to double molecules.
W. A. C.

Camphor and Nitrophenols. N. N. Efremov (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 255—286; from *Chem. Zentr.*, 1925, ii, 523—524).—The author presents the following data for the eutectic points of camphor with certain compounds, the molecular percentage in the eutectic mixture of the compound mentioned being given in each case. With *o*-nitrophenol, 11·8° and 45·5%, z=8; with *m*-nitrophenol, 16° and 41·5%; with nitrophenol, —2° and about 36%; with 2 : 4-dinitrophenol, 69·3° and 30·7%, z= 6·5; with picric acid, 66·4° and 30·5%, z=3·8; with 2-nitroresorcinol (m. p. 84·8°), 4·63° and 39·3%, z=about 11·0; with 2 : 4-dinitroresorcinol (m. p. 142·3°), 47·2° and 29%; 2 : 4 : 6-trinitroresorcinol, 82·6° and 25·3%, z=16; with nitroquinol, 26·4° and 33·2%; with 3-nitropyrocatechol (m. p. 83·8°), 25·8° and 38%. In no case was there any indication of the formation of a compound. Photomicrographs are given for some of the systems.
G. W. R.

Binary System consisting of *o*-Cresol and *p*-Cresol. A. E. HILL and I. MOSBACHER (*J. Amer. Chem. Soc.*, 1925, **47**, 2544—2545).—Evidence has been obtained of the formation of a 1 : 1 compound with a congruent m. p. of 7·8° existing between the limits of 37% and 59% of *o*-cresol. The eutectics of the compound with *o*-cresol and *p*-cresol, respectively, are at 0° and 1·57°.

W. T.

Ternary System Sodium Metasilicate–Calcium Metasilicate–Silica. G. W. MOREY and N. L. BOWEN (*J. Soc. Glass Tech.*, 1925, **9**, 226—262).—The system Na_2SiO_3–$CaSiO_3$–SiO_2 has been studied by heating the glasses at definite temperatures until in equilibrium and then quenching. From the results the ternary diagram and the binary diagrams Na_2SiO_3–SiO_2, Na_2SiO_3–$CaSiO_3$, and $Na_2Si_2O_5$–$Na_2O,2CaO,3SiO_2$ were constructed. In addition to the known compounds Na_2SiO_3, $Na_2Si_2O_5$, $CaSiO_3$, and SiO_2, three new *substances* were obtained, namely, (1) $2Na_2O,CaO,3SiO_2$, giving isometric pyritohedral crystals, refractive index (n)=1·571, which decompose at 1141° to (2) $Na_2O,2CaO,3SiO_2$; this forms crystals of indeterminate symmetry, showing twinning, with n_γ=1·599, n_α=1·596, (3) $Na_2O,3CaO,6SiO_2$, orthorhombic crystals with n_γ= 1·579, n_α=1·564, $2V$ about 75°. Many mixtures within the region solidify at the ternary eutectic CaO 5·2%, SiO_2 73·5%, and at a temperature of 725°. Outside the above region, the compounds Na_4SiO_4 and Na_2O,CaO,SiO_2 have been prepared. Comparison of the results with published surface tension and viscosity data affords no evidence of correlation between the equilibrium relations and these properties. [Cf. *B.*, 1925, 921.]

A. COUSEN.

Dehydrogenation of Methyl Alcohol and Formaldehyde with Copper as Catalyst. Conditions of Equilibrium in the System $CH_2O \rightleftharpoons CO+H_2$. J. C. GHOSH and J. N. CHAKRAVARTY (*J. Indian Chem. Soc.*, 1925, **2**, 142—149; cf. Ghosh and Mali, this vol., i, 116).—The equilibrium attained in the dehydrogenation of methyl alcohol in the presence of a copper catalyst between temperatures ranging from 155° to 350° has been studied by a static method similar to that employed by Rideal (A., 1921, i, 389). It is found that the yield of formaldehyde and its decomposition into carbon monoxide and hydrogen depend more on the nature of the catalyst than on the rate of flow. The observed equilibrium constants for the reaction $CH_3{\cdot}OH \rightleftharpoons CH_2O+H_2$ are not in agreement with the theoretical values, but for the reaction $CH_2O \rightleftharpoons CO+H_2$ the experimental data are satisfactorily represented by the equation $\log_{10}K_p=-11800/4{\cdot}571T+1{\cdot}75\log_{10}T-0{\cdot}001T+0{\cdot}3$. The most probable value for the chemical constant of carbon monoxide is 2·7.

J. W. B.

Phase Rule and its Application to Problems of Luminescence and Ionisation of Gases. M. SAHA (*J. Indian Chem. Soc.*, 1925, **2**, 49—60).—A theoretical paper in which the thermal ionisation of the elements is considered from the thermodynamic point of view. The ionisation of calcium in a closed vessel and in an

atmosphere containing an excess of electrons, as represented by $Ca \rightleftharpoons Ca^+ + e$, $Ca^+ \rightleftharpoons Ca^{++} + e$, is discussed. Reference is made to the range within which certain metastable states may occur.

J. W. B.

Thermodynamic Properties of Calcite and Aragonite. H. L. J. BÄCKSTRÖM (*J. Amer. Chem. Soc.*, 1925, **47**, 2432—2442).—The heats of solution of calcite and aragonite in *N*-hydrochloric acid and in the same acid saturated with carbon dioxide have been determined. These data give the heat of transformation of aragonite into calcite at 298° Abs. as 30 ± 20 cal./mol.; this corresponds with a change of $0{\cdot}74 \pm 0{\cdot}2$ entropy unit per mol. The third law of thermodynamics gives 22·3 and 19·9 for the entropies of calcite and aragonite under standard conditions, respectively, the difference being 2·4. This value is probably inaccurate because of an error in the specific heat curve for calcite at low temperatures, which is not in agreement with the Debye equation. The difference of entropy derived from solubility measurements is 2·9 units, but reasons are given for not accepting this value. The calibration of thermocouples for use in calorimetric work is discussed. W. T.

Higher Oxides of Silver. II. Ag_2O_2. F. JIRSA (*Chem. Listy*, 1925, **19**, 300—306).—The active oxygen content of silver dioxide may be accurately determined by means of the reaction $Ag_2O_2 + N_2H_4 = 2Ag + 2H_2O + N_2$. The heat of formation of silver perchlorate, calculated from the heats of reaction of silver perchlorate in aqueous solution with hydrochloric, hydrobromic, and hydriodic acids, is (Ag, Cl, 4O aq.)=12,622 cal. From the heats of reaction of silver monoxide and dioxide with perchloric acid the heat of formation of the dioxide is $2Ag_2O_2 = 2Ag_2O + O_2 + 2000$ cal. This value agrees with that calculated from the heats of reaction of silver oxides with nitric acid and with hydrazine. The heat of formation of the dioxide from its elements is −5440 cal., and its dissociation pressure at 25° is $1{\cdot}37 \times 10^{-3}$ derived from the Nernst equation. The dioxide yields a continuous series of solid solutions with the monoxide formed by its decomposition, and its dissociation ceases in the presence of water as soon as the liquid is saturated with silver hydroxide. A. R. P.

Decomposition of Metallic Sulphates by Heat. (MLLE.) G. MARCHAL (*J. Chim. phys.*, 1925, **22**, 412—431).—Reactions of the types (i) $RSO_4 \rightleftharpoons RO + SO_3$, (ii) $3MnSO_4 \rightleftharpoons Mn_3O_4 + 2SO_3 + SO_2$, and (iii) $2Ag_2SO_4 \rightleftharpoons 2Ag_2 + 2SO_3 + O_2$, followed by $2SO_3 \rightleftharpoons 2SO_2 + O_2$, have been studied with reference to the conditions under which the systems become univariant. Using the equation of Bodenstein and Pohl (cf. A., 1905, ii, 581) to find K_c, expressions are derived in each case for calculating the partial pressures of the sulphur trioxide, dioxide, and oxygen from the measured total pressure. The sulphates were heated in a platinum-wire-wound furnace in a vacuum and the equilibrium pressures measured. Results are quoted for the sulphates of silver, manganese, nickel, cobalt, cadmium, beryllium, and magnesium at temperatures around

1000°, showing that conditions for a univariant equilibrium are obtained. L. S. T.

Apparent Molecular Heat and Viscosity of Solutions of Naphthalene in Organic Solvents. N. DE KOLOSSOVSKY (*Bull. Soc. Chim. Belg.*, 1925, **34**, 221—231).—The method suggested for the derivation of the apparent molecular heat of dissolved substances (cf. this vol., ii, 879) has been applied to the determination of the apparent molecular heat of naphthalene in benzene, toluene, chloroform, and carbon tetrachloride solutions. Using the author's formula, the values obtained for various solvents from the data of Forch (A., 1903, ii, 632) all approximate closely to 44 cal., whence it follows that the work necessary to overcome the viscosity is equal in all solvents. Since the value calculated for the real molecular heat is 39 cal., this work is equivalent to 5 cal. Measurements of the viscosity of the pure solvents and of the naphthalene solutions give for the work necessary to overcome the viscosity of the solutions per degree rise in temperature a mean value of 3 cal. (the extreme values being 0 and 6), in good agreement with that derived above. J. W. B.

Conductivity of Uni-univalent Salts in Methyl Alcohol. J. E. FRAZER and H. B. HARTLEY (*Proc. Roy. Soc.*, 1925, **A, 109**, 351—368).—The electrical conductivity between $N/10{,}000$ and $N/500$ of fifteen uni-univalent salts in methyl alcohol has been measured. Kohlrausch's law of the independent mobility of ions has been found applicable. The empirical relation of Kohlrausch $\Lambda_0-\Lambda_c=k\sqrt{c}$ (Λ_0 and Λ_c are the equivalent conductivities at infinite dilution and at concentration c) also holds. In these respects, the results are in agreement with Debye's theory of conductivity, but some difficulties arise. If Λ_c is plotted against $\sqrt{c}$, the slope of the straight-line graph obtained varies for different salts of which the ions have approximately the same mobilities. This is not anticipated by the theory. S. B.

Calculation of the Equivalent Conductivity of Strong Electrolytes at Infinite Dilution. I. Aqueous Solutions. A. FERGUSON and I. VOGEL (*Phil. Mag.*, 1925, [vi], **50**, 971—985).—As a preliminary to a discussion of Storch's dilution formula (A., 1896, ii, 288), the values of Λ_0, the equivalent conductivity at zero concentration, have been recalculated for a series of thirty-seven electrolytes. For this purpose, the equation $\Lambda=\Lambda_0-BC^n$ has been used. A simple and direct method of determining the most probable values of the constants Λ_0, B, and n, from the experimental data, is described. For all the electrolytes considered, the available data are shown to lead to consistent values of Λ_0 over ranges of concentration C from 10^{-4} to 10^{-2} g.-equiv./litre. A further test of consistency by applying Kohlrausch's law of the independent migration of the ions gives better agreement using the present values than using Kohlrausch's own values for Λ_0. Certain regularities are observed in the variation of B and n for elements belonging to the same group of the periodic table. A. B. M.

Measurement of Single-phase Boundary Potentials. E. BAUR (*Z. Elektrochem.*, 1925, **31**, 514—517).—Cells of the type calomel electrode|KCl (1) in water|KCl (2) in amyl alcohol|$CaCl_2$ (3) in amyl alcohol|$CaCl_2$ (4) in water|calomel electrode have been measured. The potential between (1) and (2) may be neglected, whilst that between (2) and (3) may be eliminated by a bridge of 0·1*N*-hydrochloric acid in amyl alcohol. The *E.M.F.* measured is thus due to the phase boundary potential between (3) and (4).

N. H. H.

Potential of Fluorine from Measurements of the Decomposition Voltages of Fused Fluorides. B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1925, **31**, 481—488).—From measurements of the decomposition voltages of the fused fluorides of potassium, sodium, lithium, calcium, strontium, barium, magnesium, and beryllium, the value 1·923±0·01 volt at 18° has been obtained for the potential of fluorine. This has been used to obtain a new value for the potential of aluminium by measuring the decomposition voltage of aluminium fluoride. The result, 0·829 volt at 18°, when combined with those given by other methods furnishes the mean value 0·844±0·015 volt. The potential difference between hydrogen and fluorine has also been obtained directly from the decomposition voltage of fused acid potassium fluoride, the result being 1·928 volts at 18°. The heats of formation of the fluorides investigated have been calculated from the above measurements and show in many cases good agreement with calorimetric determinations.

N. H. H.

Saturated Standard Cells with Small Temperature Coefficients. W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1925, **47**, 2531—2539).—By substituting for the cadmium amalgam electrode of the normal Weston cell a cadmium–tin amalgam electrode the *E.M.F.* is increased to 1·01901 volts at 25° and the temperature coefficient is reduced to about two-fifths that of the normal Weston cell. The new cell was found to be as nearly constant over short periods of time as the Weston cell. The replacement of tin by lead is not satisfactory, the temperature coefficient being increased, whilst the presence of lead increases the tendency of cadmium to react with the hydrogen ion of the electrolyte. For the cadmium–lead amalgam the *E.M.F.* is 1·01918 volts at 25°. When a cadmium–bismuth amalgam is substituted for the cadmium amalgam the *E.M.F.* is 1·01976 volts at 25° with a positive temperature coefficient equal to the negative temperature coefficient of the cadmium–tin amalgam electrode. The presence of copper does not appreciably alter the *E.M.F.* or the temperature coefficient of the Weston cell.

W. T.

Oxidation-Reduction. VIII. Methylene-blue. W. M. CLARK, B. COHEN, and H. D. GIBBS (*U.S. Pub. Health Repts.*, 1925, **40**, 1131—1201; cf. this vol., i, 25).—Methylene-white solutions are sensitive to light; the rate of oxidation by air varies as the fifth root of the hydroxyl-ion concentration. Buffer solutions

containing citrates are described, and oxidation–reduction potentials are measured at different p_H values. Methylene-blue is a very strong base, whilst Lauth's violet has a basic dissociation constant of $1{\cdot}9\times10^{-3}$. The basic dissociation constants of the two amino groups are: for methylene-white, $K_1=1{\cdot}4\times10^{-8}$; $K_2=6{\cdot}3\times10^{-10}$; for leuco-Lauth's-violet, $K_1=3{\cdot}8\times10^{-9}$; $K_2=4{\cdot}5\times10^{-10}$. The characteristic potentials at p_H0 are 0·532 volt for methylene-blue and 0·563 volt for Lauth's violet. The corresponding free energies of hydrogenation are calculated and an equation is given for its dependence on p_H. CHEMICAL ABSTRACTS.

Streams of Gas Bubbles Directed by Electrolysis. A. COEHN (*Z. Elektrochem.*, 1925, **31**, 552—554).—When a very small platinum point electrode in the tip of a finely-drawn-out glass tube is made the anode in 0·005*N*-sulphuric acid at a high *P.D.* of approximately 300 volts, the disengaged bubbles are found to rush backwards over the electrode. The same occurs under similar conditions at the anode in 0·005*N*-potassium hydroxide solution. The explanation is offered that in the very steep potential gradient a high velocity is imparted to the ions, which then carry a stream of liquid and of gas bubbles with them. W. A. C.

Passivity of Nickel. F. EISENKOLB (*Z. Elektrochem.*, 1925, **31**, 503—507).—The potential at which nickel changes from the active to the passive state is about the same (in most cases 0·3—0·4 volt, referred to the normal hydrogen electrode) with the oxy-acids, sulphuric, nitric, perchloric, phosphoric, acetic, oxalic, citric, and tartaric, and with hydrofluosilicic acid, and is little affected by the acid concentration. With hydrochloric, hydrobromic, and hydriodic acids, much higher values are given, which vary with dilution, whilst in the most dilute solutions (0·01*N* and beyond with hydrochloric acid) the passivity ceases. With hydrofluoric acid the potential shows a maximum (1·38 volts) with a 0·1*N*-solution. The addition of potassium sulphate to sulphuric acid lowers the potential given in the latter alone, whilst addition of hydrochloric acid has the opposite effect. Mixtures of hydrochloric acid and potassium chloride give higher potentials than the former alone. In 0·1*N*-sulphuric acid rotation of the electrodes is without effect, but in hydrochloric acid the potential is increased with increasing speed of rotation and finally the passivity disappears. The theory that there is a difference in the valency of the active and passive states of a metal passing into solution is found to be without support in the case of iron and nickel. N. H. H.

Electrolytic Oxidation of Double Cyanides of Quadrivalent Molybdenum. O. COLLENBERG and B. ANDERSEN (*Z. Elektrochem.*, 1925, **31**, 558—565).—In connexion with the preparation of double cyanides of quinquevalent molybdenum, it is found that the electrolytic oxidation of tetrapotassium molybdenum octacyanide (0·06 mol./litre) proceeds smoothly and completely at platinum anodes in 0·2*N*-sulphuric acid solution, preferably at a temperature of 45° and a current density of 0·0056

amp./dm.^{2} In alkaline solutions, the oxidation can only be carried to the extent of 72%. Neutral solutions are unsatisfactory, since complex decompositions set in. W. A. C.

Electrolytic Reduction of Tungstic Acid in Presence of Oxalic Acid. O. COLLENBERG and K. WILSON (*Z. Elektrochem.*, 1925, **31**, 555—558).—Electrolysis of solutions containing 11·2 g. of potassium tungstate and 16 g. of oxalic acid in 100 c.c. at a current density of 0·01—0·03 amp./dm.^{2} and a temperature of not less than 70° with lead or tin cathodes leads to a complete reduction of tungsten to the quinquevalent stage and no further. The method is well adapted to the preparation of quinquevalent tungsten compounds. W. A. C.

Electrodeposition of Silver–Cadmium Alloys. A. H. W. ATEN and M. F. VAN PUTTEN (*Rec. trav. chim.*, 1925, **44**, 861—865).—Electrolysis of a solution containing potassium cyanide, potassium silver cyanide, and potassium cadmium cyanide with current densities up to 0·8 amp./dm.^{2} gives a deposit of silver containing not more than 2% of cadmium. With a current density of 1·2 amp./dm.^{2} and an atomic ratio of 2 : 1 of cadmium to silver in solution there is obtained a yellow deposit containing 25% of cadmium. The variation with composition of the *E.M.F.* between cadmium–silver alloys and solutions containing the above-mentioned salts in various proportions, has been determined and an expression deduced for the potential difference between silver and cadmium metals in contact with them. G. M. B.

Electrochemical Reduction of Solid Electrodes. K. FISCHBECK (*Z. anorg. Chem.*, 1925, **148**, 97—129).—A coulometer is described capable of reading to 10^{-3} coulomb, the volume of hydrogen evolved by the electrolysis of dilute sulphuric acid being measured in a capillary tube. From electrodes of platinum, mercury, and lead, theoretical volumes of hydrogen were obtained, but when a platinum cathode was covered with a reducible powder, the evolution of hydrogen was reduced by an amount which was a measure of the efficiency of the reduction process. With stannic oxide, copper pyrites, and galena, the efficiency diminished with increasing current density; with copper sulphide and copper oxide no hydrogen was evolved; in the latter case a difficultly reducible electrolyte, *e.g.*, potassium nitrate, could also be reduced. The current was varied from 0·003 to 0·05 amp. with a circular electrode of 1·5 cm. diameter. The reduction was also studied of solid electrodes of stibnite, iron pyrites, copper pyrites, galena, and cassiterite, crystals of each mineral being so mounted that one face only was exposed to the electrolyte. The following relation holds: $I_r = A \log (1 + B \cdot I)$, where I is the total current, I_r that used in reduction, and A and B are constants. In a third series of experiments, silver electrodes covered with a layer of an insoluble silver salt were reduced. Above a certain minimum value, the *E.M.F.*–current relation is linear, and the initial portion of the curve may be continued backwards by reversing the direction of

the current. The break corresponds with a change from metallic to electrolytic conduction by the salt layer, and occurs, not at zero current, but at a cathodic polarisation of the order of 0·01 volt.
A. G.

Some Electrode Phenomena in Electrolysis. J. A. CROWTHER and R. J. STEPHENSON (*Phil. Mag.*, 1925, [vi], **50**, 1066—1079; cf. *ibid.*, **50**, 86).—The phenomena occurring when an increasing potential difference is applied to an electrolytic cell, one of the electrodes of which is of comparatively small area, have been further investigated. The small electrode consisted of a platinum disc or wire of about 0·5 cm.^{2} area. Evidence is adduced to show that a contact or transfer resistance exists between the electrolyte and electrode. This resistance is inversely proportional to the external pressure on the cell. From this it is inferred that the transfer resistance is attributable to a thin gas film. When the current density exceeds a certain critical value, the resistance at the electrode is very largely increased. For solutions of sulphuric acid of varying concentration the critical voltage increases and the critical current diminishes with increasing specific resistance. The critical current diminishes with diminishing external pressure. The extra resistance of the cell when in the highly resistant state is confined to a layer which does not extend more than 0·02 mm. from the electrode. The suggestion is made that it is due to the liquid being thrown into the spheroidal state by the heat generated in the transfer resistance owing to the passage of the current through it. A. B. M.

Application of Quanta in the Theory of Chemical Reactivity. S. C. ROY (*Z. Physik*, 1925, **34**, 499—509).—In spite of the severe criticism to which the radiation theory of chemical reactivity has been subjected, its value remains great in the absence of any other valid hypothesis. The velocity of the change $AB \rightarrow A+B$ is determined by the number of collisions of AB with light quanta, and the reverse process by the number of collisions between A and B. From considerations of the effective diameter of quanta and atoms an expression is obtained for the velocity constants of the two reactions and is extended to include molecules previously activated. Ionisation of a gas is regarded as the simplest type of chemical change; thermal ionisation of gases and thermionic emission of hot bodies are treated as special cases of heat reactions. E. B. L.

Critical Increment of Chemical Reactions. W. E. GARNER (*Phil. Mag.*, 1925, [vi], **50**, 1031—1033).—Polemical, in reply to Hinshelwood (this vol., ii, 874). A. B. M.

Energy Distribution Law Appropriate to the Theory of Chemical Reaction Velocity. C. N. HINSHELWOOD and C. W. THORNTON (*Phil. Mag.*, 1925, [vi], **50**, 1135—1139).—The fraction of the total number of molecules possessing the necessary energy of activation to react is usually written $e^{-E/RT}$, where E is the critical energy. This is not rigidly true for all forms of energy, and the possibility of determining which form of molecular energy

is responsible for activation, or of distinguishing between cases in which one or other form of energy preponderates, is discussed. An examination of the data for three bimolecular reactions (cf. A., 1924, ii, 749) from this point of view, however, shows that the variations which would be observed fall within the experimental error. A. B. M.

Thermal Decomposition of Ozone. R. O. Griffith and A. McKeown (*J. Chem. Soc.*, 1925, **127**, 2086—2096).—The thermal decomposition of ozone in glass tubes at 100° follows approximately a bimolecular course although the velocity coefficients increase slightly with time. For ozonised oxygen mixtures, at pressures between 300 mm. and 1000 mm., the bimolecular coefficient k (expressed in the units litres/moles-minutes) is given by the expression $k=11,500/(300+P)$, where P is the gas pressure in millimetres of mercury. The velocity of decomposition is accelerated by the addition of argon, nitrogen, carbon dioxide, and helium, the "catalytic" efficiency being in the order given. The magnitude of the velocity coefficient varies from tube to tube and is retarded slightly by coating the walls with sulphuric acid. The reaction is therefore regarded as partly homogeneous and partly heterogeneous. A mechanism is suggested explaining the retardation of the reaction by added oxygen and its acceleration by inert gases. E. E. W.

Keeping Properties of Standard Sodium Thiosulphate Solution. E. Collard, jun. (*Ann. Chim. analyt.*, 1925, [ii], **7**, 291—292).—A 0·1*N*-solution of sodium thiosulphate remained practically unchanged in strength (24·76 as against 24·80 g. per litre) after 3½ yrs. D. G. H.

Keeping Properties of Tincture of Iodine. E. Collard, jun. (*Ann. Chim. analyt.*, 1925, [ii], 7, 292—293).—Tincture of iodine keeps well, and a sample stored in an ordinary ground glass-stoppered flask for 3 yrs. only showed a very slight loss of alcohol and a formation of hydriodic acid less than that allowed in the French Codex. [Cf. *B.*, 1925, 989.] D. G. H.

Periodic Crystallisation of Pure Substances. E. S. Hedges and J. E. Myers (*J. Chem. Soc.*, 1925, **127**, 2432—2434).—The periodic crystallisation of thin films of solutions of chrome alum and of barium nitrate has been observed on a microscope slide. With chrome alum, crystallisation proceeds at first at a fairly rapid rate with the formation of a large number of small particles, and then at a slower rate with the formation of a smaller number of larger particles, the two speeds thereafter alternating; the bands thus consist of alternate zones of small and large spherulites. Periodicity is only observed when the metastable, spherulitic form appears, and it seems probable that periodic phenomena are a general characteristic of such metastable systems. When benzoic acid is crystallised from a mixture of equal volumes of sulphuric acid and ethyl alcohol, rings about 1 cm. apart can be obtained.

These consist of layers of closely-packed crystals separated by spaces containing mostly solution with sufficient crystals to give rigidity to the whole. A. G.

Temper-colours of Iron–Carbon Alloys and of the Mixed Crystals Fe–Ni, Fe–V, Fe–Al. G. TAMMANN and G. SIEBEL (*Z. anorg. Chem.*, 1925, **148**, 297—312).—The rates of change with time of the temper-colours of primary cementite, pearlite, pearlitic cementite, and troostite, in their relation to temperature, and of nickel–, vanadium–, and aluminium–iron alloys in their relation to temperature and composition have been investigated. On plotting the thickness of the equivalent air films ($\mu\mu$) against the logarithm of the time, the resulting isotherms are in general linear or consist of two intersecting lines, indicating the validity of the equation $t=a.e^{by}-a$, where t represents time, y the thickness of the film of oxide, a a constant, and b a coefficient (Schwächungskoeffizient), correcting for the decreased availability of oxygen; b decreases with increasing temperature according to the equation $\log b_T=\log b_{T_0}-c(T-T_0)\log e$, c being a constant. The behaviour of nickel alloys is complicated. The discontinuous nature of the alteration in the b values and in the thickness of the temper-film with increasing nickel content is, however, to be explained when the changes in the nature of the alloys consequent on the passage of the iron into α- and γ- and the nickel into α- and β-modifications are considered. The discontinuity in the case of vanadium alloys is likewise connected with the $\alpha\longrightarrow\gamma$ change of iron. Addition of aluminium results in a markedly reduced rate of oxidation. J. S. C.

Mechanism of Reduction. IV. H. J. PRINS (*Rec. trav. chim.*, 1925, **44**, 876—888; cf. A., 1923, ii, 839).—A study of the action of nitrobenzene in acetic acid solution on lead gives results closely resembling those obtained with zinc, and the same formula is applicable to both. Up to a critical concentration of nitrobenzene the velocity of solution is directly proportional to the concentration of nitrobenzene, and this velocity, expressed in molecules per unit of surface, is the same for zinc as for lead. This fact and the low temperature coefficient found show that the velocity is a velocity of diffusion.

As in the case of zinc, the variation of the reaction velocity at concentrations of nitrobenzene above the critical value is attributed to the adsorption of molecules of lead acetate on the surface of the metal, and it is shown that the average life of a molecule of zinc acetate on the surface of zinc is four times that of a molecule of lead acetate on lead.

Addition of water causes first a diminution and then an increase of velocity of the reaction, and possible explanations of these effects are discussed. G. M. B.

Comparison of the Theory of Explosion Waves with Recent Experiments. E. JOUGUET (*Compt. rend.*, 1925, **181**, 546—548). —Laffitte (Thesis, Paris, 1925) has recently been able to produce

spherical combustion waves having the velocity of plane explosion waves. This is apparently in contradiction with the author's theory ("Mechanique des Explosifs," Doin, Paris, 1917, 364). The theory was only a first approximation and it is re-discussed in the light of Laffitte's work. R. A. M.

Pressures Developed in Closed Vessels by the Combustion of Explosives. E. BURLOT (*Mém. Poudres*, 1924, **21**, 403—410).—A comparison is made between the values obtained for the pressures developed by the combustion of explosives in closed vessels, measured (i) by the acceleration of a freely-moving piston, and (ii) by the deformation of "crushers." The higher results are given by (i), from which it is concluded that the frictional forces tending to diminish the acceleration of the piston are negligible, and that the pressures measured in this way correspond satisfactorily with those actually developed in the bomb. N. H. H.

Experimental Determination of the Force and Co-volume of Explosives. E. BURLOT (*Mém. Poudres*, 1924, **21**, 411—490; cf. this vol., ii, 558).—The values of the force, f, and the co-volume, α, obtained from the equation $p/\Delta=\alpha p+f$ do not agree with those obtained from the two equations $f=P_0V_0T/273$, and $\alpha=\alpha'+V_0/1000$. The reason is held to lie in the difficulty of interpreting the determinations of the pressure (p), the specific volume (V_0), and the temperature of combustion (T). The two methods of determining f and α, namely, (i) measurement of the pressures developed in the bomb, and (ii) analysis of the gases and solid residues formed, are critically examined and compared. For this the data obtained from numerous experiments of the author are utilised. It is concluded that, practically, α may be calculated by means of the expression $\alpha=\alpha'+V_0/1000$, and that as regards f an agreement between the calculation based on the pressures measured by a freely-moving piston, corrected for cooling, and that based on the laws of the specific heats of gases at high temperatures and pressures depends on a readjustment of these laws. N. H. H.

Nature of the Constant of Mass Action. R. D. KLEEMAN (*Physical Rev.*, 1924, [ii], **23**, 307—308).—Van't Hoff's assumption that the molecules formed in the reacting chamber in his process can be removed so rapidly that no dissociation takes place is inadmissible unless the process is carried out infinitely slowly, when the constant of mass action is a function, not only of the temperature, but also of the volume of the mixture and the masses of the constituents. The existence of catalytic action by contact can be deduced. A. A. E.

Laws of Unimolecular Reactions (Fermentations; Catalytic Reactions). L. AMBARD (*J. Chim. phys.*, 1925, **22**, 402—412).—A general theory of catalytic action, more comprehensive than the classical theory, is developed from experiments on catalysis by amylolytic enzymes. Univalent anions link, by adsorption, the enzyme to the substance to be transformed, in this case starch paste or glycogen. When the concentrations of starch and enzyme

are constant, and that of the anion, from sodium chloride, varies, φ, the amount of substance transformed in unit time, is proportional to the concentration of sodium chloride (when this is small), then increases less rapidly, and finally decreases. The maximum values of φ differ with the various chlorides, bromides, and iodides studied. In the absence of an electrolyte, no fermentation occurs and φ thus expresses the proportion of the enzyme activated by the anion. Further, with fixed concentration of the substrate, φ is proportional to the concentration of the enzyme only when the concentration of the univalent anion is constant. φ is proportional to the concentration of the substrate between concentrations of glycogen from 5% to 10%. Outside these limits, the law of mass action fails, and other factors, besides the number of collisions (the only factor embraced by the kinetic theory), and the concentration of catalyst and anions, intervene. These are (1) the number of collisions between catalyst and substance which can be utilised, and (2) adsorption of the enzyme, which is a function of the concentration of substance to be transformed when concentrations of enzyme and anions are constant. The hydrolysis of sucrose is also discussed. L. S. T.

Oxidation in Sea Water. H. W. HARVEY (*J. Marine Biol. Assoc.*, 1925, **13**, 953—969).—"Deep water" from the English Channel contains a catalyst which increases the rate of oxidation of easily oxidisable substances such as pyrogallol and quinol. The decomposition of hydrogen peroxide is also catalysed by deep water. Both effects are inhibited by cyanide and by glycine. It is suggested that the catalysts are organic compounds of iron and that the inactivity of surface water is due to the presence of oxidisable organic matter. When these substances are oxidised by hydrogen peroxide the surface water becomes more active. P. E.

Secondary Kinetic Salt Effect in the Case of Hydroxyl Ion Catalysis. J. N. BRÖNSTED and C. V. KING (*J. Amer. Chem. Soc.*, 1925, **47**, 2523—2531).—The decomposition of nitrosotriacetonamine catalysed by hydroxyl ions shows a negative primary salt effect (cf. A., 1924, ii, 331, 745). In piperidine–piperidinium ion and phosphate buffers the reaction shows a considerable secondary salt effect, positive in the first, and negative in the second case. An apparatus for determining the velocity of a reaction accompanied by the evolution of a gas is described. W. T.

Mechanism of Oxidation Processes. IX. H. WIELAND (*Annalen*, 1925, **445**, 181—201; cf. A., 1924, i, 1172).—I. [With H. HAUSSMANN.]—Mode of Action of Catalase.—Whilst hydrogen peroxide is to be expected as a primary product in biological oxidation processes brought about by catalases, its presence in the living cell could not be demonstrated by experiments in which the enzyme was rendered suddenly inactive by treatment with 4*N*-sulphuric acid, or hydrocyanic acid, or by cooling in liquid air, the last-named procedure being applied both to freshly-gathered leaves

and to a newly-killed 14-days-old dog (cf. Macleod and Gordon, A., 1922, i, 1095; 1923, i, 125; *J. Path. Bact.*, 1925, **28**, 155). Whilst the dilute acid extract of fresh leaves gives with titanium–sulphuric acid reagent the same coloration as hydrogen peroxide, this is derived from an unidentified substance which is not a peroxide. The following experiments on the deactivation of catalase were carried out with liver catalase prepared according to the method of Batelli and Stern (*Ergeb. d. Physiol.*, 1910, **10**, 544), except that filtration of the extract was replaced by centrifuging and decantation (cf. Morgulis, *ibid.*, 1924, **23**, 320). The standard for comparison was a clear solution obtained by extracting 0·004 g. of the crude enzyme with cold water and diluting to 100 c.c., 1 c.c. of which solution was further diluted to 100 c.c.; this volume, then containing 0·0188 mg. of dissolved material, was used to catalyse the decomposition of 5 c.c. of neutral 0·1*M*-hydrogen peroxide solution at 0°, the unimolecular reaction (cf. Senter, A., 1903, ii, 661; 1905, ii, 377; 1911, ii, 995; Waentig and Steche, A., 1911, i, 759; 1912, ii, 839) being followed by titration at intervals with 0·005*N*-potassium permanganate in presence of 2*N*-sulphuric acid. The addition of 2 c.c. of 0·001*N*-hydrocyanic acid reduces the activity of the catalase to one-sixth of its original value. Aëration of the deactivated solution, either in a vacuum through a capillary tube or at the ordinary pressure, resulted in a still further decrease in activity of the enzyme, and the fresh catalyst was deactivated by drawing air, hydrogen, nitrogen, or carbon dioxide through the solution (cf. Waentig and Steche, A., 1912, ii, 839; 1914, i, 605; Michaelis and Pechstein, A., 1913, i, 1008), by keeping the solution in a water-pump vacuum, or by mechanical agitation (cf. Abderhalden and Guggenheim, A., 1908, i, 237). Catalase deactivated by vacuum is not reactivated on subsequent aëration. Deactivation by inert gases and by agitation is ascribed to reduction of active surface by coagulation, whilst under reduced pressure the skin of gas (air) previously surrounding each particle is removed. The observedly great activity and sensitiveness of the catalase examined is ascribed to its freedom from protective colloids. Deactivation is also effected by increased pressure (of supernatant gas), but is reversible up to an excess pressure of 600 mm. of mercury, and is ascribed to the blocking of the active surface by reversible adsorption. Reactivation is considerably accelerated by diluting the pressure-deactivated solution with gas-free water, which allows the adsorption equilibrium to be established in one phase. A similar reactivation of catalase deactivated by hydrocyanic acid can be effected by dilution, indicating that this poisoning is also due to adsorption. Methylcarbylamine behaves similarly to hydrocyanic acid, its deactivating effect being of about the same order. Deactivation by carbon monoxide is of about the same order as that of indifferent gases (cf. Senter, A., 1905, ii, 377). A similar series of experiments on the deactivation of colloidal ferric hydroxide by hydrocyanic acid indicated that this also is purely an adsorption phenomenon, a result contrary to Warburg's view that the poisoning of enzymes by hydrocyanic acid is due to labile complexes formed

between the poison and the iron present in the surface of colloidal enzyme particles.

II. [With H. Lövenskiold.]—Mode of Reaction of Hydrogen Peroxide.—Oxidation of αβ-dihydroxybutyric acid (cf. Riiber, A., 1908, i, 639) in neutral (ammonium salt) aqueous alcoholic solution with hydrogen peroxide affords acetaldehyde, whilst crotonic acid yields αβ-dihydroxybutyric acid (*silver* salt, white flocks) when treated with aqueous hydrogen peroxide at 40°. The latter oxidation indicates the fission of the hydrogen peroxide into two hydroxyl groups, which become attached directly to the unsaturated carbon atoms. F. G. W.

Polymerisation of Acetylene under the Action of α-Particles. W. Mund and W. Koch (*Bull. Soc. Chim. Belg.*, 1925, **34**, 241—255).—The polymerisation of acetylene to a solid polymeride under the influence of radium emanation previously observed (cf. this vol., i, 625) has been studied quantitatively. A detailed description of the apparatus and the experimental procedure is given, whereby the velocity of polymerisation of acetylene containing approximately 5×10^{-5}% of radium emanation at 0° and 700 mm. is measured. Allowing for the effect of the radium-*A* and radium-*C* in equilibrium with the emanation and for the absorption by the walls of the containing globe, it was found that each α-particle emitted by the emanation, and having a range of 3·94 cm. in air at 0° and 760 mm., caused a disappearance of $4{\cdot}38\times10^{6}$ mols. of acetylene, and produced in the gas $2{\cdot}13\times10^{5}$ ions. Most of the molecules disappearing from the gaseous phase are assumed to become polymerised, but some may be absorbed by the polymeride, which is known to absorb considerable quantities of oxygen. J. W. B.

Catalytic Transference of Hydrogen as the Basis of the Chemistry of Decomposition Processes. A. J. Kluyver and H. J. L. Donker (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 605—618).—On the assumption that the breaking down of sugar by fermentation is the result of a number of coupled dehydrogenation and hydrogenation reactions, along with intramolecular changes and condensation reactions (cf. this vol., i, 1215), the probable mechanism of these reactions is discussed. Activation of the hydrogen atoms in the substrate is brought about by the affinity of the protoplasm for hydrogen, which thus loses part of its affinity for the substrate residue. The latter becomes to a certain extent unsaturated, and a rearrangement takes place consisting in a transference of hydrogen from one part of the molecule to another, succeeded by a splitting up into acids and aldehydes of small mol. wt., and, in some cases, by partial recondensation of the products. There is an optimum degree of affinity, since if the latter is too small there will be no activation of hydrogen, if too great the hydrogen will be bound by the protoplasm. The affinity of the protoplasm for oxygen may also give rise to hydrogen activation, owing to the action on the hydroxyl group. Not only the fermentation of sugars, but all the chemical reactions brought

about by aërobic respiratory processes and anaërobic fermentation processes, appear capable of explanation by the catalytic transference of hydrogen under the influence of the protoplasm of the organisms. The difference between aërobic and anaërobic processes, therefore, is apparently not fundamental, but one of degree only. It is not necessary to ascribe the intermediate steps in any complete fermentation process to the agency of separate enzymes, but simply to manifestations of a definite degree of affinity of the protoplasm for the hydrogen of the various intermediate products. The affinity for hydrogen of the protoplasm of a given organism must vary to a certain extent with the hydrogen-ion concentration of the protoplasm. M. S. B.

Aluminium Oxide as a Condensing Agent and the Rôle of Carriers in Catalysis. K. W. ROSENMUND and A. JOITHE.—(See i, 1403.)

Catalysis by Alumina of the Reaction between Ethyl Alcohol and Ammonia. G. W. DORRELL (*J. Chem. Soc.*, 1925, **127**, 2399—2407).—Ammonia and ethyl alcohol vapour in known concentrations were carried by a stream of nitrogen over alumina. The effects of varying the temperature of the reaction, the speed of the gases, and the ratio of alcohol to ammonia on the proportion of ammonia aminated were observed. The optimum temperature is about 300°. The amination of ammonia is small when the reacting gases travel slowly, but increases as the time of contact decreases. This fact is traced to the decomposition of ethylamine into ethylene and ammonia when passed slowly over alumina. The amination of ammonia per mol. of alcohol decreases in the presence of excess of alcohol probably on account of the formation of secondary and tertiary amines. Ammonia is readily absorbed by alumina at 344°, but no decomposition into its elements could be detected. E. E. W.

Oxidation of Dihydroxyacetone and Glyceraldehyde in Phosphate Solutions and Acceleration of Oxidation by Heavy Metals. F. WIND (*Biochem. Z.*, 1925, **159**, 58—67).—The rate of oxidation of dihydroxyacetone and glyceraldehyde by molecular oxygen in the presence of phosphate is 26—27 times that of lævulose (cf. Meyerhof and Matsuoka, A., 1924, i, 1045). The oxidation of lævulose is accelerated by cupric and ferrous salts, is inhibited by potassium pyrophosphate and cyanide in the presence of cupric salts, but is accelerated by potassium pyrophosphate in the presence of ferrous salts. The oxidation of dihydroxyacetone is accelerated by 0·001*N*-copper (125%), ferrous iron (61%), and manganese (63%), and is inhibited by 0·001*N*-potassium cyanide (40%). E. C. S.

Composition of Reduced Nickel as a Catalyst. B. KUBOTA and K. YOSHIKAWA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 223—232).—Reduced nickel used as a catalyst contains numerous unstable hydrides which may coexist. They may be classified into three groups, (*a*) hydrides capable of effecting hydrogenation of the aromatic nucleus, (*b*) hydrides reducing ethylenic

compounds, (*c*) hydrides capable of reducing groups such as the nitro group. When benzene containing thiophen is passed over the catalyst a limiting amount of nickel sulphide is formed and no further hydrogenation of the nucleus occurs. The percentage of nickel thus converted is a measure of the percentage capable of affecting the aromatic nucleus. The catalyst retains its activity towards ethylene compounds. Ethyl sulphide is now passed over and an additional amount of nickel sulphide is formed, reaching a limit when hydrogenation (*b*) ceases. Hydrogen sulphide is now passed over and the final percentage of nickel existing as sulphide is a measure of the percentage entering into the reduction of nitrobenzene. If nitrobenzene is reduced at 180° with a catalyst poisoned by thiophen, a theoretical yield of aniline is obtained, whereas only 38% is obtained from the unpoisoned catalyst.

A table shows the percentages of nickel reduced at various temperatures effective in the three classes of reactions, and hydrides the presence of which would account for the percentage of nickel effective in the reduction of nitrobenzene. R. A. M.

Catalytic Formation of Methane from Carbon Monoxide and Hydrogen. I. K. M. CHAKRAVARTY and J. C. GHOSH (*J. Indian Chem. Soc.*, 1925, **2**, 150—156).—A sugar charcoal–nickel (73 : 27) catalyst for the reaction $CO+3H_2=CH_4+H_2O$, prepared by the carbonisation of a mixture of solutions of sucrose and nickel acetate under prescribed conditions, retains its activity undiminished for months when the theoretical ratio of hydrogen and carbon monoxide is used. The critical space velocity (c.c. of gas per c.c. of catalyst material per min.) below which no carbon monoxide is found in the outflow gases is large and increases considerably with temperature. This catalyst entirely suppresses the reaction $2CO=C+CO_2$ and prevents the deposition of carbon on the nickel surface. Ceria acts as a promoter for this catalyst, *e.g.*, at 355° the critical space velocity is 3·5 without ceria, whilst with ceria it is greater than 4·4. The presence of carbon dioxide in the outflow gases is due mainly to the reaction $2CO+2H_2=CO_2+CH_4$, and partly to the reaction $C+2H_2O=CO_2+2H_2$, the latter being suppressed at high space velocities. J. W. B.

Catalytic Formation of Methane from Carbon Monoxide and Hydrogen. II. Production of Fuel Gases Rich in Methane. K. M. CHAKRAVARTY and J. C. GHOSH (*J. Indian Chem. Soc.*, 1925, **2**, 157—164).—The application of the sugar charcoal–nickel catalyst (cf. preceding abstract) in pumice to the production of methane in accordance with the equations $CO+3H_2=CH_4+H_2O$ and $2CO+2H_2=CO_2+CH_4$ from mixtures of hydrogen and carbon monoxide (1 : 1) has been studied; its efficiency is small unless a promoter is employed. Ceria (cf. Medsforth, T., 1923, **123**, 1452) is without influence in promoting the second reaction, but vanadic acid is very efficient, its activity rapidly increasing with rise in temperature. The activity of this catalyst remains steady for months if the reaction temperature be maintained below 500°, and at 400° the exothermic reactions involved maintain the temperature

of the catalyst without external heating. Ferric oxide is also an efficient promoter, but the substitution of coconut charcoal for sugar charcoal yields a catalyst which, although possessing initial high activity at low temperatures, does not remain steady and has a small temperature coefficient. Examination of the composition of the incoming and effluent gases shows that equivalent quantities of methane and carbon dioxide are produced by the second reaction, the excess of methane found resulting from the first reaction, which is favoured by a high space volume. The calorific value of the resulting gas is slightly lower than that of carburetted water-gas, the large volume of carbon dioxide produced acting as a diluent. J. W. B.

Activity of Contact Substances. II. Catalytic Synthesis of Water by Metals of the Iron Group and their Binary Alloys with One Another and with the Platinum Metals, in so far as they are Catalytically Active at the Ordinary Temperature. H. REMY and H. GÖNNINGEN (*Z. anorg. Chem.*, 1925, **148**, 279—292; cf. this vol., ii, 563).—An extension of previous work. Iron, cobalt, nickel, their binary alloys with one another and with ruthenium and osmium, and also rhodium–cobalt alloys possess no catalytic activity at the ordinary temperature against a hydrogen–oxygen mixture. As previously noticed (*loc. cit.*), the activities of the various catalysts are markedly influenced by previous treatment with hydrogen or oxygen. Rhodium–nickel alloys are only active catalytically after previous treatment with hydrogen and rhodium–iron and iridium–iron alloys after oxygen treatment. Data are given for the relative catalytic activities of the various active alloys against a mixture of 2 vols. of hydrogen and 1 vol. of oxygen systematically diluted with hydrogen, oxygen, or nitrogen. The following numbers represent the relative catalytic efficiencies of the various alloys etc. against a mixture of 2 vols. of hydrogen and 1 vol. of oxygen after previous exposure to hydrogen, the figures in parentheses representing the corresponding activities after exposure to oxygen: rhodium–iron 0 (24); rhodium–nickel 111 (0); palladium–iron 77 (95); palladium–cobalt 87 (71); palladium–nickel 118 (71); iridium–iron 0 (71); iridium–cobalt 65 (31); iridium–nickel 118 (71); platinum–iron 91 (111); platinum–cobalt 111 (65); platinum–nickel 105 (74); platinum 118 (115). The remarkable dependence of the catalytic efficiency on the previous treatment with oxygen or hydrogen is readily seen; iron alloys, which are the least active after exposure to hydrogen, are the most efficient after exposure to oxygen. It is remarkable that an iron–iridium alloy, previously exposed to hydrogen, possesses an activity about 40% of that of platinum against a gas mixture of the composition ($2H_2,O_2,6N_2$). The alloy is otherwise inactive as a catalyst. J. S. C.

Effect of *X*-Rays on the Platinum Catalyst in the Contact Sulphuric Acid Reaction. G. L. CLARK, P. C. MCGRATH, and M. C. JOHNSON (*Proc. Nat. Acad. Sci.*, 1925, **11**, 646—651).—Preliminary investigations have shown that *X*-rays do not activate

the platinum catalyst in the oxidation of sulphur dioxide when it is exposed to the radiation in dry air. When exposed in a moist atmosphere containing 0·013 part of water per 1 part of dry air, it was activated and an increase in conversion obtained over the first period of use. The activity then fell to a minimum and finally returned to its normal value before irradiation. Subsequent irradiation gave less activation and a slower return to the normal. The decreased effect of *X*-rays after the first exposure is regarded as being due to the building up of a film of sulphuric acid which is not easily ionised by the radiation. A. E. M.

Gaseous Catalysis by Means of Metals of the Platinum Group. L. Duparc, P. Wenger, and C. Urfer (*Helv. Chim. Acta*, 1925, **8**, 609—631; cf. Wenger and Urfer, A., 1918, ii, 230).—The relative efficiency of rhodium and platinum as catalysts is studied in the cases of the oxidation of sulphur dioxide and ammonia, and the reduction of carbon monoxide, carbon dioxide, nitric oxide, and nitrous oxide, and the effects of the alteration of conditions have been observed. In the catalytic oxidation of ammonia, using platinum-black as a catalyst, the best yields are obtained when the concentration of the catalyst is 3%. Above 700°, the yields are considerably reduced, and in this region at a given temperature the yield is inversely proportional to the concentration of the catalyst. At 520°, the yields are not altered appreciably by a variation in the rate of passing the gases between the limits of 10 and 60 litres per hr., the yield increasing with increasing concentration of the catalyst. A rhodium-black catalyst is much more reactive than platinum, and consequently a much lower concentration of catalyst must be employed. At a rate of 45 litres per hr. the yields are almost as large with a rhodium catalyst concentration of 0·1% (optimum) as with a 3% platinum catalyst. When the former is employed, the heat of reaction is sufficient to maintain the catalyst in a state of incandescence, whereas external heat must be continually applied in the case of the platinum catalyst. Data relevant to the theory of catalytic action are discussed and a theory of the mechanism is deduced in each case. In the catalytic oxidation of sulphur dioxide the intermediate is the oxide Rh_2O_3:—$Rh_2O_3+3SO_2=3SO_3+2Rh$; $4Rh+3O_2=2Rh_2O_3$, since the reaction which proceeds slowly below 600° reaches its maximum efficiency at this temperature, at which the rhodium-black most rapidly absorbs oxygen, whereas at 650° and above, when the dissociation of the rhodium oxide is appreciable, the yields of sulphur trioxide decrease owing to the difficulty with which the metal oxide is reformed. A similar mechanism applies to the case of platinum, the maximum absorption of oxygen and the maximum yield of sulphur trioxide coinciding at 400° and diminishing at 500° and above. In the case of the oxidation of ammonia, maximum yields are obtained at 560° and consequently the oxide of the catalyst cannot be the intermediate in this case. The ammonia reduces the catalyst oxide to yield the metal and water, and the former then reacts with the ammonia to form

its hydride and highly reactive nascent nitrogen, which immediately combines with oxygen to form nitrogen peroxide, which with excess of ammonia yields a mixture of ammonium nitrite and nitrate. With a 0·1% rhodium catalyst and the (theoretical) mixture of 2 vols. of ammonia and 3·5 vols. of oxygen, the rhodium is not oxidised, but immediately takes up the hydrogen from the ammonia and the nascent nitrogen is completely oxidised to nitrogen peroxide. With a 5% rhodium catalyst, carbon monoxide mixed with an equal volume of hydrogen is reduced in accordance with the equation $3CO+3H_2=CH_4+H_2O+CO_2+C$ when a slow current of the mixed gases is passed, and in accordance with the equation $3CO+3H_2=CH_4+H_2O+2CO$ when a rapid stream is employed. With a mixture of 1 vol. of carbon monoxide and 3 vols. of hydrogen, a theoretical yield of methane is produced in accordance with the equation $CO+3H_2=CH_4+H_2O$. Reduction of carbon dioxide is difficult, the yields being only 20—25%. In the case of nitric oxide, the catalyst becomes incandescent at 320°, and quantitative reduction in accordance with the equation $2NO+5H_2=2NH_3+2H_2O$ occurs with a concentration of catalyst between 5% and 0·5%. No reduction occurs if the gases be passed at a rate of less than 9 litres per hr., and the reaction is too violent when it exceeds 45 litres per hr., but with a sufficiently high rate raising the temperature above 320° does not influence the yield. With nitrous oxide, when a mixture of 1 vol. of nitrous oxide and 4 vols. of hydrogen is passed at a rate of 40 litres per hr. the catalyst becomes incandescent at 330°, reduction being quantitative in accordance with the equation $N_2O+H_2=N_2+H_2O$; no trace of ammonia is produced.

J. W. B.

Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. I. M. Crespi and R. W. Lunt (*J. Chem. Soc.*, 1925, **127**, 2052—2057).—The behaviour of carbon monoxide in the corona due to alternating electric fields of frequency 250 has been investigated. It decomposes yielding a solid substance containing carbon and oxygen and a gaseous mixture of carbon monoxide and dioxide of approximately constant composition. The composition of the solid is independent of the electrical potential and varies solely with the initial pressure of the carbon monoxide. The solid is a dark brown, hygroscopic powder, having an acid reaction in aqueous solution; it is readily soluble in alcohol and sparingly soluble in ether.

E. E. W.

Anode Phenomena in the Electrolysis of Potassium Ethyl Malonate. J. B. Robertson (*J. Chem. Soc.*, 1925, **127**, 2057—2067; cf. this vol., ii, 312).—The formation of ethyl succinate on electrolysis of potassium ethyl malonate is shown to be an oxidation reaction. It takes place only when the anode is of suitable material and when its potential exceeds 2·3—2·4 volts referred to the normal hydrogen electrode standard. Grey platinum and smooth platinum anodes both favour the occurrence of synthesis, but platinised platinum and gold anodes do not. Anodes of all four materials used cause what appears to be complete oxidation of a portion of

the electrolyte. The extent of this oxidation is small with platinised platinum and still smaller with gold, but is more considerable with smooth platinum and grey platinum. E. E. W.

Photochemical Union of Hydrogen and Chlorine. R. G. W. Norrish (*J. Chem. Soc.*, 1925, **127**, 2316—2334).—The rate of combination of hydrogen and chlorine is uninfluenced by desiccation down to a water-vapour pressure of 10^{-4} mm. It approaches zero between 10^{-4} and 10^{-7} mm. (Coehn and Jung, this vol., ii, 142). It is shown that at 10^{-4} mm. the surface of the reaction vessel under the conditions of experiment was no longer completely saturated with water molecules. The photochemical dissociation of chlorine molecules occurs only at the water film covering the walls of the vessel, and the reaction spreads outwards into the gas phase by "Nernst chains," its rate being constant so long as the surface of the vessel is saturated with water molecules, but decreasing when it becomes unsaturated. The anti-catalytic effect of hydrogen and oxygen (this vol., ii, 572) is explained on the basis of this hypothesis, which is further extended to account for the observed photochemical induction period. Ammonia formed from traces of nitrogenous impurities is assumed preferentially to combine with the water film, and to require removal by photochemical reaction with the chlorine before the primary reaction can occur. Quantitative observations on the effect of the addition of known quantities of ammonia on the induction period have been made, and it is shown that its duration can be calculated from the expression $(1-b/P)apv/s$, where p and P are the pressures of ammonia and chlorine, v and s the volume and surface of the reaction vessel respectively, and a and b are constants; the expression is in agreement with the hypothesis proposed. E. E. W.

Photochemical Reaction between Bromine and Tartaric Acid in Aqueous Solution. I. J. C. Ghosh and J. Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 165—178).—The photochemical reaction between bromine and tartaric acid in aqueous solution (resulting in the formation of hydrobromic acid, carbon dioxide, and aldehydotartronic acid) has been studied for blue light (450—490 μμ). The velocity of the dark reaction is negligible, but with light of an incident intensity of 5400 ergs per cm.^{2} per sec. there is a period of induction of 120—150 mins. No induction period is observed when the reaction mixture is exposed to an intense light source. The rate of disappearance of the bromine is at first slow, reaches a maximum, and then continually falls, the velocity constants in the last portion of the curve being those of a unimolecular reaction. The velocity constant depends only on the intensity of the light and is independent of its state of polarisation. The temperature coefficient of the reaction is between 1·7 and 2·0. A photochemical after-effect was observed when the reaction mixture was exposed to intense sunlight for 5 mins. and then kept in the dark at 30°, the reaction proceeding at a velocity much greater than that observed in the ordinary photochemical reaction at the same temperature, but ceasing at the end of 1 hr. Hence an intermediate

compound of bromine and tartaric acid, in which the bromine is available for iodometric titration, must be formed initially, and this decomposes in the dark with a velocity great in comparison with that of the initial photochemical reaction. By a mathematical analysis of the reaction, it is shown that when the pressure p of the acceptor molecules (osmotic pressure) is constant (tartaric acid in excess) the curve plotted between $1/k$ and $1/p$ should be a straight line, and this is the case when the initial concentration of the bromine is $0{\cdot}0147N$, but it is not so for higher concentrations of bromine. For an infinite concentration of tartaric acid, the velocity constants of the reaction will be independent of the concentration of the photoactive component, bromine, the life period of the activated bromine molecules being less for higher initial concentrations of this component than for lower, the diminution of the velocity coefficient with increase in the initial concentration of the bromine being due to this cause. The application of Einstein's law of photochemical equivalence is discussed. J. W. B.

Photochemical Studies. V. Actinoscopic Reactions. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1925, **34**, 236—241).—The action of light in effecting the liberation of iodine from a solution of potassium iodide in the presence of potassium dichromate and eosin (cf. Straub, A., 1920, i, 896) has been investigated. The presence of both the potassium dichromate and the eosin is necessary in order that the liberation of iodine may proceed with an appreciable velocity, the latter increasing with increasing intensity of the light. No reaction occurs in the dark. Since the same amount of iodine is liberated in an atmosphere of carbon dioxide as in air, atmospheric oxidation plays no part in the reaction. J. W. B.

Formation of Active Hydrogen in the Creepage Corona Discharge. F. O. ANDEREGG and W. N. HERR (*J. Amer. Chem. Soc.*, 1925, **47**, 2429—2431).—Glass wool in the discharge space tends to increase the yield of active hydrogen. The tube exhibits fatigue effects which may be removed by discharging in nitrogen. A trace of air admitted and then swept out produced a similar result, probably due to an adsorbed film of gases on the glass, since traces of nitrogen or oxygen admitted with the hydrogen were without effect. Disuse of the tube allows it to recover very slowly from fatigue. Earthenware, flint, or platinum in the discharge space gave no appreciable yield of active hydrogen; they may promote decomposition of the active form. W. T.

Effect of Ultra-violet Light on Dried Hydrogen and Oxygen. H. B. BAKER and (MISS) M. CARLTON (*J. Chem. Soc.*, 1925, **127**, 1990—1991).—The work of Coehn and Tramm indicated that the mixture of hydrogen and oxygen dried to the point at which no explosion took place, but only slow combination on heating, would combine as readily in the dried as in the undried condition, under the action of ultra-violet light.

The work has been repeated with six pairs of quartz tubes filled with the gaseous mixture produced by the electrolysis of very

pure barium hydroxide, one of each pair containing some distilled phosphorus pentoxide. In every case, whether the drying lasted 8 weeks or 2 weeks, there was a difference in the rate of union of the dried and the wet gases. After drying for 7 weeks and 8 weeks, respectively, the dried gas gave no measurable contraction after 6¼ hrs.' and 5 hrs.' exposure to the light from a quartz mercury lamp, the comparative wet tubes showing a considerable amount of union with the same exposure. No ozone was produced in either the wet or the dry gas. E. E. W.

Decomposition of Hydrogen Peroxide. W. P. DAVEY (*Science*, 1925, **61**, 388—389).—Ditman's statement (this vol., ii, 51) on the decomposition of hydrogen peroxide by a single electrical conductor the ends of which are immersed in solutions of hydrogen peroxide and colloidal platinum, respectively, cannot be substantiated when precautions are taken to prevent contamination of the hydrogen peroxide by any agent tending to decompose it. A. A. E.

Mercury and Ionised Helium. S. C. LIND and D. C. BARDWELL (*Science*, 1925, **61**, 344—345).—No evidence could be obtained of the formation of a compound of helium and mercury when the helium was ionised by means of radon. The result, however, is not necessarily at variance with those obtained using an electrical discharge (cf. Manley, this vol., ii, 57, 314, 696; Boomer, *ibid.*, ii, 144), since electron bombardment frequently produces chemically active resonance states, which are not known to be produced by α-particles. A. A. E.

Explosions with Alkali Metals. H. STAUDINGER (*Z. Elektrochem.*, 1925, **31**, 549—551).—When an alkali metal is brought into contact with bromine or with a halogenated hydrocarbon, little or no immediate reaction takes place; but the system explodes when subjected to a minimal mechanical impact, which may be measured. Thus with chloroform the requisite priming energy is 1·5 kg. metre for lithium, 0·6 for sodium, 0·02 for potassium, and 0·0007 for sodium–potassium alloy. This latter is in general by far the most sensitive form of alkali metal. The results with various halogen compounds indicate that the limit of priming energy has no connexion with the energy of reaction. Sodium–potassium is found to explode similarly with silver halides, solid carbon dioxide, mercuric oxide, ammonium nitrate, and organic nitro compounds, and the priming energies have been measured. It is suggested that a layer of a labile unpolymerised molecular compound of alkali metal with the other substance, comparable with the primary labile peroxides of organic compounds, is first formed. This protects the metal from immediate attack, but is susceptible to explosive decomposition, which is then imparted to the whole system. W. A. C.

Lithium. V. Alkali Polybromides and Polychlorides. G. F. HÜTTIG and O. SCHLIESSMANN (*Z. anorg. Chem.*, 1925, **148**, 87—92; cf. Hüttig and Krajewski, this vol., ii, 296; Hüttig and Keller, this vol., ii, 963).—Alkali bromides were heated with excess of bromine in a bomb tube at 500—700° and the tube was cooled to the temper-

ature of liquid air. The tube was then opened, inserted in a special apparatus, evacuated, and the bromine vapour-pressure curve determined. No polybromide of lithium was found; rubidium formed a tribromide which decomposed between 30° and 90°, and ammonium formed a tribromide which was already partly decomposed at 0°. Lithium, potassium, cæsium, and calcium do not form polychlorides. A. G.

Complex Salts of Stannous Iodide with Rubidium and Cæsium Iodides. V. AUGER and T. KARANTASSIS (*Compt. rend.*, 1925, **181**, 665—666).—The double *salt*, $RbSnI_3$, is obtained as yellow needles by cooling the pale-yellow liquid obtained when stannous iodide is added to excess of a solution of rubidium iodide acidified with hydriodic acid. Cubic *crystals* of $RbSn_2I_5$ are obtained when excess of stannous iodide is used. The corresponding *cæsium* salts are prepared similarly. The dry salts are fairly stable; they oxidise in the air, partly to rubidium (or cæsium) iodostannate. S. K. T.

Systematic Doctrine of Affinity. XXXVI. Ammoniates of Cupric Halides. W. BILTZ [with H. BRÖHAN and W. WEIN] (*Z. anorg. Chem.*, 1925, **148**, 207—216; cf. this vol., ii, 1183).—Corresponding data are tabulated. The compounds investigated were: $CuCl_2,10NH_3$; $CuCl_2,6NH_3$; $CuCl_2,5NH_3$; $CuCl_2,3\frac{1}{3}NH_3$; $CuCl_2,2NH_3$; $CuBr_2,10NH_3$; $CuBr_2,6NH_3$; $CuBr_2,5NH_3$; $CuBr_2,3\frac{1}{3}NH_3$; $CuBr_2,2NH_3$; $CuI_2,10NH_3$; $CuI_2,6NH_3$; $CuI_2,5NH_3$; $CuI_2,3\frac{1}{3}NH_3$. Heats of solution of some of these compounds and of the pure halides in hydrochloric acid solutions are recorded. J. S. C.

Higher Oxides of Silver. I. Ag_2O_3. F. JIRSA [with J. JELINEK] (*Z. anorg. Chem.*, 1925, **148**, 130—140).—The decomposition of the substance $2Ag_2O_3,Ag_2O_2,AgNO_3$ (cf. this vol., ii, 314), obtained by the anodic oxidation of silver nitrate to silver nitrate, pure silver peroxide, Ag_2O_2, and oxygen, was followed by measuring the oxygen evolved; at 64·3° the higher oxide was half decomposed in about 1 hr. and at 77·6° in about 4 hrs. A summary of the literature on the higher oxides of silver is included. A. G.

Systematic Doctrine of Affinity. XXXV. Ammoniates of Aurous Halides. W. BILTZ [with W. WEIN] (*Z. anorg. Chem.*, 1925, **148**, 192—206; cf. this vol., ii, 1183).—Corresponding data for the following aurous halide ammoniates are recorded: $AuCl,6NH_3$; $AuCl,2NH_3$; $AuCl,NH_3$; $AuBr,6NH_3$; $AuBr,4NH_3$; $AuBr,3NH_3$; $AuBr,2NH_3$; $AuBr,NH_3$; $AuI,6NH_3$; $AuI,3NH_3$; $AuI,2NH_3$; AuI,NH_3. The existence of $AuCl,12NH_3$, and of $AuI,8NH_3$ is demonstrated. Heats of solution of the pure halides and of the lower ammoniates in 5% potassium cyanide solution are recorded. J. S. C.

Compounds of Gold with Carbon Monoxide. W. MANCHOT and H. GALL (*Ber.*, 1925, **58**, [*B*], 2175—2178).—Compounds of carbon monoxide with the halides of all the metals of the eighth

and of related metals of the first group of the periodic system have been described with the exceptions of cobalt, nickel, palladium, and gold. Anhydrous auric chloride combines with carbon monoxide at about 95°, giving the *product*, AuCl,CO. Very considerable reduction of auric chloride occurs simultaneously, but this can be avoided to some extent by mixing the carbon monoxide with about 10% of chlorine. The new product is extraordinarily sensitive towards moisture. Replacement of auric chloride by aurous chloride or cæsium chloroaurate brings no advantage. The bromides of gold do not yield volatile compounds with carbon monoxide. H. W.

Vaterite and μ-Calcium Carbonate. R. E. GIBSON, R. W. G. WYCKOFF, and H. E. MERWIN (*Amer. J. Sci.*, 1925, **10**, 325—333).—The material originally obtained by Vater by diffusion of calcium chloride (containing barium chloride) into potassium carbonate and named vaterite-*A*, when examined by the *X*-ray powder method, proved to be calcite. A second form (vaterite-*B*) obtained by Heide on crystallising colloidal calcium carbonate at 5°, was found by similar means to be identical with the μ-calcium carbonate of Bütschli, Spannenberg, and Rinne. The latter substance was prepared by slowly dropping solutions of calcium chloride and potassium carbonate into water (with stirring) at 60°, but better by slowly dropping a 0·1*M*-solution of calcium chloride into stirred solutions of potassium carbonate (ranging from 10 to 50 g. per 700 c.c.) maintained at 60°. A. COUSEN.

New Peroxide of Barium. (MISS) M. CARLTON (*J. Chem. Soc.*, 1925, **127**, 2180—2184).—When excess of hydrogen peroxide is added to a solution of barium hydroxide at temperatures below 20°, the hydrate $BaO_2,8H_2O$ first formed changes in appearance, forming a granular precipitate which turns buff-coloured on keeping. This substance is a cream-coloured, non-crystalline powder. It does not contain hydrogen peroxide, for this substance cannot be extracted with ether or liberated by heat. The solid substance decolorises potassium permanganate more rapidly than the oxide BaO_2; it liberates iodine from potassium iodide and bromine from potassium bromide in the presence of dilute nitric acid. It reacts with sulphur, but does not form sulphur dioxide. The substance was analysed by heating at 500—600° in a current of nitrogen, and by titrating the substance dissolved in dilute nitric acid with potassium permanganate. It is concluded that the new substance has the formula BaO_3. E. E. W.

Systematic Doctrine of Affinity. XXXIII. Ammoniates of Beryllium Halides. W. BILTZ and C. MESSERKNECHT (*Z. anorg. Chem.*, 1925, **148**, 157—169; cf. this vol., ii, 1191).—The existence of the following compounds has been demonstrated, the values of the heat of dissociation and of the total heat of formation, as calculated from tensimetric data and the values of the heats of solution of the pure halides and of the lower ammines in hydrochloric acid being tabulated: $BeCl_2,12NH_3$; $BeCl_2,6NH_3$; $BeCl_2,4NH_3$; $BeCl_2,2NH_3$; $BeBr_2,10NH_3$; $BeBr_2,6NH_3$;

$BeBr_2,4NH_3$; $BeI_2,13NH_3$; $BeI_2,6NH_3$; $BeI_2,4NH_3$. The lower ammoniates are stable compounds, dissociating only at relatively high temperatures, the dissociation being always accompanied by the formation of varying amounts of the corresponding ammonium halide. J. S. C.

Analytical-synthetic Researches on Zincite. E. DITTLER (*Z. anorg. Chem.*, 1925, **148**, 332—344).—Analytical and synthetical experiments are described with the object of determining the cause of the red colour in zincite. The conversion of zinc ore into zincite is a metamorphic change produced by carbon dioxide under pressure. Under suitable temperature conditions, it is considered that the equilibrium $3MnO+CO_2 \rightleftharpoons Mn_3O_4+CO$ is set up, and that the higher manganese oxide separates almost completely from the molten zinc oxide, leaving traces of manganites, which confer the characteristic colour to the mineral. Natural zincite melts at $1670\pm10°$; increase in the manganous and ferrous oxide contents rapidly depresses the m. p. to 1550°. S. K. T.

Systematic Doctrine of Affinity. XXXIV. Ammoniates of Cadmium and Mercury Halides. W. BILTZ and C. MAU (*Z. anorg. Chem.*, 1925, **148**, 170—191; cf. this vol., ii, 1191).—The following cadmium compounds have been investigated and the corresponding data as for the iron-group metal compounds calculated and tabulated: $CdCl_2,10NH_3$; $CdCl_2,6NH_3$; $CdCl_2,4NH_3$; $CdCl_2,2NH_3$; $CdCl_2,NH_3$; $CdBr_2,12NH_3$; $CdBr_2,6NH_3$; $CdBr_2,2NH_3$; $CdBr_2,NH_3$; $CdI_2,6NH_3$; $CdI_2,2NH_3$. Some evidence was also obtained for the existence of $CdCl_2,5NH_3$. From the values of d_4^{25}, the molecular volumes of some of these compounds are calculated.

Similar data are given for the following mercuric compounds: $HgCl_2,9{\cdot}5NH_3$; $HgCl_2,8NH_3$; $HgCl_2,2NH_3$; $HgBr_2,8NH_3$; $HgBr_2,2NH_3$; $HgI_2,6NH_3$; $HgI_2,2NH_3$; $HgI_2,4/3NH_3$. Some evidence for the existence of $HgI_2,12NH_3$ was obtained.

Of the mercurous compounds, the existence of $HgCl,NH_3$ and $HgBr,NH_3$ is definitely established, the approximate heats of formation being calculated, whilst some indication for the existence of $HgCl,5NH_3$ and $HgBr,4NH_3$ was obtained. J. S. C.

Amides of Mercurous Salts. F. FEIGL and A. SUCHARIPA (*Z. anal. Chem.*, 1925, **67**, 134—140).—The action of ammonia on mercurous chloride is usually represented by the equation $Hg_2Cl_2+2NH_3=NH_4Cl+HgNH_2Cl+Hg$. That this is not a true representation of the reaction is shown by the fact that the black product yields less mercuric chloride when treated with hydrochloric acid than corresponds with half the mercury in the mercurous chloride used. The quantity of mercury dissolved by acid increases with the age of the precipitate to a maximum of about 47·5% when the reactions are carried out at 20°, but only 16% is dissolved if the reactions are conducted at 100°, showing that an amide of mercurous chloride is first formed and that this decomposes reversibly into mercuric amidochloride and metallic mercury. The reaction therefore takes place in two stages, viz.: (1) $Hg_2Cl_2+2NH_3 \rightarrow NH_2Hg_2Cl+$

NH_4Cl and (2) $NH_2Hg_2Cl \rightleftharpoons NH_2HgCl + Hg$. Mercurous amidochloride is formed by heating an intimate mixture of the mercuric compound with metallic mercury. A. R. P.

Composition of a Precipitated Aluminium Hydroxide. J. SHIDEI (*Mem. Coll. Sci. Kyōtō*, 1925, **9**, 43—73).—Precipitated aluminium hydroxide has been alleged by a number of investigators to form a definite hydrate when kept for a long time under water. Measurements have been made of the vapour tension of precipitated alumina (kept for 17 months under water), the composition varying from $Al_2O_3,5{\cdot}639H_2O$ to $Al_2O_3,2{\cdot}544H_2O$. Mündells' differential manometer was used, giving an accuracy of 0·01 mm. The rate of dehydration at constant temperature of a number of samples of the hydrated oxide was also observed. All measurements were made at 30°, and it was found that the dehydration in a vacuum of the former hydroxide is continuous, without any sudden change in its velocity, until the composition has been reduced to $Al_2O_3,2{\cdot}494H_2O$. Further hydration would be extremely slow. The pressure of the aqueous vapour from the hydroxide in a vacuum increases rapidly at first and then gradually, taking a long time to reach equilibrium.

The vapour tensions decrease continuously with the diminution in the water content of the substance. It was concluded that the precipitated hydroxide which had been kept under water for 17 months was not a definite hydrate, but remained as an oxide absorbing water. L. L. B.

Sulphates of Neodymium and Thallous Thallium. F. ZAMBONINI and V. CAGLIOTI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 153—158; cf. this vol., ii, 222, 579).—The 25° isotherm for the system $Nd_2(SO_4)_3$–Tl_2SO_4 indicates the existence of the compounds $Nd_2(SO_4)_3,4{\cdot}5Tl_2SO_4$, $Nd_2(SO_4)_3,Tl_2SO_4,8H_2O$, and $Nd_2(SO_4)_3,Tl_2SO_4,3H_2O$. The last is in equilibrium with a solution containing 3·8% of neodymium sulphate and 0·26% of thallous sulphate, and forms minute, violet crystals. The second compound is in equilibrium with solutions containing 3·78—0·30% of neodymium sulphate and 0·28—3·0% of thallous sulphate. It is isomorphous with the double sulphates

$$X_2(SO_4)_3,(NH_4)_2SO_4,8H_2O,$$

where X=La, Ce, Di. The reddish-violet compound

$$Nd_2(SO_4)_3,4{\cdot}5Tl_2SO_4$$

is in equilibrium with solutions containing 0·26—0·19% of neodymium sulphate and 3·85—4·70% of thallous sulphate.

F. G. T.

Behaviour of Zirconium Phosphate towards Acids and Bases. J. H. DE BOER and A. E. VAN ARKEL (*Z. anorg. Chem.*, 1925, **148**, 84—86).—Zirconium phosphate is dissolved by oxalic acid, and by concentrated sulphuric and phosphoric acids; unlike hydrofluoric acid (this vol., ii, 705), these acids dissolve only the freshly precipitated or moist phosphate, and the solutions are less stable. The oxalic acid solution is decomposed by heating

or by the addition of alcohol or mineral acids, and zirconium phosphate is reprecipitated from the sulphuric or phosphoric acid solutions by dilution. Zirconium phosphate is converted into the hydroxide by alkalis, but the action is only superficial; complete dissolution may be brought about by the addition of a substance capable of dissolving the hydroxide in alkaline solution. Such substances are the aliphatic oxy-acids (*e.g.*, tartaric, malic, and lactic acids), alcohols with at least two hydroxyl groups on neighbouring carbon atoms (*e.g.*, glycerol, dextrose, sucrose, pyrocatechol, and pyrogallol), and hydrogen peroxide. The solution in hydrogen peroxide precipitates the hydroxide when heated and the perzirconate by addition of alcohol. From the other solutions the hydroxide is obtained by partial neutralisation with acid, preferably after previous precipitation of the phosphoric acid with barium chloride. Hafnium phosphate behaves similarly, but the solutions are less stable; by this means the two metals can be readily separated. A. G.

Formula of Cerium Hydride. E. J. WEEKS (*Chem. News*, 1925, **131**, 245—246).—Theoretical reasons are given to show that cerium hydride formed by heating the metal in a current of hydrogen is a mixture of Ce_2H_2 and CeH_4. A. R. P.

Ionium. I. Recovery of Ionium from Carnotite. II. Adsorption of Ionium–Thorium by Barium Sulphate. III. Ionium–Thorium Ratio in Carnotite. G. D. KAMMER and A. SILVERMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2514—2522).—The direct precipitation of ionium from an acid solution of carnotite ore is impracticable on a large scale. With large quantities of ore, precipitation with oxalic acid is unsuccessful; precipitation with hydrofluoric acid gives good results, but the precipitate is bulky and difficult to handle. Ionium is strongly adsorbed by barium sulphate, 1 g. of barium sulphate adsorbing 16% of its own weight of thorium sulphate (thorium is an isotope of ionium). Radium–barium sulphate obtained in the production of radium contains considerable ionium, which can be recovered either by fusing or by boiling the sulphates with sodium carbonate. In the commercial treatment of low-grade carnotite, most of the ionium remains in the ore residue; this can be rendered soluble by heating with sulphuric acid. Ionium can be extracted from high-grade carnotite (containing more than 15% of uranium oxide) with hydrochloric acid. The radioactive substance adsorbed by barium sulphate in addition to radium is chiefly ionium, accompanied by a small amount of actinium, and not solely actinium, as often assumed. The average Colorado carnotite contains ionium–thorium in the ratio 1 : 15·8. W. T.

Action of Gaseous Ammonia on Phosphorus Chlorides. H. PERFEROT (*Compt. rend.*, 1925, **181**, 662—664).—From a study of the solid *products*, $PCl_n,2nNH_3$, obtained by mixing solutions of pentachloride, trichloride, or oxychloride of phosphorus in carbon tetrachloride with similar solutions of ammonia, it is concluded

that the primary action of gaseous ammonia on these chlorides proceeds according to the general equation: $PCl_n+2nNH_3=PCl_n,2nNH_3=P(NH_2)_n+nNH_4Cl$. S. K. T.

Reduction of Inorganic Halides. IV. Tantalum Pentachloride. O. Ruff and F. Thomas (*Z. anorg. Chem.*, 1925, **148**, 1—18; cf. A., 1921, ii, 508; 1923, ii, 868).—Tantalum pentachloride is reduced to lower chlorides when heated with red phosphorus, tin, magnesium, lead, zinc, or aluminium, but is not reduced by sulphur, antimony, arsenic, bismuth, or mercury. Reduction by aluminium was more fully investigated, the reaction mixture being heated at 300° in an evacuated bomb tube. At this temperature complete reduction to metallic tantalum did not occur, even with excess of aluminium. A chloride of the composition $TaCl_4$ was obtained when somewhat less than the calculated amount of aluminium for reduction to this stage was taken, and the aluminium chloride and excess of tantalum pentachloride were distilled off at 250°. It is uncertain whether this is a compound of quadrivalent tantalum or whether it is a complex of tri- and penta-chlorides. On further heating, more pentachloride is lost and the residue becomes progressively richer in tantalum. Thus at 350—400° the trichloride is obtained and at 600° the dichloride, these being definite compounds, and at 680—700° the proportion of tantalum is still higher and the product is pyrophoric. The dichloride dissolves in water with evolution of hydrogen and formation of an oxychloride of tervalent tantalum, and is thus distinguished from the trichloride, which dissolves without evolution of gas. In alkaline solutions, both chlorides are oxidised to the quinquevalent state with evolution of hydrogen, the measurement of which is a convenient method of determining the state of oxidation of the tantalum. When the pentachloride, prepared by chlorinating the pentoxide, is sublimed in a vacuum at 500° an *oxychloride*, TaO_2Cl, is obtained. A. G.

Reduction of Inorganic Halides. V. Derivatives of Tantalum Trichloride. O. Ruff and F. Thomas (*Z. anorg. Chem.*, 1925, **148**, 19—24; cf. preceding abstract).—When a tantalum trichloride solution is evaporated under reduced pressure with hydrochloric acid a crystalline salt is obtained which is formulated as $Ta_3^{III}Cl_7O,3H_2O$. Lindner and Feit (A., 1924, ii, 768) proposed the formula $(HTa_3^{II}Cl_7,H_2O),3H_2O$, believing it to contain bivalent tantalum on the basis of valency determinations by oxidation with permanganate and reduction of silver. Both these methods are, however, untrustworthy, and measurements of the hydrogen evolved when the substance is oxidised to the quinquevalent state in alkaline solution (see preceding abstract) show that the tantalum is tervalent. Only 3 mols. of water are lost when it is heated, and the evolution of hydrochloric acid on further heating is ascribed to traces of water having been retained. The formulæ of the derivatives described by Lindner and Feit require similar modification. A. G.

Bismuth Trihydride and Silver Bismuthide. E. J. Weeks and J. G. F. Druce (*Nature*, 1925, **116**, 710).—When heated in a vacuum, bismuth dihydride decomposes thus: $3Bi_2H_2=4Bi+2BiH_3$; when heated in hydrogen, the reaction is $2Bi_2H_2+H_2=2BiH_3+2Bi$. The bismuth trihydride was detected by interaction with silver nitrate solution, whereby a black precipitate of silver bismuthide is produced: $BiH_3+3AgNO_3 \rightleftharpoons 3HNO_3+BiAg_3$.

A. A. E.

Effect of Vacuum and of Heat on the Neutral and Basic Bismuth Nitrates. Determination of Water of Constitution and of Nitric Acid in these Salts. Picon (*Compt. rend.*, 1925, **181**, 516—518).—A glass T-tube was connected with a mercury pump; in one arm was placed phosphorus pentoxide, and in the other, one of the bismuth nitrates which were to be dehydrated. After evacuation, the T-piece was sealed. In order to minimise loss of nitric acid, the arm containing the neutral salt was cooled to −80° during evacuation. The nitric acid was determined by Dumas' method, and by titration with ferrous salts, which alone among volumetric methods gave consistent results. The neutral nitrate yielded the compound $Bi_2(NO_3)_6,3H_2O$, which retained its water after 6 months' drying. The nitrate, $Bi(OH)_2NO_3$, gave the compound $12(BiO,NO_3),5H_2O$. Another nitrate, $18(BiO,NO_3),Bi_2O_3,7H_2O$, yielded the compound

$$18(BiO,NO_3),Bi_2O_3,6H_2O.$$

The salt $10(BiO,NO_3),Bi_2O_3,8H_2O$ lost 4 mols. of water.

The same salts (with the exception of the neutral nitrate which decomposed) were heated at 100° for 10 days. Salts containing 6, 2·45, and 4·87% of water lost 3·64, 0·5, and 2·85%, respectively, leaving products agreeing well with those obtained by vacuum desiccation. The neutral nitrate cannot be completely dehydrated by phosphorus pentoxide without decomposing, and the effect of heat on this salt is complex.

R. A. M.

Acid Nature of some Derivatives of Sulphur, Selenium, and Tellurium. D. D. Karve (*J. Indian Chem. Soc.*, 1925, **2**, 128—141; cf. this vol., ii, 633).—The Hantzsch criteria for pseudo-acids, viz., comparison of the absorption spectra of the acid, its salts and esters in various solvents, the velocity of reaction with ethyl diazoacetate, the velocity of inversion of sucrose in concentrated solution, and the action of the indicator, dimethylamino-azobenzene, have been used to investigate the acid properties of several derivatives of sulphur, selenium, and tellurium. The main conclusions are as follows: methyl- and ethyl-sulphuric acids are true acids $[RO\cdot SO_3]H$ in dilute aqueous solution, but react as pseudo-acids, $RO\cdot SO_2\cdot OH$, in dilute alcoholic and concentrated ethereal solutions. Selenious acid in the pure condition and in relatively concentrated alcoholic solutions, is an associated pseudo-acid, aqueous solutions containing a large proportion of the pseudo-acid and only a very small percentage of the hydrate of the true (monobasic) acid. Selenic acid (98%) is a true acid, $[HSeO_4]H$, and in water and alcohol forms the true oxonium salt,

$$[HSeO_4]\cdot H_2OR \ (R=H \text{ or Et}),$$

salt formation increasing with dilution. Benzenesulphinic acid is a pseudo-acid in the solid state, in alcoholic solution (50 mols.), and in more concentrated ethereal solution, but in aqueous solution it is present as a true acid. Ethylsulphinic acid is a weaker acid than the phenyl derivative (but is still stronger than sulphurous acid) and in 12·5 mols. of alcohol and 4·5 mols. of ether exists entirely as the pseudo-acid. Ethylseleninic acid is present as a pseudo acid even in aqueous solution. Tellurous acid is a very weak pseudo-acid and its salts can be titrated directly with strong acids. All three telluric acids (cf. Mylius, A., 1901, ii, 550) were investigated. Ordinary telluric acid is inactive towards ethyl diazoacetate and the indicator, and therefore possesses the formula $Te(OH)_6$; *allo*telluric acid is a true acid, but pure telluric acid, H_2TeO_4, is represented as a pseudo-acid of the constitution $(OH)_2Te\leqslant^{O}_{O}$. J. W. B.

Constitution of the Thionic Acids. I. Vogel (*J. Chem. Soc.*, 1925, **127**, 2248—2249).—The following formulæ are proposed for the thionic acids: dithionic acid, $OH{\cdot}SO_2{\cdot}SO_2{\cdot}OH$; trithionic acid, $S{:}(SO_2{\cdot}OH)_2$; tetrathionic acid, $S{:}S{:}(SO_2{\cdot}OH)_2$; pentathionic acid, $S{:}S{:}S{:}(SO_2{\cdot}OH)_2$. These formulæ explain the formation of tri-, tetra-, and penta-thionic acids from sulphur sesquioxide (this vol., ii, 890) in various circumstances, the liberation of two atoms of sulphur from pentathionates by bromine and by mercuric cyanide, the conversion of tetrathionates into pentathionates by acidified thiosulphate solution, and other reactions and properties of these acids. E. E. W.

Polythionates. I. Decomposition of Polythionates in Aqueous Solution. A. Kurtenacker and M. Kaufmann (*Z. anorg. Chem.*, 1925, **148**, 43—57).—The decomposition of aqueous solutions of polythionates has been followed by the analytical methods previously described (this vol., ii, 239, 434). Potassium trithionate decomposes according to the equations: $S_3O_6''+H_2O=S_2O_3''+SO_4''+2H^{\cdot}$ and $S_2O_3''+S_3O_6''+H^{\cdot}=S_4O_6''+SO_3H'$. Sulphur is not precipitated and only a little pentathionate is formed; this occurs at a later stage of the reaction and probably according to the equation: $5S_2O_3''+6H^{\cdot}=2S_5O_6''+3H_2O$. In acid solution, decomposition is much more rapid and a third reaction takes place, namely, the decomposition of thiosulphuric acid: $S_2O_3''+H^{\cdot}=HSO_3'+S$. Both the tetra- and penta-thionate are much more stable than the trithionate. The pentathionate decomposes according to the equation $S_5O_6''=S_4O_6''+S$, and the mixture of thionates resulting from this reversible reaction is, as shown by Debus (T., 1888, **53**, 278), highly stable. The tetrathionate also tends to form this stable mixture, and the necessary sulphur is obtained by the decomposition of a part of the tetrathionate to trithionate: $S_4O_6''=S_3O_6''+S$. Tri- and penta-thionate do not react to form tetrathionate, $S_3O_6''+S_5O_6''=2S_4O_6''$, even in acid solution, but trithionate, or its decomposition products, accelerates the decomposition of pentathionate to tetrathionate and sulphur. A. G.

Polythionates. II. Influence of Thiosulphate and Sulphite on the Stability of Polythionates. A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem.*, 1925, **148**, 225—234; cf. preceding abstract).—The decomposition of aqueous solutions of the alkali trithionates is only slightly influenced by the presence of sulphites or thiosulphates. Addition of thiosulphate to tetra- or penta-thionate solutions results in an increased rate of decomposition, the effect being catalytic in that the thiosulphate concentration remains unaltered. The experimental data in the case of tetra-thionate solutions are in excellent agreement with the following reaction schemes: (i) $S_2O_3'' \rightleftarrows SO_3''+S$; (ii) $S_4O_6''+S \rightleftarrows S_5O_6''$; (iii) $SO_3''+S_4O_6''=S_3O_6''+S_2O_3''$, the reaction products being mainly tri- and penta-thionate. The catalytic action of thio-sulphate in the decomposition of pentathionate solutions is likewise due to its tendency to lose sulphur according to scheme (i) above. The accelerating action of sulphites is due to the formation of thiosulphate according to the equations: $S_4O_6''+SO_3'' \rightleftarrows S_3O_6''+S_2O_3''$; $S_5O_6''+SO_3'' \rightleftarrows S_4O_6''+S_2O_3''$. J. S. C.

Polythionates. III. Action of Hydrogen Sulphide on Polythionates. A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem*, 1925, **148**, 256—264; cf. preceding abstract).—The course of the extremely slow reaction between hydrogen sulphide and trithionate is represented satisfactorily by the equations $S_3O_6''+H_2S=2S_2O_3''+2H^{\cdot}$; $S_2O_3''+2H_2S+2H^{\cdot}=3H_2O+4S$. The rate of reaction is retarded in presence of acid. The rate of the more rapid reaction between hydrogen sulphide and tetrathionate also decreases with increasing acidity. In neutral solution, the course of the reaction is represented by the equations: $S_4O_6''+H_2S=2S_2O_3''+S+2H^{\cdot}$; $S_2O_3''+2H_2S+2H^{\cdot}=3H_2O+4S$; $5S_2O_3''+6H^{\cdot}=2S_5O_6''+3H_2O$. The presence of small quantities of trithionate is ascribed to the action between thiosulphate and undecomposed tetrathionate (*loc. cit.*). In acid solution, only the first and third of the above reactions occur, sulphur and pentathionate being the principal reaction products. J. S. C.

Polythionates. IV. Action of Alkali on Polythionates. A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem.*, 1925, **148**, 369—381).—Potassium trithionate is decomposed fairly rapidly by concentrated alkali solutions: $2S_3O_6''+6OH'=S_2O_3''+4SO_3''+3H_2O$ (Fordos and Gélis, *J. pr. Chem.*, 1850, **50**, 86). The decomposition is slower in the case of dilute alkali and probably follows the equation $S_3O_6''+2OH'=S_2O_3''+SO_4''+H_2O$ (cf. Foerster and Hornig, A., 1923, ii, 23). Tetrathionates are decomposed by dilute alkali at the ordinary temperature according to the equation: (*a*) $4S_4O_6''+6OH'=5S_2O_3''+2S_3O_6''+3H_2O$ (Thatcher, A., 1904, ii, 395). Pentathionate solutions are decomposed slowly by cold dilute alkalis. The primary reaction is: $S_5O_6'' \rightleftharpoons S+S_4O_6''$; the tetrathionate then probably decomposes thus: (*b*) $2S_4O_6''+6OH'=3S_2O_3''+2SO_3''+3H_2O$; (*c*) $2S_4O_6''+2SO_3''=2S_3O_6''+2S_2O_3''$, *i.e.*, according to (*a*) above. The sulphur, which redissolves, may react with some of the sulphite produced in (*b*): S+

$SO_3'' = S_2O_3''$, or, more probably, with excess of alkali: $4S + 6OH' = 2S'' + S_2O_3'' + 3H_2O$, the sulphide then reacting with the trithionate formed in (*b*): $S_3O_6'' + S'' = 2S_2O_3''$. The net reaction producing thiosulphate, besides (*b*), is: $2S_5O_6'' + 6OH' = 5S_2O_3'' + 3H_2O$. Boiling, concentrated alkali decomposes pentathionates with formation of sulphide, since the former also decomposes the trithionate. The analytical methods of Riesenfeld and Feld (A., 1922, ii, 45) are modified; they give approximately correct results, although the indefinite end-points and the formation of sulphide in the case of pentathionates are drawbacks. S. K. T.

Selenium as Chloride Carrier. O. and C. A. Silberrad (*J. Chem. Soc.*, 1925, **127**, 2449—2450).—In addition to acting catalytically as a chlorine carrier in the chlorination of toluene by sulphuryl chloride (cf. this vol., i, 1137), selenium also acts similarly in the direct chlorination of toluene by chlorine both in the presence and absence of light. Just as with sulphuryl chloride, it accelerates substitution in the nucleus and decreases it in the side-chain. E. E. W.

Reduction of Tungstates. V. I. Spitzin (*Z. anorg. Chem.*, 1925, **148**, 69—83).—Tungstates may be reduced to constant weight by hydrogen at 650—700°, and it is shown quantitatively that the products from the ditungstate, $Na_2W_2O_7$, paratungstate, $Na_{10}W_{12}O_{41}$, tetratungstate, $Na_2W_4O_{13}$, and pentatungstate, $Na_2W_5O_{16}$, are, in every case, mixtures of sodium tungstate, Na_2WO_4, and tungsten. Above 700° a further loss in weight takes place, and at 900° each of the above acid tungstates and also sodium tungstate are reduced to tungsten. The various tungsten bronzes are also reduced to sodium tungstate and tungsten at 650—700°. The blue bronze, $Na_2W_5O_{15}$, is reduced successively to the violet, $Na_2W_4O_{12}$, the red, $Na_2W_3O_9$, and the yellow bronzes, $Na_2W_2O_6$; this reduction takes place comparatively slowly at 550° and rapidly at 650°, but at no temperature does reduction cease at any intermediate stage. The formation of bronzes by the reduction of acid tungstates is believed to take place according to equations of the type: $Na_2W_4O_{13} + H_2 = Na_2W_4O_{12} + H_2O$; $Na_2W_4O_{12} + 3H_2 = Na_2W_3O_9 + W + 3H_2O$. In this case, the molecule of bronze could never contain more atoms of tungsten than that of the tungstate from which it was prepared. This, however, is sometimes the case, but this is ascribed to impurities in the tungstate; thus sodium tetratungstate yields a blue bronze, but the metatungstate, $Na_2W_4O_{13},10H_2O$, which can be purified by crystallisation from water, yields the violet bronze. A. G.

Systematic Doctrine of Affinity. XXXII. Higher Ammoniates of Halides of the Iron Group. W. Biltz [with E. Rahlfs] (*Z. anorg. Chem.*, 1925, **148**, 145—151).—The existence of the following compounds has been demonstrated: $MnCl_2,12NH_3$; $MnCl_2,10NH_3$; $FeCl_2,10NH_3$; $CoCl_2,10NH_3$; $MnBr_2,10NH_3$. From tensimetric and thermal data the values of the heat of dissociation, the total heat of formation, and the temper-

ature at which $p_{NH_3}=100$ mm. have been calculated and are tabulated. These numbers are considered in relation to the corresponding data for the corresponding hexammine derivatives (A., 1915, ii, 465; 1920, ii, 318). The properties of cobaltous decamminechloride differ from those described by Clark, Quick, and Harkins (A., 1921, ii, 116). J. S. C.

Action of Sodium Chloride on Ferrous Metals. R. GIRARD (*Compt. rend.*, 1925, **181**, 552—555).—Plates of cast iron or steel were immersed in air-free or aërated solutions of sodium chloride. Steel suffered corrosion in both cases, whilst cast iron was affected only in air-free solutions, and in aërated solutions was partially protected by a coating of adhering ferric substances. [Cf. *B.*, 1925, 961.] R. A. M.

Various States of Beryllium Oxide. H. COPAUX and C. MATIGNON (*Compt. rend.*, 1925, **181**, 550—552).—The loss of weight of basic beryllium carbonate has been determined at different temperatures. The decomposition is practically complete at 500—550°, but further small decreases in weight occur at higher temperatures. The oxide prepared by calcination has d^{775} 2·876, d^{875} 2·926, and d^{1100} 3·010. The oxide obtained at 800° is much more readily soluble in hydrofluoric acid than is the product obtained at 1100°. The heat of solution of the former product in hydrofluoric acid is 22·06 cal. (mean) and for the more strongly heated oxide it is 22·28 cal. Although the small difference is in the sense opposite to that expected on theoretical grounds, it is considered that it may be real. Basic beryllium carbonate requires heating to about 1000° before a definite state is attained. R. A. M.

Reaction between Ferric Sulphate and Alkali. A. KRAUSE (*Z. anorg. Chem.*, 1925, **148**, 265—278).—Experiments in which varying amounts of alkali (sodium hydroxide, potassium hydroxide, ammonia, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, and aniline) were added to a fixed volume of ferric sulphate solution, show that the value of the ratio $[Fe_2O_3]/[SO_3]$ of the precipitate obtained is related to the p_H value of the resulting solution by an equation of an exponential type, a sulphate-free precipitate being obtained only when this p_H value exceeds 7·7. On adding the theoretical quantities of sodium hydroxide, ammonia, and sodium carbonate, the values of the $[Fe_2O_3]/[SO_3]$ ratio are 24·0, 11·1, and 8·8, respectively. The anomalous behaviour of ammonia, which in the more acid solutions functions as a strong base, is discussed. J. S. C.

Potentiometric Indication in the Action of Halogens on Ferrocyanides. C. DEL FRESNO (*Anal. Fis. Quím.*, 1925, **23**, 427—437).—The oxidation of ferrocyanides to ferricyanides in solution by chlorine and by bromine can be followed potentiometrically. Owing to the instability of aqueous solutions of chlorine and bromine, the method is not of practical importance. In the case of iodine, oxidation is complete only in the presence of an excess of the halogen. G. W. R.

Oxidation of Complex Sulphites of Tervalent Cobalt. G. SCAGLIARINI and G. TARTARINI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 191—194).—By oxidising, by means of a current of air, a solution containing the complex salt, $[Co(NH_3)_6][Co(SO_3)_3(H_2O)_3]$, the sulphite radicals may be oxidised to sulphate groups. It is suggested that the oxidation is progressive, giving the anions, $[Co(SO_3)_2(SO_4)(H_2O)_3]'''$, $[Co(SO_3)(SO_4)_2(H_2O)_3]'''$, and $[Co(SO_4)_3(H_2O)_3]'''$.

The first and last stages of this process have been realised by the preparation of *hexamminecobaltictriaquodisulphitosulphatocobaltiate*, $[Co(NH_3)_6][Co(SO_3)_2(SO_4)(H_2O)_3]$, and of *triaquotriamminecobaltictriaquotrisulphatocobaltiate*, $[Co(NH_3)_3(H_2O)_3][Co(SO_4)_3(OH_2)_3]$. The former is obtained as golden-yellow crystals by the atmospheric oxidation of a solution of ammonium carbonate in a solution of cobalt sulphite saturated with sulphur dioxide. From concentrated solutions, the second salt is deposited. F. G. T.

Compound of Rhodium with Carbon Monoxide. W. MANCHOT and J. KÖNIG (*Ber.*, 1925, **58**, [*B*], 2173—2174).—Hydrated rhodium chloride is converted by carbon monoxide preferably at 140° into the *compound*, $Rh_2OCl_2,3CO$, m. p. 125·5°, decomp. 300°. Anhydrous rhodium chloride does not appear to react with carbon monoxide. H. W.

Synthesis of Cristobalite in the Wet Way. R. WEIL (*Compt. rend.*, 1925, **181**, 423—424).—Precipitated silica was heated for 200 hrs. at 650—750° in a steel tube with water containing a little sodium silicate. A mixture of quartz and cristobalite in varying proportions was obtained, lower concentration giving a greater proportion of the latter. Below 650°, no cristobalite was formed. The crystals were about 0·05—0·1 mm. in length; the transition point was about 250°. E. B. L.

Preparation of Pure Metallic Titanium, Zirconium, Hafnium, and Thorium. A. E. VAN ARKEL and J. H. DE BOER (*Z. anorg. Chem.*, 1925, **148**, 345—350).—By passing the metal chloride vapour mixed with nitrogen, or carbon monoxide, etc., over a heated tungsten filament all the possible nitrides, carbides, sulphides, selenides, and phosphides of the above metals were prepared. The pure metals are formed as thick layers on the filament when the vapours of the iodides of these metals are used unmixed with other gases. Zirconium thus prepared is soft and ductile, but has the same space-lattice as ordinary zirconium; hafnium is denser, melts at a higher temperature, and has a higher electron emission than zirconium. Thorium and titanium are ductile. The pure metals obtained by Weisz's method (D.R.-P. 314791) may contain nitride, carbide, and oxide. The "metals" obtained by Fischvoigt and Koref (*Z. tech. Phys.*, 1925, **6**, 296) probably consist of nitrides, carbides, or suboxides, owing to the use of impure hydrogen. S. K. T.

Direct Reading Spectrophotometer. C. W. KEUFFEL (*J. Opt. Soc. Amer.*, 1925, **11**, 403—410).—A direct-reading spectrophoto-

meter combining a constant deviation spectrometer with its wavelength scale, and a direct-reading rotating disc photometer with its photometric scale, are described. The method of adjustment is described, and the probable precision of measurement discussed. A. E. M.

Constricted Mercury Arc as a Source of Light for Photochemical Work. G. S. FORBES and G. R. HARRISON (*J. Amer. Chem. Soc.*, 1925, **47**, 2449—2454).—The intensity, steadiness, economy, convenience, efficiency, and life of the water-cooled, constricted-column, mercury-vapour lamp run at atmospheric pressure are discussed in comparison and contrast with the standard vertical sealed electrode commercial lamp. The only disadvantage of the constricted lamp is its more rapid deterioration, but this is not serious, as the design of the lamp is such that it can be emptied, cleaned, and refitted in a very short time. W. T.

Methods of Studying the Chemical Effects of Electric Sparks on Gases at Low Pressures. P. JOLIBOIS (*Compt. rend.*, 1925, **181**, 608—610).—A simple apparatus is described with which measurements may be made of the pressure changes caused by the passage of sparks, of known energy content, through gases maintained at low temperatures. F. G. T.

Non-polarisable Electrodes for Physiological Purposes. H. C. STEVENS and E. KARRER (*J. Opt. Soc. Amer.*, 1925, **11**, 423—426).—A zinc–zinc sulphate electrode specially adapted for use in nerve-stimulating experiments is described. The cell possesses the advantages of being non-polarisable, preventing undue diffusion of the stimulating current, stimulating symmetrically around a nerve, and being capable of application to a nerve without the necessity of severing the end. A simple modification for stimulating small muscle areas is described. A. E. M.

Automatic Recorder for Measuring Size-frequency Distribution of Grains. R. H. LAMBERT and E. P. WIGHTMAN (*J. Opt. Soc. Amer.*, 1925, **11**, 393—402).—A simple automatic photographic method for determining the weight or size distribution of particles in a sedimenting liquid has been developed. The principle consists in the photographing of the liquid in the capillary of the sedimentation tube. The error in the Ostwald–Hahn–Kelley sedimentation process has been shown to be the lag in the flow of liquid in the capillary due to its viscosity and a method for its correction has been developed. By the method of calibration other sources of error are eliminated. A. E. M.

Gas Circulating Apparatus. A. R. PEARSON and J. S. G. THOMAS (*J. Chem. Soc.*, 1925, **127**, 2450—2451).—Gas is circulated through a closed system by an oscillating column of mercury combined with an arrangement of glass valves acting as in a force pump. The principle of the hot air engine is utilised to keep the mercury oscillating in a U-tube, the closed end of which is connected with a glass bulb heated by a burner. E. E. W.

Fat-free Mercury Valve with Porous Glass Plates. A. STOCK (*Ber.*, 1925, **58**, [*B*], 2058—2060).—A new type of valve is described in the two arms of which glass plates pervious to gases but impervious to mercury are sealed. The trouble arising from the sticking of the glass floats in the otherwise similarly-constructed gas valve (cf. Stock and Priess, A., 1915, ii, 339) is thus avoided. H. W.

Purification of Phosphoric Oxide. H. WHITAKER (*J. Chem. Soc.*, 1925, **127**, 2219—2221; cf. T., 1922, **121**, 692).—An improved apparatus is described for purifying phosphoric oxide by distillation in a current of oxygen. The improvements facilitate the introduction of phosphoric oxide into the retort tube, and the collection of the sublimate in a storage bottle, whereby transference from the receiver is avoided. E. E. W.

Liquid Hydrogen Sulphide as a Source of Laboratory Supply of the Gas. C. J. MOORE (*Ind. Eng. Chem.*, 1925, **17**, 1223).—The use of liquid hydrogen sulphide in cylinders for laboratory purposes is cheaper and more convenient than production of the gas in a generator. A gasometer is used in place of a reducing valve. No danger exists of the development of excessive pressure through dissociation. [Cf. *B.*, 1925, 917.] C. I.

Mineralogical Chemistry.

Helium in Earth Gases of Petrol Sources. J. CLAY (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 529—530).—The helium content of a number of samples of petroleum gas from different parts of India varies from 0·0006% to 0·0033%. The gases were first carefully freed from hydrogen by burning with a large excess of oxygen in a Drehschmidt capillary tube; the oxygen was removed by pyrogallol, the carbon dioxide by potassium hydroxide, and the remaining gases by coconut charcoal at the temperature of liquid air. The final residue, measured in a MacLeod gauge and tested spectroscopically, was found to be helium. M. S. B.

Siliceous Matter in Quaternary Clays. A. DEMOLON (*Compt. rend.*, 1925, **181**, 673—675).—Investigation of the loss of water on heating, base exchange, and adsorption of lime by quaternary clays, indicates that the aluminosilicates are the most important constituents of these clays and that they are to be classed as zeolithic silicates with a kaolinic nucleus as distinguished from true kaolinite. (Cf. *ibid.*, 1925, **180**, 1518.) S. K. T.

Composition of the Ash Evolved from the Volcano Acatenango in Guatemala on June 12th, 1925. A. GUTBIER and H. BRINTZINGER [with W. BUBAM] (*Z. anorg. Chem.*, 1925, **148**, 141—144).—Analysis gave the following results: Si, 28·37; P, 0·04; Ti, 0·29; F, trace; Cu, trace; Al, 10·51; Fe, 4·22; Ca, 4·56; Sr, 0·06; Mg, 0·48; K, 0·69; Na, 3·84%. The composition is

deduced to be: SiO_2, 60·45; P_2O_5, 0·09; TiO_2, 0·48; F, trace; CuO, trace; Al_2O_3, 19·72; $FeO+Fe_2O_3$, 6·02; CaO, 6·38; SrO, 0·07; MgO, 0·79; K_2O, 0·83; Na_2O, 5·17%. It is thus similar to the dust evolved from Santa Maria in Guatemala in 1902 (*U.S. Bull.*, 1903, **228**, 273), and is notably poor in phosphates and potassium.

A. G.

Buttgenbachite, a New Mineral. A. Schoep (*Compt. rend.*, 1925, **181**, 421—423).—The mineral consists of sky-blue crystals found in the Belgian Congo. Its physical properties are described; its chemical composition is: water 17·34, CuO 71·56, Cl 6·02, N_2O_5 5·40%, corresponding with the formula

$$18CuO,3Cl,N_2O_5,19H_2O.$$

E. B. L.

Analytical Chemistry.

Continuous Reading Hydrogen-ion Meter. K. G. Goode (*J. Amer. Chem. Soc.*, 1925, **47**, 2483—2488; cf. A., 1922, ii, 307).—To avoid the use of a telescope and scale for titration work, a device is described which, by making use of the three-electrode vacuum tube as a voltmeter, and as a direct current amplifier, serves to indicate on the scale of milliammeter the potential between any two electrodes ordinarily used in electrochemical work. This device does not draw an appreciable current from the source to be measured and is continuous and automatic in its action. W. T.

Highly Sensitive Congo Paper. F. W. Horst (*Z. angew. Chem.*, 1925, **38**, 947).—In preparing highly sensitive Congo paper the last traces of foreign dyes must be eliminated, the dye solution must contain no fixed alkali, and the dyeing of the paper must be clean and uniform. The commercial dye is dissolved in hot water, the solution filtered, and the dye reprecipitated by careful addition of pure sodium chloride. The purified dye is again dissolved in water and the dye acid precipitated by addition of dilute hydrochloric acid. After decantation and filtration, the dye acid is dissolved in hot water containing ammonia, and the paper drawn several times through the dilute solution (1—1·5 g. per litre) and finally washed off with cold distilled water. Congo paper so prepared gives a distinct blue colour with a 1/3000 *N*-mineral acid.

W. T. K. B.

Evaluation of Chlorates. E. C. Wagner (*Ind. Eng. Chem.*, 1925, **17**, 1183—1186; cf. A., 1924, ii, 563).—The methods compared were: Bunsen's evolution method (improved by the use of a new receiver obviating the need of transferring the liquid before titration); Ditz's iodometric method; Kolb and Davidson's iodometric method; the ferrous sulphate excess method; reduction to chloride by ignition with ammonium chloride; reduction to chloride by evaporation with hydrochloric acid; reduction to chloride by sulphurous acid, and precipitation as silver chloride.

All the methods investigated gave accurate results, with the

exception of that of Kolb and Davidson, the results from which were consistently about 0·4% too high. L. L. B.

Reduction of Chloric Acid and Chlorates by Ferrous Sulphate. C. O. HARVEY (*Analyst*, 1925, **50**, 538—543).—Reduction of chloric acid and chlorates in the presence of ferrous sulphate is most complete in acid solution in the presence of potassium iodide. By determining the liberated iodine volumetrically at 45°, a completeness of reaction of 99·2% of theory may be obtained, which is reduced to 97·2% in the absence of potassium iodide. Using a gravimetric determination at 100°, 96·8% is obtained in neutral solution, rising to 98·9% in acid solution at the same temperature. [Cf. *B.*, 1925, 988.] D. G. H.

Determination of Hypoiodite and Iodate, Hypobromite and Bromate, and Bromate and Iodate in the Presence of Each Other. E. SCHULEK (*Z. anal. Chem.*, 1925, **67**, 142—147).—The solution containing hypoiodite and iodate is treated with phenol to destroy the hypoiodite and, after saturation with carbon dioxide, potassium iodide is added, followed by an excess of 10% sulphuric acid; the liberated iodine, which corresponds with the iodate present, is titrated with thiosulphate. In a second portion, the two acids are determined together iodometrically in the usual way. A similar procedure serves for the determination of hypobromite and bromate in the same solution. For the determination of bromate and iodate in mixtures, the sum of the two acids is ascertained by measuring the iodine liberated from potassium iodide by a portion of the mixture, reducing a second portion to bromide and iodide by boiling with sulphur dioxide and determining the iodide formed by the method previously described (this vol., ii, 712). A. R. P.

Presence of Iodate in Surface Waters. C. F. HICKETHIER and A. JACOBUCCI (*Z. anal. Chem.*, 1925, **67**, 129—134).—The surface waters of the northern part of the province of Santa Fé, Argentine Republic, contain traces of iodate (0·13—0·38 part per million), indicating that this region is the remains of an inland sea of the tertiary period. Iodates interfere in Trommsdorf's test (zinc iodide–starch paper) for nitrites, but not in those of Ilosva and Rodillon (neutral-red). A. R. P.

Use of Hydrazine Sulphate in Iodometry. E. CATTELAIN (*J. Pharm. Chim.*, 1925, [viii], **2**, 387—391).—Hydrazine sulphate is a more satisfactory standard for iodometry than sodium thiosulphate, as it is anhydrous and readily purified and yields stable aqueous solutions. In the presence of sodium acetate iodine oxidises it quantitatively with evolution of nitrogen if a large excess is used. The excess is then titrated with thiosulphate. A. R. P.

Electrometric Titration of Fluorides. W. D. TREADWELL and A. KÖHL (*Helv. Chim. Acta*, 1925, **8**, 500—507).—The method of Greeff (A., 1913, ii, 975), based on the production of the compound Na_3FeF_6 using potassium thiocyanate as indicator, is not suitable for the determination of small quantities of fluorides. By using a potentiometric end-point in the titration, quantities of

fluorine as small as 5 mg. can be determined to 0·5 mg. The solution is neutralised, saturated with sodium chloride, diluted with an equal volume of ethyl alcohol, and titrated with 0·03*N*-ferric chloride solution containing 1% of ferrous chloride, using a platinised platinum electrode and silver chloride electrode for comparison, the solution being stirred throughout the titration by means of a rapid stream of carbon dioxide. The end-point is determined graphically from the observed readings of a millivoltmeter. Using a microburette small quantities may be determined to 0·1 mg. The use of chromous, vanadous, zirconium, or aluminium salts in place of iron for the titration does not give so satisfactory a method. G. M. B.

Qualitative Test for Oxygen. H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1925, [ii], **111**, 62—64; cf. this vol., ii, 238).—Nitric oxide, prepared by dropping saturated aqueous sodium nitrite into a solution of ferrous sulphate in concentrated hydrochloric acid, and purified by shaking with a solution of pyrogallol (2·5 g.) in aqueous potassium hydroxide (100 c.c.; *d* 1·05), is drawn into a wide-necked bottle containing water (1 c.c.) from which the air has previously been evacuated at 20—30°, and on the inside of the wall of which has been placed a drop of a solution of diphenylamine (1 g.) in sulphuric acid (75 c.c.) and water (25 c.c.), a small piece of filter-paper being held on the wall by the latter solution. The inlet tube of the bottle has connexions for barometer, filter-pump, nitric oxide, and the gas to be tested. The pressure of the nitric oxide in the bottle should not be more than 400 mm., and the filter-paper should not assume a blue colour in less than 2 mins. The gas under test is then admitted, the presence of oxygen being evidenced by the development of the usual blue coloration on the filter-paper. A dilute acetic acid solution of α-naphthylamine and sulphanilic acid may be substituted for the above diphenylamine solution. F. G. W.

Determination of Molecular Oxygen in Aqueous Solution in the Presence of Nitrous Acid. G. ALSTERBERG (*Biochem. Z.*, 1925, **159**, 36—47).—Nitrous acid, which causes considerable errors in the determination of dissolved oxygen by Winkler's method, may be removed by sodium azide. When present in a concentration of $<0·0001\%$ (as when dealing with biological material) a sufficient quantity of azide is added to the sulphuric acid solution of the manganese hydroxide precipitate. If nitrous acid is present in greater concentration, the azide is added in a concentration of 0·5% simultaneously with the alkaline potassium iodide solution at the commencement of the determination. E. C. S.

Ozone [Determination and Solubility]. H. VON WARTENBERG and G. VON PODJASKI (*Z. anorg. Chem.*, 1925, **148**, 391—396).—Dilute ozonised air may be analysed with an accuracy of 5—10% by rapidly bubbling a large volume through a small quantity of potassium iodide solution, the liberated iodine being titrated with sodium arsenite solution. Colorimetric comparison of the iodide solution with standards is unsatisfactory. Ozone

dissolves in many organic liquids in accordance with Henry's law to form fairly stable solutions. The solubility in such liquids is much higher than in water (cf. Fischer and Tropsch, A., 1917, ii, 463). S. K. T.

Separation of Selenium and Tellurium. V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, **47**, 2454—2461).—Hydroxylamine hydrochloride can be employed for the separation of selenium and tellurium in hydrochloric, tartaric, or citric acid solution. The optimal concentration of hydrochloric acid is 17% (*d* 1·085). Hydroxylamine sulphate is less satisfactory. Hydrazine hydrochloride and the sulphate tend to cause precipitation of tellurium with the selenium; this can be avoided in the method of Pellini (A., 1903, ii, 752) by proper control of temperature. The procedure of the separation by the above methods is simple, but is complicated when oxalic acid is used. Lactic acid is unsuitable. W. T.

Sensitive Reaction for Nitrate. F. L. HAHN and G. JAEGER (*Ber.*, 1925, **58**, [*B*], 2335—2340).—Nitrate is reduced in aqueous solution by metallic lead in the presence of lead salts to nitrite which can be detected by the diazo reagent (α-naphthylamine and sulphanilic acid). The sensitiveness of the test is unfortunately diminished by the impossibility of effecting a quantitative reduction of nitrate to nitrite, partly because the latter is itself further reduced by the lead reagent but mainly because the nitrate is reduced to other products. The proportion of nitrate converted into nitrite diminishes with decreasing concentration of nitrate. The test is somewhat more sensitive than the diphenylamine reaction but is specific and more trustworthy. Large quantities of foreign substances markedly diminish the yield of nitrite. Ammonium salts, free acids, and the salts of many heavy metals completely inhibit the test, which must then be performed on the "sodium carbonate extract." If nitrite is present it may be removed by carbamide and sulphuric acid or by evaporation with ammonium chloride; larger amounts are preferably removed by 2 : 4-diamino-6-hydroxypyrimidine. The determination of somewhat greater quantities of nitrate is complicated not only by the presence of foreign substances but also by the individual behaviour of different specimens of the lead reagent. The method is therefore applicable only to cases such as the determination of nitrate in potable water. The final colorimetric comparison must be made with solutions obtained by simultaneous reduction of standard nitrate solutions and not with standard nitrite solutions.

The "lead reagent" is prepared by heating lead formate, obtained by adding formic acid to a concentrated aqueous solution of lead acetate, until the surface assumes a uniformly grey colour. Directions for the preparation and preservation of the "diazo reagent" in the solid state or in solution are given. H. W.

Contradictions and Errors in Analytical Chemistry. VI. Ferrous Sulphate Test for Nitrate and Nitrite and the Diphenylamine Reaction. F. L. HAHN and G. JAEGER (*Ber.*, 1925, **58**, [*B*], 2340—2343; cf. this vol., ii, 69).—The sensitiveness

of the "ring test" for nitrate has frequently been underestimated (cf. Faurholt, A., 1923, ii, 179) but, in the absence of chlorides, 0·1 mg. potassium nitrate in 1 c.c. of solution can be detected with certainty if a mixture of the solution and a little concentrated ferrous sulphate solution is floated on sulphuric acid. In the presence of small amounts of chloride the ring loses its typical appearance, whilst with larger quantities a coloured zone appears even in the absence of nitrate. The effect is due to ferric chloride and can be obviated by addition of phosphoric acid. Small amounts of nitrate can thus be detected in the presence of much chloride or considerable quantities of bromide. Nitrite if present to the extent of 10 mg. per litre gives a distinct brown coloration if the solution is treated with a drop of concentrated ferrous sulphate solution; confusion with the colour of ferric salts is avoided by the use of phosphoric acid for acidification. A rapid qualitative method for the detection of nitrate sensitive to 0·1 μg./c.c., is afforded by moistening a granule of diphenylamine with a few drops of water and gradually adding a few c.c. of concentrated sulphuric acid. The solution under investigation is mixed with an equal volume of concentrated sulphuric acid (and a drop of hydrochloric acid if chlorides are absent) and poured on to the diphenylamine solution. A distinct blue zone is observed, since the concentration of sulphuric acid favourable to the development of the colour is automatically attained at some position between the layers. The diphenylamine test depends greatly on some ill-defined property of the concentrated sulphuric acid. H. W.

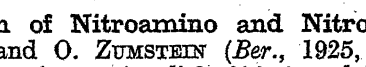
Colour Reactions of Nitrous and Nitric Acids. L. Ekkert (*Pharm. Zentr.*, 1925, **66**, 733—734).—Addition of resorcinol and concentrated hydrochloric acid to a solution of a nitrite produces an immediate saffron-yellow coloration, becoming first brownish-red and then a dark mulberry-red. After keeping for 20 mins., the solution becomes dark green if poured into an excess of sodium hydroxide; on shaking this solution with acetone, the latter becomes violet-red with a fiery-red fluorescence. If a large excess of resorcinol is used in the test and the alkali is added after 10 mins., the solution becomes blue, then green; dilution with water produces a violet colour with red fluorescence. Under the same conditions, nitrates produce only a very pale yellow coloration; on heating, however, similar colour changes to those produced by nitrites ensue, but more slowly. A. R. P.

Remarkable Behaviour of Alkali Sulphate in the Kjeldahlisation of the Nitroanilines. B. M. Margosches and E. Scheinost [with M. Frischer] (*Ber.*, 1925, **58**, [*B*], 2233—2237; cf. A., 1923, ii, 785).—When heated with sulphuric acid and potassium sulphate, *m*-nitroaniline alone of the three isomerides gives ammonia quantitatively. The effect of the addition of varying amounts of sodium, potassium, or lithium sulphate in the kjeldahlisation of *o*- and *p*-nitroaniline under otherwise standard conditions is described in detail. In general, the percentage of nitrogen converted into ammonia increases in an irregular manner as the quantity of alkali

sulphate increases, but lithium sulphate causes at first a diminution in the percentage converted. In no case is the theoretical value attained. Borax has approximately the same action as sodium sulphate. The behaviour of *o*-nitroacetanilide resembles that of *o*-nitroaniline, whereas *p*-nitroacetanilide and *p*-nitroaniline behave differently. Addition of mercuric oxide in the kjeldahlisation of *p*-nitroaniline in the presence of potassium sulphate causes low results, whereas accurate values are obtained by use of copper oxide (0·1—0·5 g.). Molybdic acid is more effective than vanadic, tungstic, or titanic acid in the kjeldahlisation of nitroanilines.

H. W.

Determination of Nitroamino and Nitroimino Groups. K. LEHMSTEDT and O. ZUMSTEIN (*Ber.*, 1925, **58**, [*B*], 2024—2027).—Treatment of tetranitrodi-2 : 2′-iminazolyl,



with boiling ferrous chloride and hydrochloric acid or with mercury and concentrated sulphuric acid causes quantitative conversion of the two *N*-nitro groups into nitric oxide, whereas the *C*-nitro groups remain unaffected. Similarly, 2-nitroaminopyridine is quantitatively reduced by ferrous chloride to nitric oxide and 2-aminopyridine; with sulphuric acid and mercury, low results for the *N*-nitro group are obtained owing to the very rapid isomerisation of the compound to the nuclear-substituted nitro-2-aminopyridine. Both methods give satisfactory results with trinitrodi-2 : 2′-iminazolyl and 5-nitro-2-nitroaminopyridine. The ferrous chloride method appears to be more generally applicable than the Lunge process, whereas the isolation of the non-volatile products is generally less difficult from the sulphuric acid solution. H. W.

Use of Liquid Amalgams in Volumetric Analysis. III. Determination of Phosphorus by Means of Lead Amalgam. K. SOMEYA (*Z. anorg. Chem.*, 1925, **148**, 58—64; cf. this vol., ii, 904).—The molybdenum in ammonium phosphomolybdate is rapidly and quantitatively reduced to the tervalent state by lead amalgam in the closed reductor previously described; by subsequently titrating with permanganate, according to the usual procedure, phosphorus may be accurately determined. The accuracy of the method was proved with pure disodium hydrogen phosphate and with a standard sample of iron. A. G.

Use of Phenolphthalein as an Indicator for the Determination of Phosphoric Acid by Titration of Ammonium Phosphomolybdate. P. NYSSENS (*Bull. Soc. chim. Belge*, 1925, **34**, 232—236).—The errors in the titration of ammonium phosphomolybdate with potassium hydroxide, using phenolphthalein as an indicator, are due to the following causes: (1) 2 mols. of ammonium hydroxide react neutral to phenolphthalein when 0·972 mol. of sulphuric acid is added, the error, therefore, being −1·4% of the ammonia present; (2) diammonium hydrogen phosphate has an

acid reaction towards this indicator, corresponding with an error of −1·70% of the phosphoric acid present. Both errors are therefore in the same sense, but since the 24 mols. of molybdic acid (MoO_3) present may be titrated exactly in the presence of this indicator, the error is reduced to −0·13%, *i.e.*, within the errors of titration, and hence the volumetric results agree with those obtained gravimetrically by the conversion of the phosphomolybdate into pyrophosphate. J. W. B.

Rapid Determination of Phosphates. R. F. Le Guyon and R. M. May (*Bull. Soc. chim.*, 1925, [iv], **37**, 1291—1293).—The phosphate is precipitated from solution, which may contain chlorides, by silver nitrate in presence of a slight excess of sodium acetate. The precipitate is then dissolved in concentrated nitric acid and the silver content of the solution determined by titration with ammonium thiocyanate. S. K. T.

Ammonium Oxalate as a Reagent for Distinguishing Sodium from Potassium Salts. J. Meyerfeld (*Z. anal. Chem.*, 1925, **67**, 150—151).—The solubility of potassium oxalate is about 40 g. and of sodium oxalate 3·2 g. per 100 c.c. of cold water, and sodium oxalate is even less soluble in a saturated solution of ammonium oxalate. Addition of the latter to a saturated solution of a sodium salt gives an immediate crystalline precipitate, whereas potassium salts have no action. The test will distinguish more than 10% of sodium in a potassium salt preparation if the dry salt mixture is added to a saturated ammonium oxalate solution. A. R. P.

Analysis of Lithium Minerals. A. Guntz and F. Benoit (*Bull. Soc. chim.*, 1925, [iv], **37**, 1294—1297).—The silica in lithium ores may be accurately determined by fusing with alkali, and boiling the water extract with ammonium carbonate solution. The precipitate is united with that obtained by boiling the filtrate with zinc oxide until all ammonia is expelled. The precipitates are then dissolved in hydrochloric acid and treated as usual. Calcination with calcium oxide is essential for the accurate determination of the water. Lithium is determined by treating the mineral with a mixture of sulphuric and hydrofluoric acids, calcining the residue at dull red heat, extracting with slightly ammoniacal dilute hydrogen peroxide solution, and boiling for 10 mins. After filtration, the solution is evaporated to dryness with a little ammonium oxalate, ignited, dissolved in water, and precipitated with an ammoniacal ammonium fluoride solution. Lithium fluoride separates and is weighed after ignition. When phosphates are present the first residue is dissolved in boiling, very dilute, hydrochloric acid and excess of litharge is added. The filtrate, after removal of lead as sulphate, is treated as before. S. K. T.

Detection of Calcium in the Presence of Barium and Strontium. G. G. Longinescu and G. Chaborski (*Bul. Soc. Română Științe*, 1924, **27**, 9—11).—The solution of the chlorides

of the metals is treated with ammonia and ammonium carbonate and a portion of the precipitate is boiled with a 25% solution of ammonium sulphate, which converts the calcium into a soluble double sulphate, leaving the barium and most of the strontium insoluble. The filtrate is tested for calcium with ammonium oxalate. All the strontium remains insoluble if no calcium is present, so that any oxalate precipitate is a sure indication of calcium. Barium and strontium may be detected in another portion of the carbonate precipitate by means of potassium dichromate and calcium sulphate, respectively. A. R. P.

Electrometric Studies of the Precipitation of Hydroxides. I. Precipitation of Magnesium, Manganous, Ferrous, Cobalt, Nickel, and Thorium Hydroxides by Use of the Hydrogen Electrode. H. T. S. Britton (*J. Chem. Soc.*, 1925, **127**, 2110—2120).—The reactions between sodium hydroxide and solutions of magnesium, bivalent manganese and iron, cobalt, nickel, and thorium salts have been studied electrometrically. In every case the precipitated hydroxide contained an appreciable proportion of the acid radical. The following p_H values were required in order that precipitation might take place: magnesium, 10·61; manganese, 8·85; cobalt, 6·92; nickel, 6·81; ferrous iron, 5·77; thorium, 3·57. These values are peculiar to the various hydroxides and are independent of both the anion and the precipitant. They are only slightly influenced in dilute solutions by changes in the concentration of the metallic salts, and are shown to depend on the solubility products of the various hydroxides. The non-precipitation of magnesium and manganous hydroxides by ammonium hydroxide in the presence of ammonium salts is discussed in the light of these results. E. E. W.

Electrometric Studies of the Precipitation of Hydroxides. II. Precipitation of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin, and Zirconium by the Use of the Hydrogen Electrode, and their alleged Amphoteric Nature. H. T. S. Britton (*J. Chem. Soc.*, 1925, **127**, 2120—2141).—Salts of the above metals are precipitated at the following p_H values: aluminium, 4·14; beryllium, 5·69; zinc, 5·20; chromium, 5·34, and zirconium, 2·79 (opalescent at 1·86) when titrated with sodium hydroxide. The electrometric titration curves indicate that, in the case of stannous and zirconium salts, colloidally dispersed basic salts are first formed and these are coagulated on the addition of further alkali. Zirconium chloride and sulphate solutions are shown to consist of highly dispersed basic particles and free acid, and no evidence could be found for the existence of the "zirconyl" radical. New light is thrown on the nature of the characteristic soluble basic salts of beryllium, chromium, and zirconium. Among the bases studied, aluminium hydroxide is the only one which is definitely amphoteric. It shows a well-marked inflection of the titration curve corresponding with the formation of the compound $NaAlO_2$. The hydrogen-ion concentration at

which zinc hydroxide (actually basic sulphate) is precipitated is not in accord with existing solubility product data. Werner's view of the difference between green and violet chromic salts is rejected, the explanation preferred involving hydrolysis and a change in the chromium hydroxide probably akin to that produced by ageing. E. E. W.

Electrometric Studies of the Precipitation of Hydroxides. III. Precipitation in the Cerite Group of Rare Earths and of Yttrium Hydroxide by Use of the Hydrogen Electrode. H. T. S. Britton (*J. Chem. Soc.*, 1925, **127**, 2142—2147).—Hydrogen electrode titrations of several of rare-earth salts with sodium hydroxide show that the hydroxides (really basic salts) are precipitated when the solutions (0·0114*M*—0·0133*M*) attain the following p_H values: samarium, 6·83; yttrium, 6·78; neodymium, 7·02 (chloride), 7·00 (nitrate); praseodymium, 7·05; tervalent cerium, 7·41; lanthanum, 8·35. The precipitation p_H values thus lie below those of magnesium and manganous hydroxides and above those of zinc. The values for samarium, yttrium, neodymium, and praseodymium lie so close together that the separation of these hydroxides by fractional precipitation is not possible. The great difference between the hydrogen-ion concentration necessary for the precipitation of thorium hydroxide and those required in the case of the rare earths accounts for some of the processes which are used to effect their separation. Ammonium chloride, if present in sufficient quantity, prevents the precipitation of lanthanum and cerous hydroxides. E. E. W.

Electrometric Studies of the Precipitation of the Hydroxides. IV. Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides by the Use of the Oxygen Electrode. H. T. S. Britton (*J. Chem. Soc.*, 1925, **127**, 2148—2159).—The interaction between sodium hydroxide and salt solutions of certain metals has been followed by means of the oxygen electrode, the hydrogen electrode being inapplicable. The results are expressed in terms of hydrogen-ion concentrations and are believed to be accurate to within 0·5 p_H unit except in the case of silver nitrate solution. The metals examined in this and previous papers are precipitated in the following order at approximately the hydrogen-ion concentrations given: magnesium, 10^{-11}; silver, bivalent manganese, lanthanum, and bivalent mercury, 10^{-9}; cerium, cobalt, nickel, cadmium, praseodymium, neodymium, and yttrium, 10^{-8}; samarium, ferrous iron (?), and lead (?), 10^{-7}; zinc, beryllium, copper, and chromium, 10^{-6}; aluminium, 10^{-5}; tervalent uranium and thorium, 10^{-4}; bivalent tin, zirconium, and ferric iron, 10^{-3}. Basic precipitates, probably containing definite basic salts, were obtained from solutions of mercuric chloride, copper sulphate, cadmium sulphate, and lead nitrate. The precipitate obtained from uranium nitrate solution was the hydroxide containing a little nitrate and not sodium diuranate. The changes in colour observed on titrating both uranic and ferric salts are regarded as being due

to the presence of colloidal basic particles which are coagulated on the addition of further alkali. E. E. W.

Determination of Small Amounts of Lead in Animal Tissues. R. NAKASEKO and I. NAKANO (*Kyōtō Med. J.*, 1925, **22**, (8)).—Organic matter is destroyed by heating with concentrated nitric acid and may afterwards be treated with concentrated sulphuric acid and mercuric oxide with additions of hydrogen peroxide, or by ignition at high temperature. The residue is dissolved in dilute acid, the lead precipitated as sulphide, re-dissolved, precipitated as chromate, and the chromate determined by liberation of iodine from iodides and titration with sodium thiosulphate. 0·005 Mg. of lead per 1 c.c. of solution may be detected by this method, phosphates in the sulphide, and chromic salts and excess of ammonium salts in the chromate interfering. Electrolytic determination of minute amounts of lead is conducted by electrolysis in a platinum vessel which itself acts as cathode. Dilute nitric acid acts as electrolyte and a current of 0·05 ampere at 0·5 volt is passed for 5—10 hrs., the lead peroxide is dissolved from the platinum wire acting as anode, and the iodine liberated from potassium iodide is titrated by means of 0·001*N*-sodium thiosulphate. Phosphates, magnesium, and ammonium salts interfere with the determination. L. F. H.

Determination of Metals Dissolved in Mercury. Rapid Method of Purifying Mercury. A. S. RUSSELL and D. C. EVANS (*J. Chem. Soc.*, 1925, **127**, 2221—2230; cf. this vol., ii, 406).—Rapid methods of determining metals in mercury and of freeing mercury from dissolved metals have been worked out on the basis of the following facts. All metals more electropositive than mercury, except cobalt, pass rapidly into solution as sulphates without the accompaniment of mercury when amalgams of them are shaken with potassium permanganate or certain other oxidising agents in dilute sulphuric acid. The point at which the last trace of the metal in the mercury has gone into solution is shown by the breaking of the surface of the mercury into bubbles. The order in which the metals pass into solution is: zinc, manganese, cadmium, thallium, tin, lead, copper, chromium and iron, bismuth and cobalt. This order is definite and independent of the oxidising agent and acid employed, but is different from that of the electrode potentials in the free state. Permanganate is reduced by all the metals mentioned except zinc and iron to the extent of 100% of the theoretical quantity. 100% efficiency is obtained with all the metals except iron when ferric sulphate is the oxidising agent. E. E. W.

Volumetric Determination of Mercuric Iodide, Mercuric Chloride, and Some Other Mercury Compounds. S. ELLMAN (*Amer. J. Pharm.*, 1925, **97**, 672—674).—Gravimetrically, mercuric iodide may be determined by solution in potassium iodide solution, and precipitation as sulphide with hydrogen sulphide; volumetrically, by treating this precipitate with standard iodine solution to

convert it into iodide and sulphur, and subsequent titration of the excess of iodine with thiosulphate. These methods should be carried out in neutral or slightly acid solution, and the volumetric one may be applied to mercuric chloride and various solutions of mercury salts. [Cf. *B.*, 1925, 989.] B. F.

Volumetric Determination of Iron by Jellinek and Winogradov's Method. H. Asmus (*Oesterr. Chem.-Ztg.*, 1925, **28**, 168—169; cf., A., 1923, ii, 871).—For the determination of small amounts of iron by titration with thiosulphate, the solution containing the iron as ferric chloride is heated to boiling in a flask through which a current of carbon dioxide is passed and thiosulphate nearly equal to that required completely to reduce the ferric salt is added rapidly, followed by the remainder drop by drop until the blue colour of the methylene-blue–magenta indicator becomes red. A preliminary colorimetric test is made to determine the approximate amount of iron present. [Cf. *B.*, Dec. 24th.] A. R. P.

Detection of Iron, Chromium, and Manganese without the Use of Nitric Acid. G. G. Longinescu and E. Petrescu (*Bul. Soc. Româna Stiinte*, 1924, **27**, 13—15).—The ammonia–ammonium sulphide precipitate of group III metals is dissolved in hot 4% hydrochloric acid and the insoluble sulphides are filtered off. The filtrate is tested for iron in the usual way and then treated with 2 c.c. of saturated ferric chloride solution, followed by an excess of sodium hydroxide solution to dissolve zinc and aluminium, leaving a granular precipitate of ferrosoferric hydroxide containing manganese and chromium hydroxides. The precipitate is tested for chromium and manganese by the hypochlorite method of Chaborski (A., 1924, ii, 278). A. R. P.

Separation of Iron from Mercury. G. Spacu (*Z. anal. Chem.*, 1925, **67**, 147—150).—The dilute solution of the two metals is treated with an excess of ammonium thiocyanate, and pyridine is added slowly until the red colour changes to yellowish-brown. A further few drops of pyridine are added and the solution is heated to boiling, whereby the iron is quantitatively precipitated as ferric hydroxide. The mercury is recovered from the solution by precipitation with hydrogen sulphide. [Cf. *B.*, Dec. 24th.] A. R. P.

Determination of Nickel as Dioxide. L. Moser and W. Maxymowicz (*Z. anal. Chem.*, 1925, **67**, 140—142).—Vaubel's method of determining nickel as the dioxide (A., 1922, ii, 875) is shown to be worthless. Calcination of nickel nitrate at 280—330° for 30 mins. yields a black powder which contains only 2·3% of peroxide oxygen, whereas nickel dioxide should contain 17·64%. A. R. P.

Determination of Molybdenum as Trioxide after Precipitation as Trisulphide. W. Hartmann (*Z. anal. Chem.*, 1925, **67**, 152—155).—In order to obtain molybdenum trisulphide in a form which filters readily, the alkaline molybdate solution is treated with freshly prepared ammonium polysulphide solution and the

mixture acidified with dilute sulphuric acid. The precipitate is collected, washed, and roasted gently to obtain the trioxide, which may contain traces of ferric oxide, silica, zinc oxide, copper oxide, and vanadium pentoxide. After weighing, it is dissolved in ammonia; zinc and copper are removed from the solution by addition of colourless ammonium sulphide, and vanadium is determined by distillation of the filtrate, after expelling ammonia by boiling with sodium hydroxide, with hydrochloric acid and potassium bromide. The sum of the impurities is deducted from the weight of crude oxide. [Cf. *B.*, Dec. 24th.] A. R. P.

Chemical Examination of Basic Eruptive Rocks. I. A. ATHANASIU (*Bul. Soc. Română Stiinte*, 1924, **27**, 17—36).—Basic eruptive rocks usually contain up to 3% or sometimes more of titanium dioxide and this introduces complications in the usual analysis when the mass obtained by fusion of the rock sample with alkali carbonate is evaporated with hydrochloric acid. On this account, it is preferable to use sulphuric acid for the evaporation as the silica is thus dehydrated more efficiently, whilst the titanium remains in solution. A further advantage claimed for this method is that the barium and zirconium are eliminated with the silica as insoluble sulphates. Titanium is separated from the filtered solution by hydrolysis in the presence of sodium sulphite; in the presence of phosphoric acid, the precipitate is contaminated with this compound and the titanium must then be determined volumetrically or colorimetrically. The other constituents of the rock are determined by the usual methods in the filtrate from the titanium. A. R. P.

Separation of Zirconium from Iron. P. WENGER and M. MÜLLER (*Helv. Chim. Acta*, 1925, **8**, 512—513).—When a mixture of ferric and zirconium oxides is fused for 2 hrs. in an open crucible with sodium carbonate and subsequently extracted with water, ignited, and again extracted with concentrated hydrochloric acid at 100°, the separation of iron from zirconium is not quantitative as claimed by Wunder and Jeanneret (A., 1912, ii, 96), since some sodium zirconate is produced (cf. A., 1920, ii, 57), but with careful working the proportion of this does not exceed 0·5%, so that the method is valuable in technical analysis or where the ratio of iron to zirconium is large. G. M. B.

Separation and Determination of Bismuth. A. GIRARD and E. FOURNEAU (*Compt. rend.*, 1925, **181**, 610—611).—Bismuth iodide gives with tetra-acetylammonium hydroxide (and other bases) strongly coloured complexes which are readily soluble in organic solvents; this property may be used for the determination of small amounts of bismuth, *e.g.*, in tissue. After destruction of organic matter by treatment with sulphuric and nitric acids, the residue is dissolved in a solution containing iodine, and this is shaken with a benzene solution of tetra-acetylammonium hydroxide, imparting to the benzene a deep red colour which is compared with standard colorations. In the presence of ferric salts the liberation of iodine is prevented by the addition of a reagent containing formic acid,

sodium formate, potassium iodide, and sodium sulphite. 0·0003 G. of bismuth may be characterised by this method. L. F. H.

Reaction between Bismuth Sulphide and Hydrochloric Acid. S. RAMACHANDRAN (*Chem. News*, 1925, **131**, 294—295).—Freshly precipitated bismuth sulphide begins to evolve hydrogen sulphide in 1 : 1 hydrochloric acid at 80°, and in 1 : 16 acid at 85°; it dissolves readily in 1 : 5 acid at 100°. A. R. P.

Proof of the Formation of Gold From Mercury. H. STAMMREICH (*Z. anorg. Chem.*, 1925, **148**, 93—96).—The presence of gold in mercury is detected by distilling off the bulk of the mercury under reduced pressure and examining the last drop. When mercury containing metals of relatively low m. p., such as lead, bismuth, zinc, cadmium, and sodium, is distilled, a quantitative separation is obtained in one operation. The last drop remaining from the distillation of gold-containing mercury is treated with nitric acid and the dissolution observed with a microscope. A spherical crystal aggregate remains, the weight of which can be calculated from its size, and by this method 1×10^{-6} mg. of gold in 1 kg. of mercury can be detected. When a base metal (*e.g.*, copper or iron) has been used for one pole of the discharge, this, or its oxide, remains as a skeleton after the dissolution of the mercury; this slowly crumbles, leaving the gold as small flakes. This may be avoided by shaking the mercury with mercuric chloride or by dissolving it in aqua regia and reducing with hydrazine sulphate. When mercury is bombarded with electrons from a cathode it may contain tungsten; this is removed by shaking with sodium hydroxide solution in the presence of air. A. G.

Spectrographic Detection of Traces of Gold. P. JOLIBOIS and R. BOSSUET (*Bull. Soc. chim.*, 1925, [iv], **37**, 1297—1304).—The detection of traces of gold in minerals by an examination of the arc and spark spectra is described. The most suitable line in the latter case is that of wave-length 2428·1 Å. About 10^{-4}% of gold may be detected. Solutions are treated with mercury or bismuth salts, precipitated with hydrogen sulphide and the gold detected in the precipitate; or else they may be electrolysed with bismuth cathodes, the spark spectra of which reveal the presence of any gold. Minerals are reduced, pure silver being added to increase the size of the metallic button, of which the arc spectrum is observed. A control must be performed on the litharge used in the reduction; a method is described for partly removing any gold it may contain. S. K. T.

Complex Base of Osmium. [Detection of Osmium.] L. TSCHUGAEV [with E. FRITZMANN].—(See i, 1395.)

Fehling's Reagent. G. PÉGURIER (*Ann. Chim. Analyt.*, 1925, **7**, 289—291).—The reagent, of which 10 c.c. are equivalent to 0·05 g. of dextrose, is made by mixing 45 c.c. of a solution of 150 g. of tartaric acid in 450 c.c. of water and 25 c.c. of a solution containing

52·5 g. of pure crystals of copper sulphate in 250 c.c. of water to which a few drops of concentrated sulphuric acid have been added, with enough sodium hydroxide solution (French Codex strength) to make up to 150 c.c. The mixture is stable for several months if kept in a yellow flask with paraffined rubber stopper. D. G. H.

Detection of Pentoses in Plant Glucosides. P. THOMAS and R. IMAS (*Compt. rend. Soc. Biol.*, **92**, 300; from *Chem. Zentr.*, 1925, **11**, 77).—By means of the reaction previously described (cf. this vol., ii, 604) pentose has been found in the hydrolysed alcoholic extract of the seeds of *Vicia angustifolia* (in agreement with von Bertrand and Weisweiller, cf. A., 1911, i, 15), but not in the seeds of *Vicia faba*, *V. sativa*, and *V. narbonensis*. A glucoside containing pentose was also found in the dried wings of the fruit of *V. angustifolia*. Primeverose gives the reaction. Investigations on convolvulin, rhamnose, rhodeose, and digitalin show that methyl- and ethyl-pentoses do not give the reaction in the form characteristic for pentose, nor do various glucosides such as salicin, amygdalin, etc. A. C.

Determination of α-Cellulose. C. G. SCHWALBE (*Papierfabr.*, 1925, **23**, 697—705; cf. this vol., ii, 720).—The usual methods for the determination of α-cellulose give results which may vary by several % when carried out by different laboratories. This may be due to variations in the ordinary temperature, in the time of treatment with sodium hydroxide, and in the wetting of the fibre. The individual fibres of a sample differ in the ease with which they are wetted, and it is possible that the addition of a wetting agent, *e.g.*, Turkey red oil, would be advantageous. Three new methods for the determination are described and have been tested in a number of laboratories, but none of them is completely satisfactory. A. G.

Identification of Drugs Containing Tannins. A. H. WARE (*Pharm. J.*, 1925, **115**, 131—135).—Aromadendrin, when dissolved in 90% alcohol, zinc or magnesium and strong hydrochloric acid being added, gives a pink colour which intensifies to red, and then fades. If neutralised with alkali, the red solution becomes yellow. An extract, *e.g.*, a kino or a cutch, is first rubbed into a paste with water, and the residue from an ethereal extract tested as above. If 5 c.c. of an aqueous extract are boiled with 10—12 drops of dilute acetic acid and 5 c.c. of 0·25% iron ammonium citrate, the liquid cooled and filtered, and 1 g. of ammonium chloride added, only pyrogallol-tannins are precipitated (from logwood, however, hæmatoxylin is precipitated). If 5 c.c. of extract are boiled with 1·5 g. of sodium dihydrogen phosphate, filtered, and the filtrate boiled with ferric citrate solution, gallotannins give a violet solution or a precipitate, ellagitannins a greenish-black precipitate, and hamamelitannins a brown solution or precipitate. If the extract is heated with a little sodium nitrite, ellagitannins give a green colour, other tannins a brown, or reddish-brown.

Extensive tables for the identification of kinos are given. B. F.

Colour Reaction for Lactic Acid. F. KUTTER (*Pharm. Zentr.*, 1925, **66**, 753).—The reaction described by Ekkert (this vol., ii, 1007) has been published by Brauer (A., 1920, ii, 517).

[Determination of] Ethyl Phthalate. III. J. A. HANDY and L. F. HOYT (*J. Amer. Pharm. Assoc.*, 1925, **14**, 219—229).—The Eilles test, employing pyrogallol, is untrustworthy, and the use of other phenols instead of pyrogallol is of no advantage. The Utz test and the Handy and Hoyt test may give positive reactions with controls; in the Andrew test, maximum fluorescence may not be produced. Dilution of an ethyl-alcoholic solution with water or 10% sulphuric acid before extraction with petroleum yields identical results, but in practice the former is preferable.

CHEMICAL ABSTRACTS.

Detection and Determination of Small Amounts of Acetone. C. BÜLOW (*Science*, 1925, **61**, 344).—The formation of acetone-2 : 4-dinitrophenylhydrazone, which is insoluble in cold water, may be used for the determination of 0·03% of acetone in urine.

A. A. E.

Determination of Vanillin, Piperonal, and Coumarin. L. G. RADCLIFFE and E. H. SHARPLES (*Perf. Ess. Oil Rec.*, 1924, **15**, 396—402, 437—439; 1925, **16**, 20—23, 51—54, 87—92, 156—162, 197—199, 271, 353—355, 387—390).—Many methods of determining these substances, when alone or in the presence of one another, have been examined, and are critically reviewed. A bibliography of the literature is given. The following methods are recommended: piperonal may be determined by reaction with excess of phenylhydrazine, and titration of the latter with hydrochloric acid, using methyl-orange as external indicator, the results being 100—101% of the theoretical. Piperonal–vanillin mixtures may be determined by conversion into a mixture of *p*-nitrophenylhydrazones, and extraction of the vanillin compound from ethereal solution by aqueous sodium hydroxide. Coumarin may be determined by boiling it with sodium sulphite to convert it into sodium dihydrocoumaric acid β-sulphonate and titrating the excess of sulphite with iodine. [Cf. *B.*, Dec. 24th.] B. F.

Determination of Hydroxymethylfurfuraldehyde, and Fiehe's Reaction. E. TROJE (*Z. Ver. Deut. Zucker-Ind.*, 1925, [828], 635—752).—Crude hydroxymethylfurfuraldehyde, obtained as a syrup by heating sucrose in an autoclave with a dilute solution of oxalic acid (cf. Middendorp, *ibid.*, 1924, [814]), is purified by distillation, in small quantities, under greatly reduced pressure (b. p. 141—142°/2 mm.). The substance crystallises in the receiver, which is cooled to about −8°, and the crystals, after removal of adherent oil by means of a centrifuge and by pressing on a porous plate and between filter-papers, melt at 32·3°. The compound suffers partial decomposition on distillation at 2 mm. and when kept. Attempts to synthesise it by the methods of Tiemann and Reimer and of Gattermann failed owing to its instability. Like furfur-

aldehyde, however, the hydroxymethyl derivative yields a variety of coloured condensation products with phenols, amines, etc. Hydroxymethylfurfuraldehyde may be determined colorimetrically by mixing its dilute aqueous solution with 10% hydrochloric acid and a few drops of dilute ethereal resorcinol and observing the time taken for the gradually deepening red coloration to attain the intensity of specified standard solutions containing magenta and methyl-orange. This method involves a correction for temperature. A gravimetric method, in which the hydroxymethylfurfuraldehyde solution is mixed with a large excess of a solution of phloroglucinol in hydrochloric acid and the resultant phloroglucide dried and weighed, gives varying results owing to the difference in the constitution of the phloroglucide according to the method of precipitation and drying. In the titrimetric method, the aldehyde is oxidised with a measured excess of iodine in alkaline solution, and the unchanged iodine is determined, after acidification, by titration with thiosulphate (1 mg. of hydroxymethylfurfuraldehyde uses, on an average, 0·1478 c.c. of 0·1*N*-iodine). Lævulose is oxidised, under the conditions specified, beyond the formation of a monobasic acid. Fiehe's colour reaction (with resorcinol) for synthetic invert-sugar and other methods of detecting the adulteration of honey and presence of artificial honey are critically reviewed. Inversion of sucrose in the cold or with invertase yields invert-sugar containing no more, and even less, hydroxymethylfurfuraldehyde than natural honey, whereas inversion with strong acids or by heating leads to values considerably higher than those for natural honey. [Cf. *B.*, Dec. 24th.] W. T. K. B.

Determination of Amino-acids formed by Hydrolysis of Proteins. I. Determination in Groups. E. Cherbuliez and R. Wahl (*Helv. Chim. Acta*, 1925, **8**, 571—582).—A new method for the proximate analysis of an amino-acid mixture is described. After hydrolysis and determination of the free ammonia by distillation with magnesia, the hexone bases and cystine are removed, as usual, with phosphotungstic acid. The remaining amino-acids are then separated as benzoylamino-acids by three successive benzoylations. The process is made more complete by evaporating the mother-liquors to recover a further small proportion of benzoylamino-acids and by determining a trace that is volatilised in this evaporation. A residue in the benzoylation which is insoluble in alkalis is shown to contain mixed anhydrides of benzoic and benzoylamino-acids. These are split at once by the action of sodium ethoxide in alcoholic solution and the acids are added to the main fraction. The nitrogen is then determined by Kjeldahl's method in each fraction. Results are quoted for an analysis of casein in which 97·45% of the nitrogen present is allocated to ammonia and amino-acids, and of ovalbumin, for which the figure is 91·35% as compared with 51% which had hitherto been accounted for. G. M. B.

Tests for Cystine and Cysteine. M. X. Sullivan (*Abstr. Bact.*, 1925, **9**, 37).—Of the amino-acids, sulphur and sulphydryl

compounds examined, cysteine is the only substance that gives a red colour with sodium β-naphthaquinone-4-sulphonate in the presence of alkali and a reducing agent, *e.g.*, sodium sulphite. Cystine gives the reaction slowly owing to gradual reduction to cysteine. Reduction of cystine to cysteine may also be effected by sodium cyanide. A. A. E.

Spectrophotometric Identification of Dyes. III. Basic Violets of the Triphenylmethane Group. W. C. HOLMES (*Ind. Eng. Chem.*, 1925, **17**, 918—919).—A spectrophotometric examination of commercial samples of methyl-violet, crystal-violet, ethyl-violet, benzyl-violet, and gentian-violet has been made with a view to their differentiation. [Cf. *B.*, 1922, 839.] A. D.

Highly Sensitive Physical Method for Detecting Proteins in a Solution. P. L. DU NOUY (*Science*, 1925, **61**, 472).—A comparison of the surface tensions of a solution containing sodium oleate (1 in 6×10^5) and egg-albumin (1 in 5×10^7) and one containing sodium oleate alone (1 in 6×10^5) shows that at these dilutions egg-albumin will prevent the lowering of the surface tension of water by sodium oleate. A. A. E.

Jaffe's Reaction for Creatinine. III. 2 : 6-Dinitrophenol. I. GREENWALD (*J. Amer. Chem. Soc.*, 1925, **47**, 2620).—No red colour is obtained when 2 : 6-dinitrophenol reacts with creatinine and sodium hydroxide (cf. Greenwald and Gross, A., 1924, ii, 508). J. W. B.

Spectrophotometric Determination of Fluorescent Substances in Solution. R. FABRE (*Bull. Soc. chim.*, 1925, [iv], **37**, 1304—1310).—The method previously described (cf. this vol., ii, 260) is applied to the determination of quinine, quinidine, and fluorescein in solution (cf. this vol., i, 609). S. K. T.

Analysis of Xanthate. W. HIRSCHKIND (*Eng. Min. J. Press*, 1925, **119**, 968—970).—Sulphide is detected with sodium nitroprusside in a 1% cold aqueous solution, and thiocarbonate by a red or brown colour of the precipitate yielded by lead acetate in a 2% solution. The available xanthate is determined in the nitrate obtained after the addition of barium chloride; in one aliquot part free alkali is determined, and in another the proportion of an added excess of acid which is not required for the liberation of unstable xanthic acid. CHEMICAL ABSTRACTS.

Reactions of Glycyrrhizin. P. BERTOLO (*Giorn. Chim. Ind. Appl.*, 1925, **7**, 404—405).—Mercury, silver, and cadmium salts of glycyrrhizinic acid were prepared; the last may be separated from the accompanying glycyramin by washing with distilled water; decomposition by means of hydrogen sulphide and recrystallisation yields the pure acid. Pure glycyrrhizin gives an immediate violet coloration in presence of sulphuric acid and aromatic hydroxy-aldehydes, owing to its glucosidic nature. With dextrose and sulphuric acid, or with sulphuric acid alone, the coloration appears more slowly, indicating the additional formation of phenolic substances through the action of the acid. G. L. R.

INDEX OF AUTHORS' NAMES.

ABSTRACTS, 1925.

Anonymous.
protein and oil content of soya beans and the iodine number of soya bean oil, i, 346.
relation of concentration of the soil solution to nitric nitrogen in soils containing large quantities of available nitrogen, and effect on plant growth, i, 347.
wild plum (*Ximenia americana*, Linn.), i, 764.

A.

Aarflot, *H.* See *H.* **Goldschmidt**, and *Erich* **Müller.**
Aarnio, *B.*, effect of temperature on the hygroscopicity of hydrogels of aluminium oxide, ferric oxide, and silica, ii, 1157.
Abakumovski, *L.* See *S. S.* **Nametkin.**
Abderhalden, *E.*, synthetic achievements of the animal organism, i, 726.
insulin, i, 753.
constitution of proteins, i, 848, 1341.
effect of growth of yeast on galactose on the fermentability of the latter by the former, i, 1362.
[degradation of proteins by hypobromite], i, 1475.
Abderhalden, *E.*, and *E.* **Gellhorn**, effect of amino-acids in producing an increase in the action of adrenaline, i, 332.
Abderhalden, *E.*, *E.* **Klarmann**, and *E.* **Komm**, structure of the protein molecule, i, 174.
Abderhalden, *E.*, and *E.* **Komm**, structure of proteins, i, 175, 320, 1475.
oxidation of polypeptides and of 2:5-diketopiperazines, i, 848.
structure of the protein molecule, i, 848.
Abderhalden, *E.*, and *H.* **Paffrath**, hormonal action of choline on intestinal movements. III. Formation of choline from phosphatides. IV. Degradation of phosphatides by intestinal juice. V. Synthesis of choline esters by an enzyme of the duodenum, i, 1016.
Abderhalden, *E.*, and *E.* **Rossner**, compounds of amino-acids with piperazines, i, 975.
Abderhalden, *E.*, and *E.* **Schwab**, structure of proteins; reduction of dipeptides and methods of isolation of reduction products given by proteins, i, 991.
methylation of tyrosine, i, 1423.
Abderhalden, *E.*, and *H.* **Sickel**, isolation from caseinogen of an amino-acid of the indole group with the composition $C_{11}H_{14}O_3N_2$, i, 846.
Abel, *E.*, and *D.* **Harasty**, formation of nitrous acid from nitric acid and nitric oxide, ii, 139.
Abel, *J. J.*, and *E. M. K.* **Geiling** [with *G.* **Alles**, and *A.* **Raymond**], insulin. I. Is insulin an unstable sulphur compound? i, 1218.
Abelin, *J.*, specific dynamic action of foodstuffs. IV. Mechanism of specific dynamic action, i, 332.
Abelin, *J.* See also *K.* **Miyakaki.**
Abelles, *N.*, and *H.* **Popper**, distribution of iodine in the hydrolytic products of the thyroid gland, i, 1489.
Abelsdorff, *R.* See *A.* **Schönberg.**
Abraham, *A.*, and *P.* **Kahn**, significance of ions in muscular function. V. Influence of ions on the lactacidogen changes during ageing, i, 728.
Abraham, *H.*, and *R.* **Planiol**, magnetic ferric oxide, ii, 587.
Abrams, *A. J. J.* See *T. L.* **Davis.**
Abramson, *H. A.*, determination of phenolsulphonephthalein in the urine of jaundice, i, 329.
Abt, *G.*, carbon of peptones, source of energy for *Bacillus diphtheriæ*, i, 1014.
Abt, *G.*, and *G.* **Loiseau**, causes of p_H variation in cultures of *Bacillus diphtheriæ*, i, 479.
Ackermann, *D.*, *F.* **Holtz**, and *H.* **Reinwein**, occurrence of methyladenine, dimethylhistamine, guanidine, betaine, and eledonine in *Geodia gigas*, i, 720.
Ackerson, *C. W.*, *M. J.* **Blish**, and *F. E.* **Mussehl**, phosphorus, calcium, and alkaline reserve of blood sera of normal and rachitic chicks, i, 609.

Adair, *G. S.*, hæmoglobin system. I. Classification of reactions, i, 849.
hæmoglobin system. II. Theory of reactions which do not obey the law of constant proportions, i, 849.
hæmoglobin system. III. Equilibrium of hæmoglobin and carbon dioxide, i, 850.
hæmoglobin system. IV. Reproduction of carbon dioxide curves of blood with an artificial mixture of hæmoglobin and sodium bicarbonate, i, 850.
hæmoglobin system. V. Relation of hæmoglobin and bases, i, 850.
hæmoglobin system. VI. Oxygen dissociation curve of hæmoglobin, i, 851.
direct method of measuring the osmotic pressure of hæmoglobin, ii, 965.
Adam, *G.* See *R.* **Stollé**.
Adam, *H. R.*, electrometric titration in the determination of ferrous and ferric iron in magnetites, ii, 717.
Adam, *N. K.*, structure of surface films on water, ii, 195.
evaporation of water from clean and contaminated surfaces, ii, 658.
[cause of surface tension], ii, 1046.
Adam, *N. K.*, and *J. W. W.* **Dyer**, synthesis of arachidic acid and some long-chain compounds, i, 354.
molecular structure of thin films. VI., ii, 32.
Adam, *N. K.*, and *G.* **Jessop**, explanation of "intertraction" phenomena between solutions, and molecular significance of surface tension, ii, 772.
angles of contact and polarity of solid surfaces, ii, 962.
Adams, *E. Q.*, luminous efficiency of chemi-luminescence reactions, ii, 1117.
Adams, *E. W.*, and *H.* **Adkins**, catalysis in acetal formation, i, 784.
Adams, *E. W.* See also *H.* **Adkins**.
Adams, *H. S.* See *W. D.* **Harkins**.
Adams, *R.*, and *J. R.* **Johnson**, trypanocidal compounds, i, 319.
Adams, *R.*, *E. H.* **Volwiler**, and *R. L.* **Jenkins**, di-*sec.*-butylaminoalkyl esters of aromatic acids, i, 399.
Adams, *R.* See also *C. L.* **Butler**, *jun.*, *W. H.* **Carothers**, *H.* **Heckel**, *E. A.* **Jacobsen**, *J. W.* **Kern**, *I. A.* **Koten**, *K.* **Ogden**, *J. S.* **Pierce**, and *C. W.* **Rassweiler**.
Addis, *T.*, determination of urea in blood and urine, i, 1113.
Adickes, *F.*, α-ketopimelic acid and α-ketosuberic acid and their behaviour towards concentrated sulphuric acid, i, 230.
addition of alkali alkoxide to esters, i, 1378.
Adinolfi, *E.*, influence of *X*-rays on the crystallisation of bismuth, ii, 485.
Adkins, *H.*, and *E. W.* **Adams**, relation of structure, affinity, and reactivity in acetal formation, i, 785.
Adkins, *H.*, and *P. P.* **Perkins**, dehydration of alcohols over alumina, i, 626.
Adkins, *H.*, and *R. N.* **Simington**, 1-phenyltetrahydro-1:4-oxazine (4-phenylmorpholine) and a new triphenylmethane dye, i, 986.
Adkins, *H.* See also *E. W.* **Adams**, *F.* **Bischoff**, *W. C.* **Child**, *L. B.* **Haines**, and *W. A.* **Lazier**.
Adler, *A.*, fluorescent oxidation products of bilirubin and their importance as sources of error in the routine detection of urobilin, i, 328.
Adler, *E.* See *S.* **Isaac**.
Adler, *M.* See *H.* **Weil**.
Adlersberg, *D.*, and *O.* **Porges**, detection of bilirubin and urobilin in the fæces with trichloroacetic acid, i, 98.
Adolf, *M.*, physical chemistry of the globulins. VI. Alteration of globulin by heat, ii, 199.
heat changes of the globulins, ii, 520.
Adolf, *M.*, and *W.* **Pauli**, electrolyte-free, water-soluble proteins. II. Effect of carbon dioxide, ii, 289.
Adolph, *E. F.*, metabolism of ammonium salts and of urea in man, i, 1353.
diffusion of water through collodion membranes between solutions of mixed electrolytes, ii, 859.
Adova, (*Mlle.*) *A. N.*, enzymes of *Utricularia vulgaris*. II. Relative amounts of proteolytic enzymes in the bladders and in the stem, i, 202.
Adova, (*Mlle.*) *A. N.* See also *I. A.* **Smorodincev**.
Aeschlimann, *J. A.*, asymmetric compounds of quinquevalent arsenic, i, 706.
Aeschlimann, *J. A.*, *N. D.* **Lees**, *N. P.* **McCleland**, and *G. N.* **Nicklin**, organic compounds of arsenic. II. Derivatives of the arsenic analogue of carbazole, i, 319.
Afanasieva, *M.* See *S.* **Kostytschev**.
Aggazzotti, *A.*, changes in the total, amino-, and ammoniacal nitrogen of hens' eggs during incubation, i, 457.
Aguirreche, *F. D.*, existence of liquid racemates, ii, 1142.

Ahlberg, *R.*, α-ethyl-αα′-thiodilactic acid, i, 885.
Ahlgren, *G.*, deamination of aspartic acid by hydrolysis, i, 235.
insulin and the oxidation of dextrose, i, 482.
Ahmad, *N.*, absorption and scattering of γ-rays, ii, 923.
Ainslie, *D. S.*, variations in the structure of the lithium red line 6708 Å., ii, 450.
Airoldi, *A.* See *G.* **Scagliarini**, and *A.* **Skrabal**.
Akashi, *K.* See *B.* **Kubota**.
Aktien-Gesellschaft für Anilin-Fabrikation, preparation of diarylthiocarbamides, i, 133.
preparation of azine derivatives, i, 304.
preparation of 4-allyloxyphenylmalonamic acid and its esters, i, 402.
preparation of safranine dyes, i, 591.
preparation of keto derivatives of the thiazine series, i, 596.
azo derivatives of β-naphthol containing *p*-substituted auxochromes, i, 988.
alkyl ethers of monohydric phenols and their halogen substitution products, i, 1145.
dyes, i, 1330.
Aktien-Gesellschaft Lignose, additive products of lead oxide with lead compounds of acidic polynitro compounds, i, 1145.
Albert, *A.*, organic compounds of mercury, i, 844.
Albritton, *E. C.*, effect of interpancreatic administration of dextrose on the blood-sugar curve, i, 463.
Alekseevski, *E. V.*, adsorption and heterogeneous catalysis. I., ii, 858.
Alexander, *J.*, simple kinetic principle of colloidal processes, ii, 779.
Alexander, *L. M.*, new determination of the constant *N* of Avogadro, ii, 364.
Ali, *B.*, surface tension of water, benzene, methyl alcohol, and ethyl alcohol, ii, 768.
Ali, *B.* See also *P. E.* **Lauder**.
Alimchandani, *R. L.* See *A. N.* **Meldrum**.
Alinari, *E.* See *F. C.* **Palazzo**.
Allaire, *H.* See *M.* **Javillier**.
Allan, *F. N.*, *B. R.* **Dickson**, and *J.* **Markowitz**, relationship of phosphate and carbohydrate metabolism. II. Effect of adrenaline and phloridzin on the excretion of phosphate, i, 726.
Allan, *James*, and *R.* **Robinson**, an accessible derivative of chromonol, i, 148.
Allan, *John*. See *E. F.* **Armstrong**.
Allen, *C. F. H.*, reactions of δ-ketonic nitriles, i, 963.
Allen, *H. S.*, static model for helium, ii, 349.
Allen, *R. P.* See *W. D.* **Bancroft**.
Alles, *G.* See *J. J.* **Abel**.
Alles, *G. A.* See *G.* **Piness**.
Allin, *K. D.* See *V. J.* **Harding**.
Allison, *F. E.*, nitrification of phosphorus nitride, i, 218.
Allison, *F. E.*, *J. J.* **Skinner**, and *F. R.* **Reid**, toxicity studies with dicyanodiamide on plants, i, 1030.
Allison, *S. K.*, reflection of *X*-rays by barytes, ii, 18.
reported $K\beta_4$ line in the *X*-ray spectra of molybdenum and palladium, ii, 724.
Allison, *S. K.*, and (*Miss*) *A. H.* **Armstrong**, experimental determination of the relative intensities of some of the molybdenum and copper *K* lines and the tungsten *L* lines, ii, 1015.
Allison, *S. K.*, and *W.* **Duane**, scattered radiation due to *X*-rays from molybdenum and tungsten, ii, 250.
experimental determination of the critical excitation frequency for the production of fluorescent *X*-radiation, ii, 930.
wave-lengths of scattered *X*-rays, ii, 1034.
Allmand, *A. J.*, Einstein's "photochemical equivalent law," ii, 1074.
mechanism of the ozone–chlorine reaction, ii, 1079.
Allmand, *A. J.*, and *A. N.* **Campbell**, electro-deposition of manganese. II., ii, 305.
Allmand, *A. J.*, *P. W.* **Cunliffe**, and *R. E. W.* **Maddison**, photodecomposition of chlorine water and of aqueous hypochlorous acid solutions, ii, 572.
Allmand, *A. J.*, and *V. S.* **Puri**, effect of superposed alternating current on the anodic solution of gold in hydrochloric acid, ii, 302.
effect of superposed alternating current on the polarisable primary cell zinc–sulphuric acid–carbon. I. Low frequency current, ii, 303.
Allpress, *C. F.*, and *W.* **Maw**, carbonates of ethylene glycol and related compounds, i, 4.
Aloy, *J.*, and *A.* **Valdiguié**, reactions produced by sunlight in the presence of uranium compounds, ii, 1081.
Alphen, *J. van*, action of ketens on hydrazine derivatives, i, 80.
action of keten on hydroxybenzoic acids and their esters, i, 1149.

Alquier, *J.* See *L.* **Randoin.**
Alsberg, *C. L.* See *D. B.* **Dill.**
Alsterberg, *G.*, determination of molecular oxygen in aqueous solution in the presence of nitrous acid, ii, 1198.
Altchidjian, *Y.* See *H.* **Gault.**
Alterthum, *H.*, kinetics of macro-crystal formation in tungsten by union of small crystals, ii, 136.
Alterthum, *H.*, *W.* **Fehse**, and *M.* **Pirani**, melting point of carbon, ii, 759.
Alterthum, *H.*, and *F.* **Koref**, heterogeneous equilibria between tungsten and oxygen, and tungsten and water vapour at high temperatures, ii, 1159.
Althammer, *W.*, reduction of magnesium sulphate, ii, 145.
Alvarado, *A. M.* See *J. N.* **Pearce.**
Amadori, *M.*, hydrated *meso*tartaric acid, i, 511.
Amagat, (*Mlle.*). See (*Mme.*) *P.* **Ramart.**
Ambard, *L.*, laws of unimolecular reactions (fermentations; catalytic reactions), ii, 1170.
Ambard, *L.*, and **Vaucher**, elimination of amylase by the kidneys, i, 609.
Amberger, *K.*, and *J.* **Bauch**, glycerides of cacao fats, i, 114.
Ambler, *H. R.*, absorption of carbon monoxide. I. Critical comparison of some methods employed in gas analysis, ii, 436.
Ambler, *H. R.* See also *T. C.* **Sutton.**
Ambler, *J. A.*, *D. F. J.* **Lynch**, and *H. L.* **Haller**, naphthalenesulphonic acids. VI. Sulphonation of naphthalene in the vapour phase, i, 126.
Ambrus, *B.* See *H.* **Thoms.**
Ames, *J. W.*, and *C. J.* **Schollenberger**, availability of phosphorus in calcareous and non-calcareous soils, i, 1524.
Ames, *J. W.*, and *R. H.* **Simon**, soil potassium as affected by fertiliser treatment and cropping, i, 1523.
Amuat, *A. M.* See *M.* **Battegay.**
Anargyros, *A.*, colloidal oxide of manganese, ii, 1152.
Anderegg, *F. O.*, and *W. N.* **Herr**, formation of active hydrogen in the creepage corona discharge, ii, 1180.
Andersen, *B.* See *O.* **Collenberg.**
Anderson, *A. K.*, plant diseases. VI. *Fusarium lini*, Bolley, i, 1522.
Anderson, *G. H.*, calcium and phosphorus content of blood in normal and rachitic children. II. Phosphorus, i, 188.
Anderson, *G. H.*, and *S.* **Graham**, etiology of tetany in children, i, 330.
Anderson, *J. A.* See *H. N.* **Holmes.**
Anderson, *L. A. P.*, *A.* **Howard**, and *J. L.* **Simonsen**, lathyrism. I., i, 1000.
Anderson, *L. C.* See *M.* **Gomberg.**
Anderson, *M. S.*, heat of wetting of soil colloids, i, 219.
Anderson, *W. T.*, *jun.*, and *F. W.* **Robinson**, oxalic acid–uranyl sulphate ultra-violet radiometer, ii, 415.
Ando, *K.* See *Y.* **Osaka.**
Andratschke, *I.* See *Z.* **Stary.**
André, *E.*, determination of the acetyl value of fats, ii, 446.
André, *E.*, and *H.* **Canal**, marine-animal oils; squalene and spinacene, i, 1373.
André, *E.*, and (*Mlle.*) *T.* **François**, additive power of iodine with regard to ethylenic compounds, i, 356.
André, *E.*, and *F.* **Guichard**, American palm tree fats; murumuru butter, i, 1124.
André, *G.*, and *E.* **Demoussy**, selective absorption of potassium by plants, i, 758.
André, *H.*, conductance by metallic colloids and its electro-technical applications, ii, 976.
Andreanelli, *M.* See *G.* **Rossi.**
Andreoly, *G.* See *A.* **Maubert.**
Andrew, *J. H.*, and *R.* **Hay**, colloidal separations in alloys, ii, 954.
Andrew, *J. H.*, and *A. J. K.* **Honeyman**, specific volume of steels, ii, 278.
Andrews, *D. H.*, solubility relations of isomeric organic compounds. III. Mutual solubility of the three dinitrobenzenes, ii, 1052.
Andrews, *D. H.*, and *J.* **Johnston**, application of the ideal solubility curve to the interpretation of equilibrium diagrams in metal systems, ii, 206.
Andrews, *D. H.*, *G. T.* **Kohman**, and *J.* **Johnston**, solubility relations of isomeric organic compounds. II. Determination of freezing temperatures of binary mixtures, ii, 852.
Andrews, *D. H.* See also *G. T.* **Kohman.**
Andrews, *J. C.*, optical activity of cystine; oxidation of cystine, i, 1389.
Andrews, *J. W.*, heat of sublimation of carbon dioxide, ii, 758.
Andrews, *J. W.* See also *W. H.* **Rodebush.**
Andrews, *M. R.*, and *S.* **Dushman**, diffusion of carbon through tungsten and tungsten carbide, ii, 500.
Andrews, *S.*, phosphate metabolism in fatigued mammalian muscle, i, 729.

Andrjuschtschenko, *A.* See *V.* **Ipatiev.**

Andrussov, *L.*, differential methods and apparatus for the determination of dissociation isochores; thermal dissociation of cadmium carbonate, ii, 538.

thermal dissociation of calcium carbonate, and the differential method. II., ii, 803.

Angelescu, *B. N.*, volumetric determination of manganese, ii, 330.

Angelescu, *E.*, and *J.* **Mircescu**, adsorption of iodine by starch, ii, 1149.

Angelescu, *E.*, and *D.* **Motzoc**, equilibrium between two liquid phases in the system, aniline–acetic acid–water, ii, 854.

Angeli, *A.* See *D.* **Bigiavi.**

Angerer, *E. von*, and *Alex.* **Müller**, spectroscopic determination of the electron affinity of the halogens, ii, 1025.

Angern, *O.* See *P.* **Pfeiffer.**

Anschütz, *R.*, *H.* **Aschenberg**, *H.* **Kuckertz**, *F.* **Krone**, *K.* **Riepenkröger**, and *C.* **Zerbe**, reciprocal changes of the isomeric *O*- and *N*-acylsalicoylamides, and the constitution of acylsalicoylimide salts, i, 666.

Anschütz, *R.*, and *K.* **Riepenkröger**, is orthoboric acid, H_3BO_3, volatile in steam? ii, 1084.

Anschütz, *R.*, and *G.* **Schultz**, constitution of the two isomeric "dehydrothio-*m*-xylidines," i, 315.

Anschütz, *R.*, *W.* **Stoltenhoff**, and *F.* **Voeller**, two mixed anhydromonohydroxybenzoic acids and their transformation into xanthonecarboxylic acids, i, 1273.

Anslow, *G. A.*, total ionisation produced in air by electrons of various energies, ii, 343, 459.

Anson, *M. L.*, and *A. E.* **Mirsky**, carbon monoxide dissociation curve of hæmochromogen, i, 456.

combination of nitric oxide with hæmoglobin, i, 1475.

hæmochromogen and the relation of protein to the properties of the hæmoglobin molecule, i, 1475.

[non-protein component of hæmoglobin], i, 1476.

helicorubin and its relation to hæmoglobin, i, 1476.

Anthony, *J. D. C.*, and *L. J.* **Hudleston**, freezing points of hydrofluoric acid, ii, 644.

Antonoff, *B.* See *A.* **Schönberg.**

Antonov, *G. N.*, molecular interaction in the liquid state, ii, 865.

Aoyama, *S.*, reaction products of ruthenium tetroxide and hydrochloric acid, ii, 816.

Applebey, *M. P.*, and *P. G.* **Davies**, physical properties of aniline and its aqueous solutions, ii, 948.

osmotic pressure by the solubility method in concentrated solutions, ii, 964.

Appleton, *E. V.*, *K. G.* **Emeléus**, and *M. A. F.* **Barnett**, experiments with an α-particle counter, ii, 10.

Araki, *S.*, equilibria in the systems, ammonium chromate–ammonium sulphate–water, and ammonium chromate–potassium chromate–water at 25°, ii, 786.

Arbuckle, *H. B.*, and *O. J.* **Thies**, *jun.*, variation of protein content of maize. III., i, 1518.

Archbold, *H. K.*, physiology of apples. II. Nitrogen content of stored apples, i, 345.

physiology of apples. III. Determination of dry weight and the amount of cell-wall material in apples, i, 345.

Archibald, *E. H.*, and *L. T.* **Hallett**, solubilities in water of rubidium and cæsium chloroplatinates, ii, 652.

Archibald, *W.* See *C. P.* **Stewart.**

Ardagh, *E. G. R.*, and *G. M.* **Broughall**, separation of nickel and copper from iron, ii, 603.

Arens, *H.*, photographic reversal, ii, 313.

Arkadiev, *W.*, magnetic spectra of iron and nickel wires at wave-lengths of a centimetre, ii, 82.

electric and magnetic spectroscopy, ii, 750.

Arkel, *A. E. van*, crystal structure and physical properties, ii, 749.

so-called lead suboxide, ii, 815.

Arkel, *A. E. van*, and *J. H. de* **Boer**, separation of zirconium from other metals, including hafnium, by fractional distillation, ii, 243.

electronegative hydrogen, ii, 734.

additive properties of boiling points. I. and II., ii, 758, 1141.

influence of hydrogen and substituted halogens on the properties of organic compounds, especially on their boiling points, ii, 758.

preparation of pure metallic titanium, zirconium, hafnium, and thorium, ii, 1193.

Arkel, *A. E. van.* See also *J. H. de* **Boer.**

Arisz, *W. H.*, and *J.* **Schweizer**, tannin of *Hevea braziliensis*, i, 875

Arland, *A.*, acidity of plant sap and methods for its determination, i, 213.
Armbruster, *G.* See *P.* **Pfeiffer.**
Armendt, *B. F.* See *L. J.* **Bircher.**
Armes, *H. P.* See *M. A.* **Parker.**
Armit, *J. W.*, and *R.* **Robinson**, polynuclear heterocyclic aromatic types. II. Some anhydronium bases, i, 1170.
Armstrong, (*Miss*) *A. H.*, *W.* **Duane**, and *R. J.* **Havighurst**, reflection of *X*-rays by alkali halide crystals, ii, 1033.
Armstrong, (*Miss*) *A. H.* See also *S. K.* **Allison.**
Armstrong, *E. F.*, *John* **Allan**, and *C. W.* **Moore**, fatty acid constituents of some natural fats. I. Oils from the coconut, i, 353.
fatty acid constituents of some natural fats. II. Palm-kernel oil, i, 504.
Armstrong, *E. F.*, and *T. P.* **Hilditch**, constitution of natural unsaturated fatty acids. I. New method of ascertaining the position of the ethylenic linking in acids of the oleic series, i, 355.
constitution of natural unsaturated fatty acids. II. Acids present in a South Georgia whale oil, i, 778.
catalytic actions at solid surfaces. XII. Particles of a catalyst which participate in chemical change, ii, 562.
catalytic actions at solid surfaces. XIII. Some factors controlling selective hydrogenation: terpene derivatives, ii, 563.
Armstrong, *H. E.*, enzyme action. XXIV. Oxydase effect and the phenomena of oxidation in general: carbon monoxide, i, 1009.
Arnaud. See *E.* **Carrière.**
Arnd, *O.* See *F.* **Zetzsche.**
Arnd, *T.*, determination and nature of the acidity of moor soils, i, 221.
influence of humic acids on bacterial life in moor soils, and a method of determining soil acidity, i, 490.
Arndt, *F.* [with *W.* **Flemming**, *E.* **Scholz**, *V.* **Löwensohn**, *S.* **Källner**, and *B.* **Eistert**], chromone and 1-thiochromone series, i, 1309.
Arndt, *F.*, *P.* **Nachtwey**, and *J.* **Pusch**, pyrone problem; 1-thiopyrones and 1-thiopyranones, i, 1307.
conversion of 4-thiopyrones into dipyrylene; dithiopyrylene, i, 1312.
Arndt, *F.*, and *J.* **Pusch**, possible existence of indigoid dyes with a hydrogenated six-membered ring, i, 1312.
Arndt, *F.*, and *J.* **Pusch** [with *R.* **Schwarz**], halochromism of hydrogenated pyrone and thiopyrone systems, i, 1304.
Arndt, *F.*, *E.* **Scholz**, and *P.* **Nachtwey**, dipyrylenes and the relationships of the linkings in pyrone ring systems, i, 57.
Arndt, *K.*, and *G.* **Ploetz**, electrical conductivity of fused sodium hydroxide, ii, 127.
Arnold, *R.*, and *E.* **Gley**, iodine content of goat's thyroid, i, 325.
Arnoldi, *W.*, and *J. A.* **Collazo**, sugar and fat in (human) blood, i, 179.
Arnoldi, *W.* See also *F.* **Kraus.**
Arnulf, *A.*, ionisation of potassium vapour under the influence of visible light, ii, 460.
Arrhenius, *O.*, lime requirement of soils. II. Soil reaction and the growth of the higher plants, i, 490.
lime requirement of soils. III. Influence of soil reaction on biological and physico-chemical soil factors, i, 766.
influence of neutral salts on soil reaction, i, 1525.
Arrhenius, *S.*, kinetics of cellulose production, ii, 560.
Arstal, *A.* See *S.* **Bodforss.**
Arzichovski, *V.*, temperature of swelling of starch granules, ii, 967.
Arzichovski, *V.*, and *O.* **Scheljakin**, effect of concentrated solutions of poisons on plant cells, i, 1227.
Asahara, *G.*, application of *X*-ray diffraction to the determination of the transformation temperature of thallium, ii, 483.
effect of allotropic change on the grain growth in thallium, ii, 637.
transformation temperature of thallium, ii, 645.
Aschan, *O.* [with *I. F. M.* **Krohn**], two homologues of diprene, i, 49.
Aschenberg, *H.* See *R.* **Anschütz.**
Ascherl, *A.* See *Erich* **Schmidt.**
Ashdown, *A. A.* See *T. L.* **Davis**, and *J. F.* **Norris.**
Asher, *L.*, and *K.* **Takahashi**, physiology of the glands. LXX. Experimental hypoglycæmia and the carbohydrate metabolism of the brain, i, 331.
Ashley, *M. F.* See *L. B.* **Loeb.**
Ashworth, *J. R.*, simple characteristic relationships among the ferromagnetics, ii, 944.
Asmas, *R.* See *Erich* **Schmidt.**
Asmus, *H.*, volumetric determination of iron by Jellinek and Vinogradov's method, ii, 1206.
Asselin. See *L.* **Randoin.**
Astengo, *R.* See *L.* **Francesconi.**
Asterblum, (*Mlle.*) *M.*, permanent modifications in fluorescent liquids, ii, 1026.

Aston, *F. W.*, rarity of the inert gases on the earth, ii, 18.
mass-spectra of chemical elements. VI. Accelerated anode rays continued, ii, 618.
photographic plates for detection of mass rays, ii, 706.
isotopes of mercury, ii, 833.
Astruc, *A.*, and *E.* **Canals**, rotating dialyser, ii, 896.
Astruc, *A.*, and **Radet**, determination of ethyl alcohol, ii, 443.
Aten, *A. H. W.*, electrical heating apparatus in the laboratory, ii, 588.
Aten, *A. H. W.*, and *M. F. van* **Patten**, electrodeposition of silver–cadmium alloys, ii, 1166.
Athanasiu, *G.*, sensitiveness of actinometers with mercury electrodes, ii, 415.
electrochemical actinometers, ii, 1067.
Athanasiu, *I. A.*, chemical examination of basic eruptive rocks, ii, 1207.
Atkin, *W. R.*, and *G. W.* **Douglas**, titration curve of gelatin, ii, 113.
Atkins, *W. R. G.*, hydrogen-ion concentration of sea-water in its relation to photosynthetic changes. III., i, 199.
filtration and other errors in the determination of the hydrogen-ion concentration of soils, i, 220.
Atsuki, *K.*, nitrates of oxycelluloses, hydrocelluloses, and cellulose hydrates, i, 120.
cellulose acetonitrate, i, 642.
dehydration of cellulose nitrate by alcohol, i, 1044.
swelling and dispersion of cellulose nitrate in ethyl alcohol, i, 1044.
Atynski, *K.* See *L.* **Moser**.
Aubel, *E.*, and *J.* **Salabartan**, mechanism of hydrogen production from dextrose by *Bacillus coli communis*, i, 747.
Aubel, *E.*, and *R.* **Wurmser**, utilisation of energy liberated by oxidations, i, 480.
Audubert, *R.*, photovoltaic phenomena, ii, 43.
photo-electric properties of silver halides and the mechanism of the formation of the photographic latent image, ii, 56.
Audubert, *R.*, and (*Mlle.*) *M.* **Quintin**, mechanism of the adsorption of ions, ii, 384.
Audubert, *R.*, and *H.* **Rabaté**, method of determination of the granular distribution of disperse systems, ii, 775.
Auerbach, *F.*, and *E.* **Smolczyk**, electrometric titration of acids, ii, 118.
Auerbach, *F.*, and *H.* **Weber**, lead salts of some fruit acids, i, 1130.
Auerbach, *R.*, technique and theory of measuring the diffusion of coloured substances, ii, 28.
method of viscosimetry with variable velocity of flow; velocity function of the viscosity of disperse systems. III., ii, 589.
Auerspergrová, *M.* See *J.* **Šterba-Boehm**.
Aufrecht, determination of uric acid in urine, i, 187.
melanin and its detection in urine, i, 1350.
Auger, *P.*, secondary β-rays produced in a gas by *X*-rays, ii, 175.
experimental study of directions of emission of photo-electrons, ii, 730.
Auger, *P.*, and *F.* **Perrin**, direction of emission of photo-electrons, ii, 618.
Auger, *V.*, determination of antimony, ii, 604.
new type of alkali borate; pentaborates, ii, 697.
Auger, *V.*, and *T.* **Karantassis**, stannic iodide complexes, ii, 814.
complex salts of stannous iodide with rubidium and cæsium iodides, ii, 1182.
Auger, *V.*, *L.* **Lafontaine**, and *C.* **Caspar**, salts of cupferron, ii, 328.
Augustson, *A. M.* See *E.* **Hägglund**.
Auméras, *M.*, degree of hydration of calcium oxalate, ii, 895.
Austin, *P. C.*, lithium arc spectrum for polarimetric use, ii, 995.
Austin, *P. C.*, and *J. R.* **Park**, rotatory dispersion of derivatives of tartaric acid. II. Acetyl derivatives, ii, 1028.
Autenrieth, *W.*, and *E.* **Bölli**, *p*-oxodiazphospholes and experiments with trimethylenedisulphonyl chloride, i, 1468.
Autenrieth, *W.*, and *H.* **Hefner**, experiments with thiocarbonyl chloride, i, 1376.
Autenrieth, *W.*, and *A.* **Meyer**, determination of bismuth in organs, blood, and excreta, i, 182.
Autenrieth, *W.*, and *W.* **Meyer**, thiophosphoryl chlorides of the general formulæ $SP(OR)Cl_2$ and $SP(OR)_2Cl$ and derivatives of pentabasic thiolphosphoric acid, $(HO)_4P{\cdot}SH$, i, 807.
compounds containing phosphorus and *p*-thiodiazphospholes, i, 989.
Auwers, *K. von*, 1-methyl-Δ^1-dihydronaphthalene, i, 241.
[formation and spectrochemical behaviour of hydrogenated naphthalene derivatives], i, 815.
alleged dimeric anils of alkylglutaric acids, i, 892.

Auwers, *K. von*, constitution of labile and stable acylindazoles, i, 1460.
Auwers, *K. von*, *T.* **Bahr**, and *E.* **Frese**, tetrahydrobenz*iso*oxazoles, i, 308.
cyano*cyclo*hexanones and their transformation products, i, 310.
Auwers, *K. von*, and *W.* **Daniel**, isomeric relationships in the pyrazole series. V. *N*-Alkyl and *N*-acyl derivatives of methylpyrazoles, i, 1180.
Auwers, *K. von*, and *E.* **Frese**, formation of indazoles from the hydrazones of 2:6-dinitrobenzaldehyde, i, 1101.
Auwers, *K. von*, and *O.* **Jordan**, Beckmann transformation. II., i, 264.
Auwers, *K. von*, and *W.* **Kohlhaas**, spectrochemistry of thiophen derivatives, i, 150.
Auwers, *K. von*, and *R.* **Kraul**, constitution of acridine, i, 578.
spectrochemistry and structure of polynuclear aromatic hydrocarbons, i, 900.
spectrochemistry of compounds containing nitrogen, ii, 847.
Auwers, *K. von*, and *A.* **Kreuder**, influence of constitution on the transformation of phenylhydrazones of unsaturated compounds into pyrazolines. II., i, 1454.
Auwers, *K. von*, *M.* **Lechner**, and *H.* **Bundesmann**, Beckmann transformation. III., i, 265.
Auwers, *K. von*, and *A.* **Lohr**, alkylated and halogenated indazoles, i, 73.
Auwers, *K. von*, and *H.* **Mauss**, isomeric relationships in the pyrazole series. IV. Alkyl derivatives of 3-phenylpyrazol-5-one, and alkyl and acyl derivatives of 5(3)-chloro-3(5)-phenylpyrazole, i, 1178.
Auwers, *K. von*, and *K.* **Möller**, formation and spectrochemical behaviour of hydrogenated naphthalene derivatives, i, 402.
Auwers, *K. von*, and *F.* **Niemeyer**, isomeric relationships in the pyrazole series. III. 5-Chloro-3-methylpyrazole and its derivatives, i, 1176.
Auwers, *K. von*, and *B.* **Ottens**, derivatives of phenylpropiolaldehyde and α-bromocinnamaldehyde, i, 1428.
formation and transformation of pyrazolecarboxylamides, i, 1459.
Auwers, *K. von*, and *W.* **Pfuhl**, tenacity of organic radicals with respect to nitrogen, i, 1100.
Auwers, *K. von*, *L. von* **Sass**, and *W.* **Wittekindt**, tetrahydroindazoles, 1181.
Auwers, *K. von*, and *W.* **Schmidt**, isomeric relationships in the pyrazole series. II. 3(5)-Phenylpyrazole and its derivatives, i, 585.
Avasare, *M. D.*, See *K. G.* **Naik**.
Avery, *O. T.* See *J. M.* **Neill**.
Avogadro, *L.*, and *G.* **Tavola**, dioximes. XXV., i, 1040.
Awerbuch, *A.* See *M.* **Centnerszwer**.
Awschalom, *M.*, rapid separation of sulphur precipitates in analytical reactions, ii, 823.
Ayyar, *P. R.* See *S. N.* **Iyer**, and *J. J.* **Sudborough**.

B.

Baas-Becking, *L. G. M.*, sulphur bacteria, i, 1217.
Baborovsky, *J.*, hydration of ions, ii, 1151.
Bach, separation of small quantities of calcium from large amounts of magnesium, ii, 825.
Bach, *A.*, active hydrogen, ii, 885.
Bach, *A.*, *W.* **Engelhardt**, and *A.* **Samyslov**, rôle of accompanying substances in immunisation with invertase preparations, i, 1506.
Bach, *D.*, toxicity and nutritive value of ammonium acetate for the lower fungi, i, 216.
Bacharach, *A. L.*, basal vitamin-*B*-free diet of Drummond and Watson, i, 1220.
Bachmann, *F. M.* See *J. C.* **Walker**.
Bachmann, *W.*, and *C.* **Brieger**, heat of wetting of oils and metal and its relationship to lubricating power, ii, 510.
Back, *E.*, Zeeman effect of neon, ii, 341.
Zeeman effects contrary to the rule for multiplets of the first stage, ii, 917.
Backeberg, *O. G.*, alkyl hypochlorites, i, 775.
Backenköhler, *F.* See *F.* **Scheibe**.
Backer, *H. J.*, and *W. G.* **Burgers**, resolution of chlorosulphoacetic acid into its optically active components, i, 359.
optically active components of chlorosulphoacetic acid, i, 631.
Backer, *H. J.*, and *H. W.* **Mook**, optical resolution of bromosulphoacetic acid, i, 632.
Backer, *J.* See *O.* **Collenberg**.
Backes, *P.* See *P.* **Pfeiffer**.
Baddiley, *J.*, *W. W.* **Tatum**, and **British Dyestuffs Corporation, Ltd.**, dyes of the anthraquinone series, i, 414.
Baddiley, *J.* See also **British Dyestuffs Corporation, Ltd.**

r, *W. L.* See *A. R.* **Carr.**
Badische Anilin- & Soda-Fabrik, preparation of nitrogenous anthraquinone derivatives, i, 414.
perylene dyes, i, 1290.
Badoche, *M.* See *C.* **Moureu.**
Badstübner, *W.* See *R.* **Stollé.**
Bäcklin, *E.*, doublet $K\alpha_{1,2}$ of the lighter elements and the dependence of the *X*-ray spectra on chemical combination, ii, 914.
Bäcklin, *E.*, *M.* **Siegbahn**, and *R.* **Thoræus**, semi-optical lines in the *X*-ray spectra, ii, 457, 614.
Bäckström, *H. L. J.*, heat of dissociation of calcium carbonate and the entropy of carbon dioxide, ii, 1140.
thermodynamic properties of calcite and aragonite, ii, 1162.
Baekeland, *L. H.*, and *H. L.* **Bender**, phenol resins and resinoids, i, 689.
Bär, *R.*, abnormal low-voltage arcs in mercury vapour, argon, and helium, ii, 254.
Baermann, *L.* See *W.* **Traube.**
Baerwald, *H.*, electron reflection in gases, ii, 731.
Bahl, *D. C.* See *S. S.* **Bhatnagar.**
Bahlke, *W. H.*, and *R. E.* **Wilson**, boiling-point correction chart for normal liquids with special application to petroleum products, ii, 73.
temperature of vapour above boiling salt solutions, ii, 514.
Bahr, *T.* See *K. von* **Auwers.**
Bahrt, *G. M.* See *J. C.* **Russel.**
Bailar, *J. C.*, *jun.* See *H. B. van* **Valkenburgh.**
Bailey, *C. R.*, condensed ternary system, phenol–water–salicylic acid, ii, 1064.
Bailey, *D. F. H.* See *K. C.* **Bailey.**
Bailey, *G. L.* See *R.* **Genders.**
Bailey, *J. R.* See *R. C.* **Goodwin**, and *C. A.* **Nau.**
Bailey, *K. C.*, synthesis of carbamide from carbon dioxide and ammonia under atmospheric pressure. I., i, 121.
reaction between ferric chloride and potassium thiocyanate, ii, 422.
identity of "alumen" in Pliny's natural history, ii, 591.
Bailey, *K. C.*, and *D. F. H.* **Bailey**, colorimetric determination of thiocyanates and cyanates, ii, 447.
Bailey, *K. C.*, and *J. D.* **Kidd**, freezing points of solutions containing ferric chloride and potassium thiocyanate, ii, 422.
Bailey, *V. A.*, attachment of electrons to gas molecules, ii, 1019.
Bailly, *O.*, application of the Denigès–Grimbert–Leclère reaction to the characterisation and determination of adrenaline in suprarenal powders, ii, 248.
Bain, *J. W.*, double salts formed by sodium and potassium carbonates, ii, 577.
Bain, *J. W.*, and *G. F.* **Kay**, effect of heat on cellulose, i, 639.
Baker, *H. B.*, and (*Miss*) *M.* **Carlton**, effect of ultra-violet light on dried hydrogen and oxygen, ii, 1180.
Baker, *J. W.*, ring-chain tautomerism. XIII. Three-carbon ring-chain tautomerism in a bridged ring system, i, 916.
formation and stability of *spiro*-compounds. XII. Further evidence for the multiplanar configuration of the *cyclo*heptane ring, i, 1277.
Baker, *S.*, and *W. N.* **Haworth**, synthesis of derivatives of γ-arabinose, i, 365.
Baker, *T. T.*, leptology of the silver bromide grain, ii, 574.
Baker, *T. T.*, and *L. F.* **Davidson**, changes in the ultra-violet absorption of gelatin, ii, 838.
Baker, *W.*, and *A.* **Lapworth**, reduction products of arylidenecyanoacetic acids, i, 30.
synthesis of substituted succinic acids containing aromatic residues, i, 670.
Baker, *W.*, and *R.* **Robinson**, β-piperonylpropionitrile and some derived substances, i, 925.
synthetical experiments in the *iso*flavone group. I., i, 1299.
Bakker, *G.*, thermodynamics of the capillary layer, ii, 789.
Bakr, *A. M.*, and *J. W.* **McBain**, sorption of toluene and acetic acid and their mixtures by carbon, ii, 193.
Bakunin, *M.*, and *F.* **Giordani**, constitution of picrotoxin, i, 691.
Balandin, *A.*, contraction constants and affinity of solid compounds, ii, 637.
Balareff, *D.*, rôle of water in reactions in the solid state. IV. and V., ii, 409, 893.
solubility and size of grain, ii, 853.
Balaš, *F.* See *J.* **Frejka.**
Balassa, *L.* See *G.* **Sachs.**
Baldet, *F.*, spectrum of carbon monoxide at very low pressures, and its relation to the spectrum of the tails of comets, ii, 180.
third negative group of carbon; spectrum of the tails of comets; extension on the red side and structure of the bands, ii, 469.

Baldet, *F.*, influence of pressure on carbon band spectra in discharge tubes; consequences for the theory of comets, ii, 469.
band spectra associated with carbon, ii, 927.
red cyanogen spectrum in Daniel's comet (1907), ii, 928.
Baldoni, *A.*, synthesis of salicyluric acid in diseased conditions, i, 330.
Bálint, *M.*, constancy of the hydrogen-ion concentration of living bacteria, i, 338.
iodometric micro-determination of sodium, ii, 158.
Bálint, *M.*, and *P.* **Ruszczynski**, micro-determination of organic substances, i, 323.
Balks, *R.*, formation and decomposition of humus in the soil, i, 1031.
Ballard, *M. P.* See *R. E.* **Oesper**.
Ballin, *O.* See *Erich* **Müller**.
Balls, *A. K.*, and *J. B.* **Brown**, yeast metabolism. I., i, 476.
Balls, *A. K.* See also *J. B.* **Brown**.
Ballye, *A. E.* See *J. B.* **Speakman**.
Baltadschieva, *M.* See *A.* **Skrabal**.
Balthazard, *V.*, spectrometric determination of the "poisoning coefficient" in carbon monoxide poisoning, i, 196.
Baly, *E. C. C.*, and *E. S.* **Semmens**, selective photochemical action of polarised light. I. Hydrolysis of starch, i, 12.
Baly, *E. C. C.* See also *R. W.* **Riding**.
Balz, *P.* See *L.* **Wöhler**.
Balzerkiewicz, *H.* See *A.* **Schaarschmidt**.
Bamann, *E.* See *R.* **Willstätter**.
Bamberger, *E.*, some data from dissertations and other literature, i, 142.
action of hydrohalogen acids (and sulphuric acid) on arylhydroxylamines, i, 388.
arylazides. V., i, 843.
Bancroft, *W. D.*, molecular weight and solution, ii, 858.
Bancroft, *W. D.*, and *R. P.* **Allen**, metallic lustre. II., ii, 658.
Bancroft, *W. D.*, and *C.* **Gurchot**, permeability of membranes, ii, 110.
Bandopadhyay, *P. C.* See *P.* **Ray**.
Banerji, *B. N.*, electric discharge in gases at low pressure, ii, 921.
Banerji, *D.*, scattering of light in mixtures of air and carbon dioxide, ii, 1118.
Bangham, *D. H.*, and *F. P.* **Burt**, sorption of ammonia and carbon dioxide by glass, ii, 284.
sorption of nitrous oxide and sulphur dioxide by glass, ii, 657.
Bangham, *D. H.*, and *W.* **Sever**, experimental investigation of the dynamical equation of the process of gas sorption, ii, 507.
Bangham, *D. H.*, and *J.* **Stafford**, velocity of oxidation of the metals and the structure of coloured oxide films, ii, 138.
"activated" graphite as a sorbent of oxygen, ii, 655.
Bangler, *B.* See *L.* **Schmid**.
Banks, *M. A. L.* See *R.* **Lessing**.
Banu, **Negresco**, and **Heresco**, cholesterol in normal infants, i, 452.
Bappert, *R.* See *K.* **Hess**.
Barat, *C.* See *H. K.* **Sen**.
Barbaudy, *J.*, boiling points of mixtures of water, benzene, and ethyl alcohol under a pressure of 760 mm. of mercury, ii, 766.
Barbieri, *O.* See *G.* **Plancher**.
Barbour, *H. G.*, *C. B.* **Ridout**, and *D.* **Claydon**, chemo-therapeutic properties of a substance with a chain of four arsenic atoms, i, 733.
Bardach, *B.*, abnormal crystal-formation and its relation to oxalate precipitation and to red blood-corpuscles, i, 1114.
Bardet, *J.*, and *C.* **Toussaint**, separation of celtium [hafnium] and its arc spectrum, ii, 826.
Bardwell, *D. C.* See *S. C.* **Lind**.
Barendrecht, *H. P.*, invertase and the second mode of action of hydrogen ions, i, 203.
Bargellini, *G.*, β-phenylcoumarins, i, 1299.
3:4-diphenylcoumarins, i, 1442.
Bargellini, *G.*, and *P.* **Leone**, glucosides of chalkones [phenyl styryl ketones], i, 1283.
Barger, *G.*, and *F. J.* **Eaton**, blue adsorption compounds of iodine. IV., i, 44.
Barger, *G.* See also *E.* **Stedman**.
Barkan, *G.*, studies of iron. I. Action of digestive ferments on the iron of hæmoglobin, i, 1482.
Barkas, *W. W.*, distribution of particles in colloidal suspensions, ii, 289.
Barkenbus, *C.*, and *J. B.* **Holtzclaw**, new substituted benzyl esters, i, 1148.
Barker, *E. F.*, and *O. S.* **Duffendack**, ionisation of hydrogen chloride by electron impacts, ii, 1017.
Barkla, *C. G.*, *J*-phenomenon in *X*-rays, ii, 456.
Barkla, *C. G.*, and *S. R.* **Khastgir**, *J*-transformation of scattered *X*-rays, ii, 456.

Barkla, *C. G.*, and *G. I.* **Mackenzie**, coherence of superposed *X*-radiations, ii, 614.
Barkus, *O.* See *S.* **Morgulis**.
Barnard, *L.* See *J.* **Oliver**.
Barnett, *E. de B.*, action of nitrogen dioxide on anthracene derivatives, i, 1258.
2-chloro-3:5-dinitrobenzamide, i, 1288.
Barnett, *E. de B.*, and *J. W.* **Cook**, mechanism of substitution reactions in the aromatic nucleus, i, 123.
reduction of the bromoanthraquinones, i, 940.
Barnett, *E. de B.*, *J. W.* **Cook**, and *M. A.* **Matthews**, mechanism of substitution reactions in the aromatic nucleus. II., III., IV., and V., i, 648, 900, 1140, 1398.
1:5-dichloroanthrone, i, 818.
Barnett, *E. de B.*, and *M. A.* **Matthews**, mechanism of substitution reactions in the aromatic nucleus. I., i, 18.
1:2-benzanthraquinone (Sirius-yellow G), i, 820.
Barnett, *M. A. F.* See *E. V.* **Appleton**.
Barnette, *R. M.*, *D. J.* **Hissink**, and *J. van der* **Spek**, determination of the hydrogen-ion concentration of the soil, i, 220.
Barratt, *S.*, absorption spectra of mixed metallic vapours, ii, 19.
absorption spectra of mixed metallic vapours. II. Spectra of volatile compounds of magnesium and the alkali metals, ii, 927.
Barratt, *T.*, and *R. M.* **Winter**, thermal conductivity of wires and rods, ii, 756.
Barrenscheen, *H.* See *E.* **Fromm**.
Barrenscheen, *H. K.*, and *O.* **Weltmann**, fluorescent oxidation products of bilirubin and their importance as sources of error in tests for urobilin, i, 187.
Barrett, *F. L.* See *H. F.* **Coward**.
Barrett, *W. R.* See *W. R.* **Orndorff**.
Barriga Villalba, *A. M.*, yajeine, a new alkaloid, i, 828.
Bartels, *H.*, distribution of transition probabilities in the atoms of alkali metals, ii, 624.
Bartens, *K.* See *K.* **Fries**.
Bartholomé, *W.* See *Erich* **Schmidt**.
Barthoux, *J.*, new mineral: dussertite, ii, 235.
pyrites of Majdan-Pek (Serbia), ii, 429.
Barton, *H. A.*, negative and doubly-charged positive ions in argon, ii, 6.
single and double ionisation of argon by electron impacts, ii, 459.
negative ion emission from oxide-coated filaments, ii, 1020.
Barton, *V. P.*, and *F. L.* **Hunt**, molecular dimensions of "celluloid," ii, 21.
Bartlett, *R. S.*, photo-resistance effect for metals at low temperatures, ii, 943.
Bartunek, *R.* See *E.* **Heuser**.
Barus, *C.*, density and diffusion measurement by interferometry, ii, 25.
diffusion of hydrogen into air, measured by the interferometer U-gauge, ii, 27.
Baruttschisky, *I.* See *A.* **Rosenheim**.
Bary, *P.*, physico-chemical composition of glasses, ii, 380.
Basini, *A.* See *G.* **Rossi**.
Bassanoff, *D.* See *H.* **Scheibler**.
Bastings, *L.*, decay of radium-*E*, ii, 9.
decay constant of radium emanation, ii, 621.
Basu, *K.* See *J. C.* **Ghosh**.
Basu, *S. K.* See *H.* **Freundlich**.
Batchelor, *H. W.* See *W. M.* **Gibbs**.
Batscha, *B.*, thoron, ii, 177.
phosphorescent powers of fluorescein, ii, 181.
Batschinski, *A.*, molecular fields and their volumes, ii, 932.
Battegay, *M.*, and *A. M.* **Amuat**, acylhydrazidoanthraquinones, i, 169.
Battegay, *M.*, and *J.* **Véchot**, piaselenazonium salts, i, 1466.
Batuecas, *T.*, compressibility of methyl ether and molecular weight of the gas, ii, 16.
compressibilities of gases at 0° and below one atmosphere, and the divergence from Avogadro's law. III. Ethylene, nitrous oxide, nitric oxide, and methyl ether, ii, 497.
revision of weight of normal litre of methyl chloride vapour, ii, 753.
revision of the compressibility of methyl chloride and the molecular weight of this gas, ii, 753.
Batuecas, *T.*, *G.* **Maverick**, and *C.* **Schlatter**, compressibilities of gases at 0° and below one atmosphere, and the divergence from Avogadro's law. IV., ii, 497.
Bauch, *J.* See *K.* **Amberger**.
Baude, *P.* See *M.* **Javillier**.
Baudisch, *O.*, formation of organic from inorganic substances under the influence of light, ii, 1082.
Baudisch, *O.*, and *D.* **Davidson**, oxidation of thymine; 4:5-dihydroxythymine, i, 1100.
Baudisch, *O.*, and *L. A.* **Welo**, catalysis; active and inactive iron oxide, ii, 881.
ageing of ferrous carbonate and ferrous hydroxide; ageing of natural mineral waters, ii, 992.

Baudisch, *O.* See also *D.* **Davidson**, and *L. A.* **Welo.**
Bauer, *C.* See *A.* **Haller.**
Bauer, *K. H.*, and *G.* **Kutscher**, oxidation of unsaturated fatty acids with hydrogen peroxide and perbenzoic acid, i, 630.
Bauer, *O.*, and *O.* **Vollenbruck**, hardness of copper–tin alloys, ii, 104.
Bauer, *W.* See *E.* **Philippi.**
Baukovac, *O.* See *R.* **Kremann.**
Bauman, *L.*, *M.* **Chudnoff**, and *G. M.* **Mackenzie**, attempted separation of the active constituent of ragweed pollen, i, 1028.
Baumann, *A.* See *H.* **Wieland.**
Baumberger, *J. P.*, hydrogen electrode technique, ii, 236.
Baumecker, *W.*, influence of narcotics on the rate of sinking of blood corpuscles, i, 321.
Baumeister, *L.* See *G.* **Grube.**
Baumgarten, *P.*, action of halogen on the enolates of glutacondialdehyde and synthesis of 3-halogenopyridines, i, 1381.
Baumgarten, *P.* See also *W.* **Traube.**
Baur, *E.*, is the solution of cellulose in ammoniacal copper oxide a peptisation? ii, 662.
light-sensitiveness of potassium ferrocyanide, ii, 884.
photolysis of methylene-blue, sensitised by zinc oxide, ii, 1082.
measurement of single-phase boundary potentials, ii, 1164.
Baur, *H.*, and *R.* **Kuhn**, insulin and its action. III. Lactic acid content of muscle in death due to insulin or to starvation, i, 482.
Baur, *H.* See also *R.* **Kuhn.**
Baur, *K.* See *C.* **Bülow.**
Bausch, *H.* See *A.* **Binz.**
Baxter, *G. P.*, and *H. W.* **Starkweather**, density of oxygen, ii, 188.
density and atomic weight of helium, ii, 1045.
Baxter, *W. P.* See *A. A.* **Noyes.**
Bayen, spark spectra of tungsten and mercury in the extreme ultra-violet, ii, 168.
Bayer, *O.* See *J. von* **Braun.**
Bayerle, *V.*, dropping mercury cathode. V. Deposition of arsenic, antimony, and bismuth, ii, 675.
Bayerle, *V.*, and *M.* **Tamele**, preparation of pure hydrogen, ii, 233.
Bayle, *E.*, and *R.* **Fabre**, urinary elimination of *iso*quinoline alkaloids, in particular of hydrastine, i, 609.
fluorescence as a criterion of purity in organic compounds, ii, 604.
Bayle, *E.*, *R.* **Fabre**, and *H.* **George**, fluorescence and its applications, ii, 260.
Bayley, *C. H.* See *M. C.* **Boswell.**
Bayley, *P. L.*, coloration of the alkali halides by *X*-rays, ii, 21.
Baylis, *J. R.*, influence of curvature on air-saturation of water and its relation to the air-binding of filters, ii, 980.
Beaber, *N. J.* See *H.* **Gilman.**
Beal, *G. D.* See *E. O.* **North.**
Beals, *C. S.*, arc spectrum of palladium, its Zeeman effect, and spectral type, ii, 1015.
Beams, *J. W.* See *F. L.* **Brown.**
Beans, *H. T.*, and *L. P.* **Hammett**, hydrogen electrode, ii, 694.
Beard, *H. G.* See *H. H.* **Hodgson.**
Bearden, *J. A.* See *A. H.* **Compton.**
Beauchamp, *L.* See *L.* **Lematte.**
Becherer, *F.*, preparation of optically active primary alcohols, i, 664.
Bechert, *K.*, structure of the nickel spectrum. II., ii, 1014.
Bechert, *K.*, and *L. A.* **Sommer**, arc spectrum of nickel, ii, 913.
Bechhold, *H.*, electro-ultrafiltration, ii, 1158.
Bechhold, *H.*, and *A.* **Rosenberg**, electro-ultrafiltration of gelatin and glue, ii, 668.
Bechhold, *H.*, and *V.* **Szidon**, ultrafiltration of non-aqueous solutions, ii, 529.
Beck, *A.* See *H.* **Biltz.**
Beck, *W.*, sensitisation and protection by lipoids, ii, 527.
Beckenkamp, *J.*, fine structure of the free benzene molecule, ii, 90.
relationship between the fine structures of the two crystalline forms of carbon and zinc sulphide, ii, 271.
electrostatic and electrodynamic significance of electrons in the crystallisation of the elements of the fourth periodic group, ii, 358.
Becker, *A.*, electron emission excited by α-rays, ii, 8.
cathode rays, ii, 251.
electron emission of metals. I., ii, 616.
photo-electric action of total radiation of a solid body, ii, 1107.
Becker, *B.* See *L.* **Schmid.**
Becker, *E.*, and *H.* **Hilberg**, passivity of metals, ii, 405.
Becker, *G.*, dispersion of electrical double refraction of some organic liquids, ii, 755.
effect of pressure on the infra-red absorption of hydrogen chloride, ii, 1114.

Becker, *H. G.*, mechanism of absorption of moderately soluble gases in water, ii, 106.
Becker, *J.* See *B.* **Helferich.**
Becker, *J. A.*, soft *X*-rays and secondary electrons, ii, 8.
Compton and Duane effects, ii, 17.
Becker, *J. A.*, *E. C.* **Watson**, *W. R.* **Smythe**, *R. B.* **Brode**, and *L. M.* **Mott-Smith**, reality of the Compton effect, ii, 1128.
Becker, *J. E.* See *E. V.* **McCollum.**
Becker, *M. L.*, equilibrium at high temperatures in the iron–carbon–silicon systems, ii, 973.
Becker, *R.*, simple kinetic derivation of the ionisation and vapour pressure equations, ii, 342.
Becker, *R.* See also *W.* **Hieber.**
Becker, *W.* See *G.* **Linck.**
Beckett, *E. G.*, *J.* **Thomas**, and **Scottish Dyes, Ltd.**, anthraquinone derivatives, i, 685.
Bedell, *H. L.* See *T. J.* **Thompson.**
Bedos, *P.*, a new racemic menthone and the two corresponding menthols, i, 1078.
Bedos, *P.* See also *M.* **Godchot.**
Bédowé, *J.*, acyclic acetals and their azeotropic properties, i, 513.
Bedr-Chan, *S.*, analysis of alvite, ii, 710.
Bedreag, *C. G.*, physical structure of the elements, ii, 863.
Beduwé, (*Mlle.*) *J.* See *A.* **Verley.**
Bedworth, *R. E.* See *N. B.* **Pilling.**
Beekley, *J. S.*, and *H. S.* **Taylor**, adsorption of silver salts by silver iodide, ii, 855.
Beeman, *N.* See *W. D.* **Harkins.**
Beeny, *H.*, electrochemical corrosion tests on iron and steel, ii, 1068.
Beeson, *J. W.*, and *J. R.* **Partington**, explosion of ammonia with carbon monoxide and oxygen, ii, 682.
Behner, *K.*, arc spectrum of titanium from 7496 to 2273 Å., ii, 1100.
Behr, *H.* See *P.* **Pfeiffer.**
Behrend, *R.*, history of the synthesis of uric acid, i, 441.
Behrens, *K.* See *O.* **Mumm.**
Behrens, *W. U.*, and *C.* **Drucker**, method for the determination of the specific heat of metals, ii, 24.
Beisler, *W. H.*, and *J. L.* **Bray**, preparation and properties of 1-benzamido-2-methylanthraquinone, i, 1288.
Belaiew, *N. T.*, inner crystalline structure of ferrite and cementite in pearlite, ii, 768.
Belfanti, *S.*, hæmoleucolysin of the pancreas and its relation to Delezenne and Fourneau's lysocithin, i, 326.
Bell, *F. K.*, infra-red absorption spectra of organic derivatives of ammonia. I. Aniline and some mono- and di-alkylanilines, ii, 928.
Bell, *G. E.*, and *F. Y.* **Poynton**, dielectric constants of some liquids and their variation with temperature. I., ii, 477.
Bell, *H.*, the CuH molecule and its band spectrum, ii, 470.
Bell, *H. C.*, and *C. S.* **Gibson**, ββ′-dichloro- and ββ′-dibromo-diethyl selenides and their simple halogen derivatives, i, 1126.
Bell, *R. W.*, effect of heat on solubility of calcium and phosphorus compounds in milk, i, 998.
Bellenot, *H.* See *A.* **Berthoud.**
Beller, *H.* See *H.* **Fischer.**
Beloglazov, *K. F.*, a property of van't Hoff's plane diagram, ii, 788.
Beloglazov, *K. F.* See also *N. S.* **Kurnakov.**
Beltz, *L.*, and *E.* **Kaufmann**, interferometric studies. I. Determination of the refractive index and protein content of blood-serum by the interferometer, i, 1200.
Benatt, *A.*, and *M.* **Händel**, effect of potassium and calcium on the acidity of urine, i, 722.
Bencowitz, *I.*, and *H. T.* **Hotchkiss**, preparation of conductivity water, ii, 817.
Bencowitz, *I.*, and *R. R.* **Renshaw**, basis for the physiological activity of certain -onium compounds; the mobilities of the -onium ions. I. Sulphonium ions, ii, 872.
Benda, *O.* See *R.* **Kremann.**
Bender, *H. L.* See *L. H.* **Baekeland.**
Benedicks, *C.*, hardness of manganese steel, ii, 188.
Benedict, *F. G.*, and *E. L.* **Fox**, oxycalorimeter, ii, 998.
Benedict, *S. R.*, determination of blood-sugar, i, 994.
determination of uric acid in the blood, i, 995.
reaction given by insulin solutions *in vitro*, i, 1512.
Benedict, *S. R.* See also *R. C.* **Theis.**
Benedik, (*Miss*) *I.* See *J.* **Klimone.**
Bener, *C.* See *F.* **Kehrmann.**
Benesch, *E.*, determination of copper value of celluloses, ii, 74.
Benevolenskaja, *S. V.* See *A. E.* **Tschitschibabin.**
Bengough, *G. D.*, and *R.* **May**, [corrosion of copper, brass, and zinc in sea-water]; seventh report to the Corrosion Research Committee of the Institute of Metals, ii, 218.

Bengtsson, *E.*, and *E.* **Svensson**, conditions for appearance, and structure, of bands of silver between $\lambda = 3330$ and $\lambda = 3358$, ii, 166.

Benguerel, *C.*, determination of chlorides in blood, i, 455.

detection of urobilin and urobilinogen in urine, i, 460.

Bennett, *C. T.*, and *D. C.* **Garratt**, *iso*propyl, propyl, and ethyl alcohols: refractive indices, i, 498.

Bennett, *G. M.*, hepto- and nono-dilactones, i, 883.

Bennett, *G. M.*, and *W. A.* **Berry**, Ráy's supposed triethylene trisulphide, i, 695.

Bennewitz, *K.*, theory of degraded gases and null point energy, ii, 97.

Benoit, *F.* See *A.* **Guntz**.

Benton, *A. F.*, and *P. H.* **Emmett**, reduction of nickelous and ferric oxides by hydrogen, ii, 216.

Berckmans, *V. S. F.*, and *A. F.* **Holleman**, tetrachloronitrobenzenes, tetrachlorodinitrobenzenes, and their reaction with sodium methoxide, i, 1136.

Berczeller, *L.*, and *H.* **Wastl**, sinking of red blood-corpuscles in flowing blood, i, 452.

viscosity of suspensions of blood-corpuscles. I., i, 452.

Bere, *C. M.*, and *S.* **Smiles**, derivatives of aniline disulphoxide, i, 21.

Bérenger, (*Mlle.*), and *A.* **Tian**, heats of solution and heats of incomplete reactions, ii, 790.

Beretta, *A.* [with *N.* **Jacoob**], synthesis of 1-*p*-sulphophenyl-1:2:5-triazole-3:4-dicarboxylic acid, i, 589.

Beretta, *A.* See also *G.* **Charrier**.

Berg, *A.*, brominated additive products of Schiff's bases, i, 817.

Berg, *O.* See *W.* **Noddack**.

Berg, *O. W.* See (*Mlle.*) *E.* **Gleditsch**.

Bergami, *G.* See *F.* **Bottazzi**.

Bergeim, *O.*, intestinal chemistry. I. Determination of intestinal reductions. II. Intestinal reductions as a measure of putrefaction; influence of diet, i, 99.

Berger, *G.*, photocatalytic effect of neutral salts, ii, 313.

Berger, *G.* See also *S. C. J.* **Olivier**.

Berger, *Gottfried.* See *Heinrich* **Schulze**.

Berger, *J.*, Van der Waals' equation and the liquid state of aggregation. II., ii, 376.

Bergerhoff, *K.* See *H.* **Thoms**.

Bergh, *A. A. H. van den*, and *H.* **Wieringa**, formation of sulphæmoglobin, i, 1475.

Bergheimer, *E.* See *R.* **Lorenz**.

Berglund, *V.* See *G. von* **Hevesy**.

Bergmann, *M.*, constitution of proteins, i, 848.

unsaturated reduction products of the sugars. X. ψ-Glucal and dihydro-ψ-glucal, i, 887.

Bergmann, *M.*, and *H.* **Ensslin**, compounds of formaldehyde with glycine, i, 1046.

Bergmann, *M.*, *H.* **Ensslin**, and *L.* **Zervas**, aldehydic compounds of amino-acids, i, 890.

Bergmann, *M.*, and *E.* **Knehe**, chemistry of substances of high molecular weight. I. An anhydride of cellobiose, i, 1384.

Bergmann, *M.*, *A.* **Miekeley**, and *E.* **Kann**, transformations of peptide substances. V. Conversion of serine into pyruvic acid and alanine, i, 1134.

high-molecular bodies. II. "High-molecular" amino-acid anhydrides of the piperazine type, i, 1474.

Bergmann, *M.*, *A.* **Miekeley**, and *F.* **Stather**, unsaturated reduction products of the sugars and their transformations. IX. Anhydride of a disaccharide from δ-hydroxy-δ-acetylbutyl alcohol, i, 227.

Bergmann, *M.*, *A.* **Miekeley**, *F.* **Weinmann**, and *E.* **Kann**, transformations of peptide substances. IV. Hydrolytic deamination of amino-acids, i, 795.

Bergmann, *M.*, and *A.* **Miekeley** [with *C.* **Witte**], transformations of peptide substances. III. Derivatives of *dl*-serine; new anhydrides of glycylserine, i, 235.

Bergmann, *M.*, and *F.* **Stather**, action of alkalis on keratin, i, 847.

Bergstrom, *F. W.*, reaction between potassamide and salts of cobalt and iron in liquid ammonia, ii, 231.

acid properties of ammonium salts in liquid ammonia, ii, 315.

electronegative potential series in liquid ammonia, ii, 794.

displacement of metals from solutions of their salts by less electro-positive elements. II. Reaction between amides of the alkali and alkaline-earth metals and elements more electro-positive than tin, ii, 885.

action of ammonia and of a solution of potassamide in liquid ammonia on certain halides of molybdenum and tungsten, ii, 1083.

Bering, *F.*, effect of adsorption compounds on infectious diseases, i, 858.

Berk, *J.*, and *P. H.* **Hermans**, action of nitrous acid on aliphatic primary amines, and formation of aliphatic diazo compounds, i, 794.
Berkhoff, *G.* See *F. A. H.* **Schreinemakers.**
Berkhout, *P. J. T. van*, determination of dextrose, non-protein nitrogen, uric acid and total phosphorus in normal human blood in tropical regions, and in the blood of birds suffering from avitaminosis, i, 453.
Berkmann, *S.* See *N.* **Isgarischev.**
Berl, *E.*, and *H.* **Fischer**, explosive limits of mixtures of gas or vapour with air, ii, 413.
Berl, *E.*, and *F.* **Rau**, determination of molecular weight by aid of the gas-interferometer of Haber and Löwe, ii, 24.
Berl, *E.*, and *E.* **Wachendorff**, adsorption experiments with solutions, ii, 507.
Berlin, *L. W.* See *K.* **Brand.**
Berliner, *J. F. T.*, and *O. E.* **May**, vapour pressure. I. Nitroanilines, ii, 1045.
Berliner, *J. F. T.* See also *R. M.* **Hann.**
Bernal, *J. D.*, structure of graphite, ii, 17.
Bernardi, *V.* See *G.* **Ponzio.**
Berner, *E.* See *C. N.* **Riiber.**
Bernfeld, *A.* See *A.* **Fodor.**
Bernhard, *A.*, uric acid content of cerebrospinal fluid, i, 326.
Bernhard, *X.* See *O.* **Keller.**
Bernhardt, *F.*, saturation pressure of mercury up to 2000 kg./cm.^{2}, ii, 493.
Bernhardt, *H.*, determination of very small quantities of lead in animal tissues and the ageing of very dilute solutions of lead nitrate, ii, 1003.
Bernhardt, *H.*, and *C. H. R.* **Rabl**, effect of yellow phosphorus (on rats) with varying mineral nutrition, i, 1357.
Bernhardt, *H.*, and *H.* **Ucko**, bromine content of blood; detection of minute quantities of bromine, i, 454.
Bernhauer, *E.* See *E.* **Späth.**
Bernhauer, *K.*, acid formation by *Aspergillus niger*, i, 205.
Bernoully, *O.* See *F.* **Straus.**
Bernstein, *J. K.* See *M.* **Coblens.**
Bernton, *A.*, aliphatic hydroxyphosphinic acids. I. α-Carboxy-α-hydroxyethylphosphinic acid, i, 646.
Berrer, *E.* See *L.* **Kalb.**
Berry, *A. J.*, thallous thallic halides, ii, 59.
Berry, *W. A.* See *G. M.* **Bennett.**
Bert, *L.*, preparation of aromatic γ-chloroallyl derivatives and their use in the synthesis of aromatic acetylenic hydrocarbons, alcohols, and aldehydes, i, 803.
general method of synthesis of allyl compounds, i, 1052.
Bert, *L.*, *P. C.* **Dorier**, and *R.* **Lamy**, homologues of γ-phenylpropinene, i, 1373.
Berthelot, *A.*, and *G.* **Ramon**, agents for the transformation of toxins into anatoxins, i, 481.
Berthelot, *D.*, law of photochemical equivalents and the place of the quantum theory in relation to the atomic theory and energetics, ii, 1022.
Bertho, *A.*, general method of formation of 1-phenyl-4-alkyl-1:2:3-triazoles, i, 840.
Berthold, *R.*, photographic and ionisation effect of *X*-rays of different wavelengths, ii, 252.
Berthoud, *A.*, photochemical sensitisation, ii, 1083.
Berthoud, *A.*, and *H.* **Bellenot**, photochemistry of the halogens; action of light on the reactions of iodine or bromine with potassium oxalate, ii, 141.
Bertolo, *P.*, action of iodine on desmotroposantonin: artemisic acid, i, 546.
genesis of artemisic acid from desmotroposantonin, i, 921.
reactions of glycyrrhizin, ii, 1212.
Berton, *A. L.* See *G.* **Vavon.**
Bertrand, *G.*, determination of the different forms of manganese present in arable soil, i, 223.
new reaction of the pentoses, i, 790.
Bertrand, *G.*, and *A.* **Compton**, so-called reversibility of enzyme action; complete hydrolysis of salicin by emulsin, i, 738.
Bertrand, *G.*, and *M.* **Mâchebœuf**, presence of nickel and cobalt in animals, i, 719.
amount of cobalt in organs of animals, i, 996.
Bertrand, *G.*, and *M.* **Mokragnatz**, general occurrence of nickel and of cobalt in arable land, i, 492.
presence of nickel and cobalt in vegetables, i, 873.
Bertrand, *G.*, and *H.* **Nakamura**, comparative physiological importance of iron and zinc, i, 1114.
Besler, *E.* See *B.* **Helferich.**
Bessaritsch, *R.* See *W.* **Steinkopf.**

Best, *C. H.*, and *J. H.* **Ridout**, blood lactic acid after insulin, i. 754.
Best, *C. H.* See also *D. A.* **Scott**.
Bestehorn, *H.* See *K.* **Feist**.
Bettzieche, *F.*, action of Grignard reagents on amino-acids. III. Deamination of tertiary amino-alcohols by acetic acid and sodium nitrite: conversion into carbonyl compounds with migration of groups, i, 251.
action of Grignard reagents on amino-acids. V. Wandering of acyl groups in amino-alcohols and glycols, i, 1147.
Bettzieche, *F.* See also *K.* **Thomas**.
Beuker, *H.* See *H. C.* **Kremers**.
Beust, *R. von.* See *M.* **Busch**.
Beyne, *E.*, volumetric determination of zinc, ii, 69, 438.
Bezssonoff, *N.*, colour reactions of the fat-soluble vitamins. i, 107.
nature of the antiscorbutic principle, vitamin-*C*, i, 751.
Jendrassik reaction for vitamin-*B*, i, 1220.
Bezssonoff, *N.* See also *G.* **Truffaut**.
Bhagwat, *V. K.*, and *F. L.* **Pyman**, 4- and 5-nitro-1:2-dimethylglyoxalines, i, 1174.
Bhatnagar, *S. S.*, *M.* **Prasad**, and *D. C.* **Bahl**, protective action of soaps and further evidence in favour of the chemical theory of adsorption. III., ii, 1155.
Bhatnagar, *S. S.*, *M.* **Prasad**, *N. G.* **Mitra**, and *D. L.* **Shrivastava**, electrical resistance of thin films of organic liquids on paper, ii, 948.
Bhatnagar, *S. S.*, *M.* **Prasad**, and *D. M.* **Mukerji**, surface tension of sodium and potassium amalgams at the amalgam–benzene interface, ii, 194.
effect of light on the interaction of water and sodium and potassium amalgams, ii, 811.
Bhatnagar, *S. S.*, *M.* **Prasad**, and *D. D.* **Ohri**, effect of water on dried and pressed silica gel. I., ii, 966.
Bhatnagar, *S. S.* See also *D. L.* **Shrivastava**.
Bhide, *B. V.*, and *J. J.* **Sudborough**, esterification, i, 1127.
Bialosuknia, *V.*, rôle of different nitrogenous compounds as sources of nitrogen for higher plants in pure cultures, i, 1366.
cyanamide, its derivatives, and hexamethylenetetramine as sources of nitrogen for wheat, cabbage, and white mustard in pure cultures, i, 1366.
Bianchessi, *M.* See *G.* **Charrier**.
Bianu, *M. V.*, number of ions produced by the α-particle from polonium, ii, 348.
Biata, (*Mlle.*) *M.* See *A.* **Chrząszczewska**.
Bichowsky, *F. V.*, generation of hydrocyanic acid, i, 236.
Bidault, *C.*, and *S.* **Blaignan**, bacterium producing ethyl butyrate, i, 1216.
Biedermann, *W.*, and *C.* **Jernakoff**, hydrolysis of starch by salts. IV. Hydrolysis by blood pigments and plant peroxydases, i, 11.
Biehler, *W.*, concentration in the blood and excretion of alcohol at high altitudes, i, 1115.
Bielecki, *J.*, and *J.* **Sztencel**, investigation of the phosphorus compounds in the fruit of the walnut (*Juglans regia*), i, 215.
Bieler, *E. S.*, band spectra of lead isotopes, ii, 732.
Bielozerski, *A. N.* See *A. V.* **Blagoveschenski**.
Bielz, *F.*, direct measurement of mean free path of uncharged silver atoms in nitrogen, ii, 668.
Bierich, *R.*, and *A.* **Rosenbohm**, biochemistry of cancer formation, i, 328.
Bierman, *H. R.*, and *F. J.* **Doan**, colorimetric picric acid method for determining lactose, ii, 245.
Bierry, *H.*, and *L.* **Moquet**, microdetermination of free sugar in total blood, i, 179.
glycolysis and changes of the inorganic phosphorus in blood *in vitro*, i, 454.
Bierry, *H.*, and *F.* **Rathery**, excretion of ketone substances and β-hydroxybutyric acid in depancreatised dogs, i, 856.
Bierry, *H.*, *F.* **Rathery**, and *E.* **Kourilsky**, is glycolysis diminished in diabetic blood? i, 1207.
Bierry, *H.*, *F.* **Rathery**, and *L.* **Levina**, variations in the blood-sugar of splenectomised dogs. i, 857.
Bierry, *H.* See also *A.* **Desgrez**.
Biester, *A.*, *M. W.* **Wood**, and *C. S.* **Wahlin**, carbohydrates. I. Relative sweetness of pure sugars, i, 1498.
Biester, *A.* See also *J. J.* **Willaman**.
Bigelow, *L. A.*, reaction between benzylideneaniline and carbon disulphide at high temperature and pressure, i, 242.
Bigiavi, *D.*, and *A.* **Angeli**, action of nitrous acid on azoxyphenols, i, 316.
Bigiavi, *D.*, and *G.* **Kindt**, oxidation of benzeneazophenol [*p*-hydroxyazobenzene], i, 597.

Bigwood, *E. J.*, p_H limits of normal blood; regulation of p_H in normal and pathological conditions, i, 1342.
Biilmann, *E.*, *A. L.* **Jensen**, and *K. O.* **Pedersen**, method of measuring reduction potentials of quinhydrones, ii, 404.
Biilmann, *E.* See also *G. E.* **Cullen**.
Bijvoet, *J. M.* See *N. H.* **Kolkmeijer**.
Bikerman, *J. J.*, organic sols of arsenic trisulphide, ii, 522.
Billeter, *O.*, rearrangement of thiocyanates into thiocarbimides, i, 1051.
Billig, *K* See *K.* **Fries**.
Billon, *P.*, primary β-amino-alcohols having the general formula $R{\cdot}CH(NH_2){\cdot}CR^1R^2{\cdot}CH_2{\cdot}OH$, i, 120.
Bills, *C. E.*, resistance to reagents of the antirachitic substance in cod-liver oil, i, 1019.
Biltz, *H.*, simultaneous electrolytic determination of copper and lead, ii, 715.
Biltz, *H.*, and *A.* **Beck**, action of phenylcarbimide on methylcarbamide, i, 1393.
Biltz, *H.*, and *E.* **Peukert**, 3-ethyluric acid and 3-ethylxanthine, i, 1462.
Biltz, *W.*, volume of the water in the hydrates of calcium sulphate, ii, 356.
theory of swelling and reversibility phenomena of colloids, ii, 520.
aluminium sulphide, ii, 986.
Biltz, *W.* [with *H.* **Bröhan** and *W.* **Wein**], systematic doctrine of affinity. XXXVI Ammoniates of cupric halides, ii, 1182.
Biltz, *W.* [with *E.* **Rahlfs**], systematic doctrine of affinity. XXXII. Higher ammoniates of halides of the iron group, ii, 1191.
Biltz, *W.* [with *W.* **Wein**], systematic doctrine of affinity. XXXV. Ammoniates of aurous halides, ii, 1182.
Biltz, *W.*, and *H. G.* **Grimm**, lattice energy of ammines, ii, 842.
Biltz, *W.*, and *W.* **Holverscheit**, systematic doctrine of affinity. XXX. Heats of formation of intermetallic compounds. VI. Tin alloys, ii, 268.
Biltz, *W.*, and *E.* **Keunecke**, systematic doctrine of affinity XXXI. Thiohydrates, ii, 986.
Biltz, *W.*, and *W.* **Klemm**, fused electrolytes, ii, 127.
Biltz, *W.*, and *C.* **Mau**, systematic doctrine of affinity. XXXIV. Ammoniates of cadmium and mercury halides, ii, 1184.
Biltz, *W.*, and *C.* **Messerknecht**, systematic doctrine of affinity. XXXIII. Ammoniates of beryllium halides, ii, 1183.
Biltz, *W.* See also *C.* **Messerknecht**.
Binder, *K.*, potassium ferritripyrocatecholoxide as an indicator for acidimetry and alkalimetry, ii, 596.
Bing, *H. J.*, and *H.* **Heckscher**, quantitative determination of the "primary ether extract" of blood, i, 995.
fat + cholesterol content of the blood in cases of Basedow's disease, i, 999.
Bingham, *E. C.*, Shimer filter tube, ii, 432.
plasticity in colloid control, ii, 1157.
Binz, *A.*, and *H.* **Bausch**, sulphoxyl compounds. XIV. Aldehydesulphoxylates as protective colloids, i, 991.
Binz, *A.*, *H.* **Bausch**, and *E.* **Urbschat**, arseno-metallic compounds. IV. Silver salvarsan, i, 1195.
Binz, *A.*, and *C.* **Räth**, constitution of sulphur-blue, i, 445.
Birch, *C. F.*, and *W. S. G. P.* **Norris**, petroleum. I. Occurrence of compounds of sulphur in the light distillate from the crude oil of Maidan-i-Naftun, i, 628.
petroleum. II. Action of sodium hypochlorite on sulphur compounds of the types found in petroleum distillates, i, 1229.
Bircher, *L. J.*, graphic comparison of potential scales and electrode potentials, ii, 711.
Bircher, *L. J.*, *W. D.* **Harkins**, and *G.* **Dietrichson**, two types of overvoltage and the temperature effect, ii, 211.
Bircher, *L. J.*, *A. W.* **Ingersoll**, *B. F.* **Armendt**, and *G.* **Cook**, electrolytic preparation of semicarbazide sulphate, i, 525.
Birckenbach, *L.*, and *K.* **Kellermann**, pseudohalogens. I., ii, 568.
Birge, *R. T.*, further spectra associated with carbon, ii, 829.
band spectra associated with carbon, ii, 836.
Birge, *R. T.*, and *J. J.* **Hopfield**, quantum analysis of new nitrogen bands in the ultra-violet, ii, 787.
Birtwell, *C.*, *D. A.* **Clibbens**, and *B. P.* **Ridge**, chemical analysis of cotton; oxycellulose. I., i, 234.
Bischoff, *F.*, oil of *Echinacea angustifolia*, i, 760.
Bischoff, *F.*, and *H.* **Adkins**, organic reactions at the surface of titania; adsorption of certain gases by titania, ii, 568.
Bishop, *G.* See *O. L.* **Brady**, and *J. N.* **Collie**.
Bissinger, *E.*, *E. J.* **Lesser**, and *K.* **Zipf**, mechanism of the action of insulin, i, 209.

Bistrzycki, *A.*, and *J.* **Risi**, action of benzilic and anisilic acids on thiophenols, i, 1426.
Bittner, *K.* See *A.* **Kurtenacker.**
Bizzell, *J. A.* See *T. L.* **Lyon.**
Bjeljaeva, *W.* See *A.* **Palladin.**
Bjerregaard, *A. P.*, crystallising point of paraffin wax, i, 769.
Bjerrum *N.*, theory of osmotic pressure, membrane potential, and coagulation of colloids; colloidal chromium hydroxide, ii, 111.
Bjerrum, *N.*, *A.* **Unmack**, and *L.* **Zechmeister**, dissociation constant of methyl alcohol, ii, 1062.
Björkesen, *A.*, *X*-ray radiation from hot sparks, ii, 830.
Björkesen, *A.* See also *L.* **Pauling.**
Black, *A.* See *H.* **Steenbock.**
Black, *A. P.* See *H. W.* **Doughty.**
Black, *C. A.* See *A. T.* **Larson.**
Black, *D. H.*, β-ray spectrum of mesothorium. II., ii, 10.
electrical properties of liquid sulphur, ii, 24.
high-energy γ-ray from thorium disintegration products. ii, 177.
β-ray spectra of thorium disintegration products, ii, 922.
Blackburn, *C. M.*, application of the quantum theory of band spectra to the first negative Deslandres group of carbon, ii, 260.
Blackett, *P. M. S.*, ejection of protons from nitrogen nuclei, photographed by the Wilson method, ii, 256.
Blackett, *P. M. S.*, and *J.* **Franck**, excitation of the hydrogen spectrum by electron impact, ii, 1097.
Blackshaw, *G. N.*, silage, its composition and value as a farm food, i, 1523.
Blagoveschenski, *A. V.*, ripening of seeds, i, 756.
Blagoveschenski, *A. V.*, and *A. N.* **Bielozerski**, specific action of plant ferments. II. Specific conditions of action of leaf peptases, i, 1009.
Blagoveschenski, *A. V.*, and *N. I.* **Sossiedov**, specific action of plant ferments. I. The specific conditions of action of leaf invertases, i, 1007.
Blaignan, *S.* See *C.* **Bidault.**
Blair, *E. W.*, and *W.* **Ledbury**, partial formaldehyde vapour pressures of aqueous solutions of formaldehyde. I., ii, 400.
Blaise, *E. E.*, and (*Mlle.*) *M.* **Montagne**, preparation of acyclic δ-diketones, i, 633.
formation of pyridine derivatives from acyclic δ-diketones, i, 835.
Blaise, *E. E.*, and (*Mlle.*) *M.* **Montagne**, conversion of dialkyl*cyclo*hexenones into dialkylbenzenes, i, 1071.
Blake, *F. C.*, precision *X*-ray measurements by the powder method, ii, 844.
Blake, *F. C.* See also *R. J.* **Havighurst.**
Blanchetière, *A.*, evolution of knowledge of the chemical structure of protein compounds, i, 602.
colour reactions of tryptophan with aldehydes, i, 963.
sodium, potassium, and calcium in blood after ovariectomy and in the menopause, i, 1207.
Blanchetière, *A.*, and *H.* **Cardot**, mineral composition of the blood of dogs (under narcosis), i, 455.
Blanck, *E.*, and *W.* **Lohmann**, conversion of quicklime into calcium carbonate in soils, i, 223.
Blanck, *E.*, and *A.* **Rieser**, chemical alteration of granite beneath peat, ii, 820.
Blanck, *E.*, and *F.* **Scheffer**, conversion of calcium oxide into calcium carbonate in the soil and the causes of its combination, i, 491.
Blanco, *J. G.* See *F.* **Knoop.**
Blank, *H. R.* See *J. H.* **Müller.**
Blaschko, *H.*, heat of combustion of pyruvic acid and its physiological significance, i, 1011.
Blaszkovska, (*Mlle.*) *Z.*, heats of formation of quinonechloroimines and quinonedichlorodi-imines, ii, 1042.
Blaszkovska, (*Mlle.*) *Z.* See also *W.* **Swientoslawski.**
Blatt, *H.* See *P.* **Landrieu**, and *C.* **Moureu.**
Blau, *M.*, photographic action of H-particles from paraffin and aluminium, ii, 1111.
Bleeker, *C. E.*, and *I. A.* **Bongers**, intensity measurements in flame spectra, ii, 77.
Blencke, *W.* See *R.* **Fricke.**
Blessl, *H.* See *G.* **Sachs.**
Bleyer, *B.*, and *O.* **Kallmann**, less studied constituents of cows' milk. I., i, 184.
less studied constituents of cows' milk. II. The water-soluble yellowish-green colouring matter, i, 457.
Bleyer, *L.*, changes of buffering and the amino-nitrogen increase in nutrient media by bacterial action, i, 746.
Blicke, *F. F.*, reaction between metallic sodium and aromatic aldehydes, ketones, and esters. I. Aldehydes, i, 37.

Blicke, *F. F.*, reaction between metallic sodium and aromatic aldehydes, ketones, and esters. II. Esters, i, 662.
dissociation of benzopinacol derivatives, i, 811.
Blindow, *K.* See *E.* **Koehler.**
Blish, *M. J.*, and *A. J.* **Pinckney**, identity of gluten proteins from various wheat flours, i, 176.
Blish, *M. J.* See also *C. W.* **Ackerson.**
Bloch, *E.* See *L.* **Bloch.**
Bloch, *L.*, and *E.* **Bloch**, spark spectrum of iron in the Schumann region, ii, 78.
spark spectrum of tungsten in the Schumann region, ii, 168.
chlorine spark spectra, ii, 611.
spark spectra in the Schumann region, ii, 726, 829.
Bloch, *L.*, *E.* **Bloch**, and *G.* **Déjardin**, spark spectrum of neon, ii, 334.
Bloch, *W.* See *W.* **Herz.**
Blok, *C. J.*, determination of the p_H "spectrum" for bacteria, and application to *Bacillus coli*, i, 615.
Blom, *J. H.* See *O.* **Diels.**
Bloor, *W. R.*, plasma lipoids in experimental anæmia, i, 609.
biochemistry of the fats, i, 1346.
Blümmel, *F.* See *K.* **Freudenberg.**
Bluker, (*Miss*) *C. E.*, flame spectra and chemical reaction, ii, 1025.
Blum, *L.*, and *L.* **Delaville**, modification of the blood and secretions by ultrafiltration, i, 605.
mechanism of acidosis, i, 723.
Blum, *L.*, *M.* **Delaville**, and *V.* **Caulaert**, modifications of the blood during anaphylactic shock, i, 188.
Blum, *W.*, "electrolytes" and "ionogens," ii, 402.
Blumberger, *J. S. P.* See *J.* **Böeseken.**
Blunck, *R.*, and *P. P.* **Koch**, determination of intensity ratios in systems of Debye–Scherrer rings; application to the investigation of the photographic process, ii, 940.
Boas, *F.*, and *F.* **Merkenschlager**, plant tyrosinases (with particular regard to the action of quinine), i, 474.
Boas, *M. A.*, value of egg-white as sole source of nitrogen for young growing rats, i, 211.
Boas, *I.*, determination of pepsin in gastric juice, i, 1213.
Bobilioff, *W.*, hydrogen-ion concentration in the latex of *Hevea braziliensis*, i, 622.
Bobko, *E. W.*, and *D. W.* **Druschinin**, influence of individual factors on the reaction of the soil solution, i, 1525.
Bobrownicki, *W.*, action of hydrogen on calcium cyanamide, i, 526.
Bock, *A. V.*, and *H.* **Field**, *jun.*, carbon dioxide equilibrium in alveolar air and arterial blood, i, 93.
Bock, *J. C.* See *M.* **Gilbert.**
Bock, *R.*, dielectric constants and absorption-coefficients of glycerol, ii, 355.
Bockstahler, *L. J.*, specific heat of incandescent tungsten, ii, 643.
Bodansky, *M.*, distribution of unsaturated fatty acids, cholesterol, and cholesterol esters in experimental anæmia, i, 724.
Bodansky, *O.* See *J. M.* **Nelson.**
Bode, *K.* See *R.* **Ruer.**
Boden, *E.*, *P.* **Neukirch**, and *F.* **Wankell**, insulin-like behaviour of oat bran extract, i, 483.
Bodenstein, *M.*, theory of catalytic hydrogenation by means of platinum, ii, 216.
Bodenstein, *M.*, mechanism of photochemical reactions, ii, 1075.
Bodenstein, *M.*, *P.* **Harteck**, and *E.* **Padelt**, chlorine hexoxide, ii, 991.
Bodenstein, *M.*, and *G.* **Kistiakovski**, photochemical decomposition of chlorine monoxide, ii, 883.
Bodenstein, *M.*, and *H.* **Lütkemeyer**, photochemical formation of hydrogen bromide and velocity of formation of the bromine molecule from the atoms, ii, 218.
Bodenstein, *M.*, and *H.* **Plaut**, formation and thermal decomposition of carbonyl chloride, ii, 135.
Bodforss, *S.*, mechanism of Fischer's synthesis of indoles, i, 698.
Bodforss, *S.*, and *A.* **Arstal**, formation of perborates by electrolysis using unsymmetrical alternating current, ii, 414.
Bodine, *J. H.*, and *D. E.* **Fink**, microelectrode for determination of hydrogen-ion concentration, i, 1201.
Bodó, *R. von*, determination of iodides in urine, i, 1490.
Boechi, *C.* See *G.* **Rossi.**
Boedecker, *F.*, and *O.* **Wunstorf**, constitution of hydrargyrum salicylicum and related substances, i, 1107.
Boedtker, *E.*, presence of lecithin in fats, i, 1114.
Böeseken, *J.*, complex compounds of boron and the asymmetry of borosalicylic acid, i, 449.
transformations of a new type, i, 1237.
repulsive action of mutually equal and mutually differing groups in saturated organic compounds, ii, 1031.

Böeseken, *J.*, and *J. S. P.* Blumberger, action of iodine in chloroform solution on some ethylenic hydrocarbons, i, 225.
velocity of oxidation of aromatic ethylene derivatives by Prileschaeff's reagent, i, 240.
Böeseken, *J.*, *W. D.* Cohen, and *S. L.* Langedijk, reaction of ketones with alcohols under the influence of light. I. Absorption spectra of some ketones, i, 408.
Böeseken, *J.*, and *H.* Gelissen, action of benzoyl peroxide on chloroform and on carbon tetrachloride (a new synthesis of ω-trichlorotoluic acids), i, 30.
Böeseken, *J.*, and *J. A.* Mijs, asymmetric derivatives of boron, i, 911.
Böeseken, *J.*, and *A. E. J.* Peck, *cis*- and *trans-cyclo*hexane-1:3-dicarboxylic acids; separation of the *trans*-acid into its optically active components, i, 1150.
Böeseken, *J.*, and (*Mlle.*) *H. J.* Ravenswaay, refractive index of Chinese wood oil and the structure of α- and β-elæostearic acids, i, 507.
constitution of α-elæostearic acid from Chinese wood oil and from its isomeride β-elæostearic acid, i, 1129.
Böhme, *E.* See ***W.* Ostwald.**
Boehringer Sohn, *C. H.*, preparation of α-lobeline, i, 425.
preparation of papaverine nitrite, i, 427.
preparation of compounds of lecithin with bile acids and their alkali salts, i, 824.
Bölli, *E.* See ***W.* Autenrieth.**
Boer, *J. H. de*, detection of ortho-, pyro-, and meta-phosphate occurring together, and in presence of sodium fluoride, ii, 67.
Boer, *J. H. de*, and *A. E. van* Arkel, separation of zirconium and hafnium by crystallisation of the double ammonium fluorides, ii, 243.
separation of zirconium from its ores as phosphate, ii, 705.
behaviour of zirconium phosphate towards acids and bases, ii, 1185.
Boer, *J. H. de*. See also ***A. E. van* Arkel.**
Börjeson, *G.*, electric synthesis of colloids, ii, 197.
Börnegg, *C. E. von*, rapid determination of solid matter in liquids, ii, 324.
Boeters, *H.* See ***C.* Paal.**
Bogatsky, *W.* See ***P.* Petrenko-Kritschenko.**
Bogert, *M. T.*, and *M.* Chertcoff, new group of dyes from poison gases through the 2-aminothiazoles as intermediates; preparation of thiazole dyes of Doebner-violet type, i, 80.
thiazoles. VI. New group of dyes from poison gases through the 2-aminothiazoles as intermediates; preparation of thiazole dyes of Doebner violet type, i, 315.
Bogert, *M. T.*, and *J. J.* Ritter, constitution of the "Pechmann dyes," and the mechanism of their formation from β-benzoylacrylic acid, i, 36.
unsaturated ketonic acids. I. Constitution of the so-called "Pechmann dyes" and the mechanism of their formation from β-benzoylacrylic acid, i, 255.
Bogert, *M. T.*, and *J. J.* Ritter, unsaturated ketonic acids. II. Experiments with β-benzoylacrylic acid and related compounds, i, 816.
Boggio-Lera, *E.* See ***A.* Piutti.**
Bogue, *R. H.*, plasticity and structure in gelatin systems, ii, 1058.
Bogue, *R. H.*, and *M. T.* O'Connell, influence of hydrogen-ion concentration on the optical rotation of gelatin, ii, 744.
Bohanes, *A.*, determination of volatile organic acids, ii, 605.
Bohn, *G.* See ***A.* Drzewina.**
Bohn, *P. R.*, presence of calcium oxalate crystals on the surface of certain *Caryophyllaceæ*, i, 1124.
Bohne, *A.* See ***A.* Windaus.**
Bohr, *N.*, action of atoms in collision, ii, 1022.
Boitard, *G.*, chemical theory of corresponding states, ii, 865.
Bokhorst, *S. C.*, and *H. van der* Zee, allotropy of mercuric iodide, ii, 490.
Bokorny, *T.*, bases as [plant] growth-promoting substances and the pickling of seed with bases and other substances, i, 489.
Bolin, *I.*, conditions of maximum stability for some organic substances, ii, 411.
Bolliger, *A.*, and *F. W.* Hartman, relation of blood phosphates to carbohydrate metabolism, i, 1000.
Bollmann, *J. L.*, *F. C.* Mann, and *T. B.* Magath, physiology of the liver. X. Uric acid following total removal of the liver, i, 1496.
Bom, *T. van der*. See ***C.* Dhéré.**
Bonath, *K.* See ***G.* Giemsa, and *A.* Papendieck.**

Bondi, *J.* See *H.* **Pringsheim.**
Bone, *W. A.*, *D. M.* **Newitt**, and *D. T. A.* **Townend**, gaseous combustion at high pressures. V. Explosion of hydrogen–air and carbon monoxide–air mixtures at varying initial pressures up to 175 atmospheres, ii, 800.
Bonem, *P.* See *S.* **Edlbacher.**
Bongards, *H.*, determination of the radioactive content of the air by streaming, ii, 621.
Bongers, *I. A.* See *C. E.* **Bleeker.**
Bonhoeffer, *K. F.*, active hydrogen, ii, 52.
behaviour of active hydrogen, ii, 52.
chemical luminescence with active hydrogen, ii, 839.
Bonino, *G. B.*, spectro-chemistry in the ultra-red. VII. Absorption of certain homologous ketones, ii, 838.
spectro-chemistry in the ultra-red. VIII. Absorption of certain halogenated hydrocarbons, ii, 838.
spectro-chemistry in the ultra-red. IX. Origin of the absorption bands incorrectly attributed to the groups $-CH_3$ and $-CH_2-$, ii, 1032.
Bonnet, *A.* See *L.* **Meunier.**
Bonnet, *R.* See *E. F.* **Terroine.**
Booge, *J. E.* See *J.* **Kendall.**
Boomer, *E. H.*, chemical activity of helium, ii, 144, 925.
Booth, *H.*, and *E. J.* **Bowen**, heats of solution and of decomposition of chlorine dioxide, ii, 299.
action of light on chlorine dioxide, ii, 573.
Bordas. See **D'Arsonval.**
Bordas, *F.*, **François-Dainville**, and **Roussel**, elimination of benzoic acid and benzoates from the body, i, 1206.
Bordas, *F.*, and *F.* **Touplain**, conductivity of water, ii, 155.
Bordet, *J.*, and *M.* **Bordet**, bacteriolytic power of colostrum and of milk, i, 616.
Bordet, *M.* See *J.* **Bordet.**
Borelius, *G.*, electrical conductivity of mixed crystal alloys, ii, 749.
Borelius, *G.*, and *C. H.* **Johansson**, coefficient of expansion at low temperatures, ii, 27.
Borge, *E.* See *K. A.* **Vesterberg.**
Borissov, *P.* See *N. D.* **Zelinski.**
Borkenstein, *W.* See *R.* **Schenck.**
Born, *F.*, dissociation of several metallic oxides, ii, 785.
vapour pressure of the volatile constituents of glass at the ordinary temperature, ii, 785.
Born, *M.*, electrical meaning of chemical affinity, ii, 482.
Born, *M.*, and *J.* **Franck**, quantum theory and molecule formation, ii, 266.
dissipation of heat of reaction, ii, 365.
Bornet, *L.*, colour reactions of cryogenine with heavy metals, ii, 164.
Bornträger, *A.*, detection of small quantities of lactic acid in fruit [tomato] juice as calcium lactate, ii, 1007.
Borsook, *H.*, and *H.* **Wasteneys**, enzymic synthesis of protein. II. Effect of temperature on synthesising action of pepsin, i, 472.
enzymic synthesis of protein. IV. Effect of concentration on peptic synthesis, i, 864.
Borsook, *H.* See also *H.* **Wasteneys.**
Bosányi, *A.*, and *J.* **Csapó**, acid-combining power of the serum of healthy and diseased children, i, 188.
Bosch, *J. C. van der.* See *E.* **Cohen.**
Bose, *P. K.*, thiodiazines. I. Condensation of thiosemicarbazide with ω-bromoacetophenone, i, 167.
thiodiazines. II. Condensation of ω-bromoacetophenone with 4-substituted thiosemicarbazides; constitution of thiosemicarbazides, i, 1465.
Bossuet, *R.* See *P.* **Jolibois.**
Bost, *R. W.* See *A. S.* **Wheeler.**
Boswell, *M. C.*, and *C. H.* **Bayley**, mechanism of the inhibition of the catalytic action of platinum black and partly reduced nickel oxide by chlorine, ii, 215.
action of promoters in catalysis, ii, 805.
Bothe, *W.*, and *H.* **Geiger**, experimental test of the theory of Bohr, Kramers, and Slater, ii, 1.
Botolfsen, *E.* See *E.* **Gleditsch.**
Bott, *T. H.* See *F.* **Challenger.**
Bottazzi, *F.*, and *G.* **Bergami**, effect of low temperatures on liquid colloidal systems, ii, 965.
Bougault, *J.*, α-hydroxy-γ-phenylcrotonamide, i, 921.
an anhydride (ether) of a ketone hydrate; benzyl-β-phenylethylsuccinic acids, i, 1152.
Bouma, *T.*, intensity ratios of some inter-combination lines, ii, 915.
Bouman, *N.*, electrochemical behaviour of chromium, ii, 46.
Bourgeaud, *M.*, and *A.* **Dondelinger**, affinity constant of some organic bases, ii, 117.
Bourguel, *M.*, preparation of true acetylenic hydrocarbons, i, 1, 770.

Bourguel, *M.*, action of phosphorus pentachloride on certain aldehydes and ketones, i, 864.
hydrogenation of triple linkings; formation of *cis*-ethylenic compounds, i, 883.
Bourion, *F.*, and *J.* **Picard**, kinetic study of the reduction of mercuric bromide by sodium formate, ii, 685.
Bourjau, *W.* See *H.* **Ohle**.
Bourne, *C. L. C.* See *J. B.* **Harrison**.
Bourne, *W.* See *R. L.* **Stehle**.
Boutaric, *A.*, flocculation of colloidal solutions, ii, 393.
Boutaric, *A.*, and *G.* **Corbet**, critical solution temperature of ternary mixtures, ii, 103.
Boutaric, *A.*, and (*Mme.*) *Y.* **Manière**, influence of radiations on the flocculation of colloidal solutions, ii, 394.
influence of very small quantities of foreign substances on the stability of colloidal solutions, ii, 778.
Boutaric, *A.*, and (*Mlle.*) *G.* **Perreau**, protection of colloidal solutions by the addition of electrolytes in quantities insufficient to produce flocculation, ii, 526, 863.
influence of some stable colloids on the flocculation of sols and suspensions, ii, 1155.
Boutaric, *A.*, and *M.* **Vuillaume**, colloidal arsenic sulphide, ii, 112.
Bouyoucos, *G. J.*, heat of wetting as a new means of determining the colloidal materials in soils, i, 348.
heat of wetting of soils dried at different temperatures and the force with which soils absorb water, i, 1228.
factors influencing the heat of wetting of soil colloids, i, 1228.
Bovalini, *E.* See *U.* **Sborgi**.
Bowen, *A. R.* See *G. T.* **Morgan**.
Bowen, *E. J.*, dissociation theory and photochemical thresholds, ii, 1074.
photo-activation of chlorine, ii, 1079.
Bowen, *E. J.*, and *J. F.* **Sharp**, photochemical decomposition of nitrosyl chloride, ii, 695.
Bowen, *E. J.* See also *H.* **Booth**.
Bowen, *I. S.*, and *R. A.* **Millikan**, series spectra of two-valency-electron systems and of three-valency-electron systems, ii, 252.
series spectra of the stripped atoms of phosphorus (P V), sulphur (S VI), and chlorine (Cl VII), ii, 342.
series spectra of two-valency-electron atoms of phosphorus (P IV), sulphur (S V), and chlorine (Cl VI), ii, 610.
Bowen, *I. S.*, and *R. A.* **Millikan**, *pp'* groups in atoms of the same electronic structure, ii, 916.
series spectra of two-valency-electron atoms of boron (B II) and carbon (C III), ii, 1013.
Bowen, *I. S.* See also *R. A.* **Millikan**.
Bowen, *N. L.*, and *J. W.* **Greig**, crystalline modifications of $NaAlSiO_4$, ii, 997.
Bowen, *N. L.* See also *G. W.* **Morey**.
Bowler, *J. P.*, and *W.* **Walters**, toxicity and rate of excretion from the blood stream of calcium chloride, i, 723.
Boyce, *J. C.* See *J. H.* **Jones**.
Boyd, *W. J.*, action of mixtures of nitric acid and hydrochloric acid on acetone, i, 788.
Boynton, *L. C.* See *H. C.* **Sherman**.
Bozorth, *R. M.*, orientations of crystals in electrodeposited metals, ii, 1038.
Bozorth, *R. M.*, and *L.* **Pauling**, crystal structures of cæsium tri-iodide and cæsium dibromoiodide, ii, 748.
Brachmann, *W.* See *E.* **Rupp**.
Brackett, *F. S.*, atomic force fields, ii, 2.
Bradford, *S. C.*, kinetic theory of vaporisation. I. and II., ii, 26, 1142.
Bradley, *A. J.*, crystal structure of lithium potassium sulphate, ii, 638.
allotropy of manganese, ii, 1124.
Bradley, *F.*, and *W. C. M.* **Lewis**, ionisation of two electrolytes in alcohol–water mixtures; influence of environment on ionisation, ii, 868.
Bradley, *H. C.* See *A. B.* **Hertzmann**.
Brady, *O. L.*, and *G.* **Bishop**, isomerism of the oximes. XXII. Configuration of the aldoximes, i, 930.
Brady, *O. L.*, and *J.* **Harris**, phenylcarbamyl derivatives of nitrophenols, i, 1261.
Brady, *O. L.*, *S. W.* **Hewetson**, and *L.* **Klein**, reactions of the unsymmetrical trinitrotoluenes, i, 16.
Brady, *O. L.*, and *H. V.* **Horton**, alcoholysis of trinitroanisole and trinitrophenetole, i, 1409.
Brady, *O. L.*, and *L.* **Klein**, isomerism of the oximes. XXI. Action of picryl chloride and of chloro-2:4-dinitrobenzene on aldoximes, i, 674.
Brady, *O. L.*, and *R. P.* **Mehta**, isomerism of the oximes. XX. Isomeric *p*-nitrobenzophenoneoximes and their four methyl esters, i, 43.
Brady, *O. L.*, *W. G. E.* **Quick**, and *W. F.* **Welling**, nitration of phthal- and succin-*p*-tolil, i, 1400.

Braecke, *M.*, changes in the composition of *Rhinanthus crista galli*, L., *Melampyrum arvense*, L., and *M. pratense*, L., during a year's growth, i, 619.

Bragg, (*Sir*) *W. H.*, structure of quartz, ii, 1131.

Bragg, *W. L.*, influence of atomic arrangement on refractive index, ii, 92.

interpretation of intensity measurements in *X*-ray analysis of crystal structure, ii, 735.

Bragg, *W. L.*, and *S.* **Chapman**, theoretical calculation of rhombohedral angle of calcite etc., ii, 92.

Brahm, *C.*, volatile fatty acids formed by the acid fermentation of foodstuffs. I. "Electrosilage" of maize, i, 623.

Braicovic, *A.* See *P.* **Leone**.

Bramley, *A.*, velocity of the synthesis of hydrogen bromide by capacity change, ii, 802.

multiplet structure, ii, 831.

Brammall, *A.*, and *H. F.* **Harwood**, tourmalinisation in the Dartmoor granite, ii, 819.

Branch, *G. E. K.*, and *H. E. H.* **Branch**, action of halogens on pyrrole to give coloured solutions, i, 66.

Branch, *H. E. H.* See *G. E. K.* **Branch**.

Brand, *E.* See *M.* **Sandberg**.

Brand, *K.*, and *W.* **Krey**, coloured phenol ethers of the diphensuccindene group, i, 904.

Brand, *K.*, and *O.* **Loehr**, compounds of the diphensuccindene series. VII. Oxidation of diphensuccinda-9:12-dione to phthalic acid and benzil-*oo'*-dicarboxylic acid, i, 683.

compounds of the diphensuccindene series. VIII. Dinitrodiphensuccinda-9:12-dione, i, 684.

Brand, *K.*, *H.* **Ludwig**, and *L. W.* **Berlin**, coloured hydrocarbons of the diphensuccindene group; an abnormal Grignard reaction, i, 904.

Brand, *K.*, and *W.* **Mühl**, 9:12-diaryl-Δ^{10}-diphensuccindenes and 9:12-diaryldiphensuccindanes, i, 903.

Brand, *K.*, *O.* **Stallmann**, *W.* **Groebe**, and *H.* **Stein**, halochromism of triphenylmethane and azo compounds. X. Thiophenols and the bathochromic effect of the alkylmercapto group, i, 397.

Brandt, *A.* See *A.* **Stock**.

Brandt, *L.* See *G.* **Jander**.

Brandt, *P. M.* See *H. G.* **Miller**.

Brass, *K.*, and *G.* **Nickel**, diazido-, diaminodihydroxy-, and tetrahydroxy-phenanthraquinones, i, 273.

phenanthraquinonyl-8-azide and its acid decomposition, i, 446.

Brass, *K.*, and *O.* **Ziegler**, monoazides of anthraquinone, i, 685.

Brauch, *W.* See *A.* **Gigon**.

Braun, *G.* See *G.* **Zemplén**.

Braun, *J. von*, and *O.* **Bayer**, catalytic hydrogenation of indole bases, i, 428.

dihydrazines. VI. Further experiments in the sugar group with diphenylmethanedimethyldihydrazine, i, 1382.

Braun, *J. von*, *O.* **Bayer**, and *W.* **Kaiser**, cyclic sulphides. III., i, 1445.

Braun, *J. von*, and *O.* **Engel**, ring closures in the meta position in the benzene series. III., i, 382.

Braun, *J. von*, *R.* **Fussgänger**, and *M.* **Kühn**, tenacity of organic radicals. III., i, 1401.

Braun, *J. von*, and *W.* **Kaiser**, syntheses in the fatty-aromatic series. XV. *o*-γ-Bromopropylbenzyl bromide, i, 1414.

Braun, *J. von*, and *M.* **Kühn**, halogenated allyl halides, i, 1374.

Braun, *J. von*, and *H.* **Reich**, syntheses in the aliphatic-aromatic series. XVI. Chlorinated amines and amino-acids, i, 1405.

Braun, *J. von*, and *L.* **Schörnig**, hydrogenated carbazoles, i, 1449.

Braun, *J. von*, and *F.* **Zobel**, action of ammonia on bisimmonium bromides, i, 1455.

Braun, *J. von*. See also *R.* **Willstätter**.

Braune, *H.* [with *H.* **Hellweg**], diffusion in mixed crystals, ii, 103.

Brauner, *M.* See *L.* **Kofler**.

Brauns, *D. H.*, optical rotation and atomic dimension. IV. and V., ii, 633.

Bray, *J. L.* See *W. H.* **Beisler**.

Bray, *W. C.* See *R. S.* **Livingston**, and *A. A.* **Noyes**.

Breckenridge, *J. M.* See *W. M.* **Walker**.

Breckpot, *R.*, action of organo-magnesium compounds on nitriles; γ-ethoxybutyronitrile, i, 14.

Bredée, *H. L.* See *E.* **Cohen**.

Bredemeier, *H.* See *G.* **Tammann**.

Bredig, *G.*, and *A. von* **Goldberger**, example of photochemical reaction-coupling ($COCl_2+H_2$) and the photochemical decomposition of formaldehyde, ii, 142.

Bredig, *G.*, and *L.* **Teichmann**, critical constants and vapour pressures of hydrogen cyanide, ii, 950.
Bredig, *M. A.* See *S.* **Goldschmidt.**
Bredt, *J.*, camphor-*sec.*-*tert.*-nitrilic and chlorocamphor-*sec.*-*tert.*-nitrilic acids, i, 255.
Bredt, *J.*, and *A.* **Ivanov**, formation of camphor-*sec.*-*tert.*-nitrilic chloride and chlorocamphor-*sec.*-*tert.*-nitrilic chloride from camphorimide by means of phosphorus pentachloride, i, 254.
Breguet, *A.* See *L.* **Meunier.**
Brehme. See **Opitz.**
Brehme, *T.*, and *P.* **György**, calcium fixation by animal tissues. XI., i, 717.
Breit, *G.*, polarisation of resonance radiation in weak magnetic fields, ii, 629.
Breit, *G.*, and *H. K.* **Onnes**, dielectric constants of liquid hydrogen and liquid oxygen, ii, 631.
Breit, *G.* See also *E. O.* **Hulburt**, and *A. E.* **Buark.**
Brenchley, *W. E.*, and *H. G.* **Thornton**, relation between the development, structure, and functioning of the nodules on *Vicia faba* as influenced by the presence or absence of boron in the nutrient medium, i, 1368.
Brennen, *H.*, chemical studies on the isotopes of lead, ii, 174, 1109.
Brennen, *J. H.*, adsorption of polonium by various substances and its reversibility, ii, 770.
Brentano, *J.*, focussing method in crystal powder analysis by *X*-rays, ii, 483.
Brewer, *A. K.*, ionisation produced in gaseous reactions, ii, 919.
Brewster, *C. M.*, Schiff's bases from 3:5-dibromosalicylaldehyde, i, 38.
Brewster, *R. Q.* See *F. B.* **Dains.**
Brezina, *J.*, dropping mercury cathode. VI. Electro-deposition of manganese and the complexity of manganous ions in ammoniacal solutions, ii, 676.
Bridel, *M.*, enzymic hydrolysis of gentiacaulin; production of a xyloglucose, primeverose, i, 336.
presence of monotropitin in fresh roots of three species of *Spiræa*: *S. ulmaria*, *S. filipendula*, and *S. gigantea* (var. *rosea*), i, 347.
enzymic hydrolysis of monotropitin; production of primeverose, i, 615.
presence of large quantities of free maltose in the fresh tubers of *Umbilicus pendulinus*, DC, i, 620.
primeverose, the primeverosides, and primeverosidase, i, 760.
Bridel, *M.*, primeverosidase and primeverase in emulsin from almonds, i, 1438.
Bridel, *M.*, and *C.* **Charaux**, blackening of Orobanches in the course of their desiccation, i, 488.
unstable glucoside complex obtained from bark of *Rhamnus cathartica*, i, 621.
hydrolytic products of fermentation of rhamnicoside: primeverose and rhamnicogenol, i, 636.
rhamnicoside, a new glucoside, the source of China green, found in the bark of the stem of the purgative buckthorn, i, 690.
chemical composition of the bark of the purgative buckthorn (*Rhamnus cathartica*, L.), i, 1224.
Bridel, *M.*, and *P.* **Picard**, preparation and properties of monotropitoside, i, 1027.
Bridge, *L. A. du*, positive rays produced by ultra-violet light, ii, 251.
Bridgman, *P. W.*, thermal conductivity and thermo-electric force of single metal crystals, ii, 1136.
viscosity of liquids under pressure, ii, 1143.
Brieger, *C.* See *W.* **Bachmann.**
Brieger, *F.*, silicon metabolism of diatoms, i, 341.
Briggs, *D. R.*, crystalline cuprous bromide, ii, 319.
Briggs, *D. R.* See *F. N.* **Peters**, *jun.*
Briggs, *G. E.*, plant yield and intensity of external factors; Mitscherlich's "Wirkungsgesetz," i, 1222.
Briggs, *G. E.*, and *J. B. S.* **Haldane**, kinetics of enzyme action, i, 736.
Briggs, *G. H.*, electric charge carried by thorium-*X* and thorium emanation recoil atoms in gases, ii, 922.
Briggs, *S. H. C.*, potassium chlororuthenates and the co-ordination number of ruthenium, ii, 703.
Brighton, *T. B.* See *D. A.* **MacInnes.**
Brill, *H. C.*, properties of aryl esters and ethers of *N*-piperidinoalkyl compounds, i, 833.
Brillouin, *L.*, surface tension: interpretation of the Eötvös expression, ii, 496.
Briner, *E.*, *T.* **Egger**, and *H.* **Paillard**, oxidations with ozone. II. Preparation of camphor i, 274.
Briner, *E.*, *W.* **Plüss**, and *H.* **Paillard**, catalytic dehydration of phenol–alcohol systems, i, 248.
Briner, *E.*, *H. von* **Tscharner**, and *H.* **Paillard**, oxidations with ozone. III. Preparation of methylvanillin, piperonal, and anisaldehyde, i, 1069.

Brings, *L.*, nitrogen distribution in the hydroxyproteic acid fraction of urine, i, 328.

Brinkman, *R.*, and *J. von der* **Velde**, quantitative investigation in biological fluids of substances with great surface activity, i, 468.

Brinkmann, *E.* See *W.* **Hückel.**

Brinkworth, *J. H.*, measurement of the ratio of the specific heats, using small volumes of gas; ratios of the specific heats of air and of hydrogen at atmospheric pressure and at temperatures between 20° and −183°, ii, 373.

Brinsmaid, *W.*, double-reacting turmeric paper, ii, 435.

Brinton, *P. H. M.-P.*, and *R. B.* **Ellestad**, determination of uranium in carnotite, ii, 72.

Brinton, *P. H. M.-P.*, and *A. E.* **Stoppel**, ignition of precipitates. II. Conversion of molybdenum sulphide into oxide and the volatility of molybdenum trioxide, ii, 72.

Brinton, *P. H. M.-P.* See also *A. E.* **Stoppel.**

Brintzinger, *H.* See *A.* **Gutbier.**

Brioux, *C.*, influence of urea, used as fertiliser, on the reaction of the soil, i, 491.

Brioux, *C.*, and *J.* **Pien**, use of the quinhydrone electrode for determination of p_H in soils, i, 1227.

Briscoe, *H. V. A.*, and *P. L.* **Robinson**, redetermination of the atomic weight of boron, ii, 346.

Briscoe, *H. V. A.*, *P. L.* **Robinson**, and *G. E.* **Stephenson**, electrical explosion of tungsten wires, ii, 348.

use of fused borax in the determination of the atomic weight of boron, ii, 619.

Briscoe, *H. V. A.* See also *P. L.* **Robinson**, and *L. A.* **Sayce.**

British Dyestuffs Corporation, Ltd., *J.* **Baddiley**, and *W. W.* **Tatum**, new dyes of the anthraquinone series, i, 145.

British Dyestuffs Corporation, Ltd., *W. H.* **Perkin**, *jun.*, and *G. E.* **Clemo**, preparation of 4-tetrahydroquinolone and of intermediate products, i, 697.

British Dyestuffs Corporation, Ltd. See also *J.* **Baddiley.**

Britton, *H. T. S.*, hydrogen and oxygen electrode titrations of some dibasic acids and of dextrose, ii, 977.

electrometric studies of the precipitation of hydroxides. I. Precipitation of magnesium, manganous, ferrous, cobalt, nickel, and thorium hydroxides by use of the hydrogen electrode, ii, 1203.

Britton, *H. T. S.*, electrometric studies of the precipitation of hydroxides. II. Precipitation of the hydroxides of zinc, chromium, beryllium, aluminium, bivalent tin, and zirconium by the use of the hydrogen electrode, and their alleged amphoteric nature, ii, 1203.

electrometric studies of the precipitation of hydroxides. III. Precipitation in the cerite group of rare earths and of yttrium hydroxide by use of the hydrogen electrode, ii, 1204.

electrometric studies of the precipitation of hydroxides. IV. Precipitation of mercuric, cadmium, lead, silver, cupric, uranic, and ferric hydroxides by the use of the oxygen electrode, ii, 1204.

Briusova, *L. J.* See *S. S.* **Nametkin.**

Brode, *R. B.*, absorption coefficient for slow electrons in gases, ii, 617.

absorption coefficient for slow electrons in vapours of mercury, cadmium, and zinc, ii, 1020.

Brode, *R. B.* See also *J. A.* **Becker.**

Brodkorb, *F.* See *G. F.* **Hüttig.**

Brodmann, *L.* See *F.* **Weigert.**

Brodsky, *A.*, corresponding temperatures of solids, ii, 26.

Bröhan, *H.* See *W.* **Biltz.**

Brönsted, *J. N.*, theory of the velocity of chemical reactions, ii, 681.

Brönsted, *J. N.*, and *A.* **Delbanco**, velocity of saponification of ionic esters, ii, 684.

Brönsted, *J. N.*, and *H. C.* **Duus**, catalytic decomposition of nitroamide. II. Catalysis by simple amino-bases, ii, 982.

Brönsted, *J. N.*, and *C. V.* **King**, secondary kinetic salt effect in the case of hydroxyl ion catalysis, ii, 1171.

Broglie, *L. de*, and *A.* **Dauvillier**, semi-optical lines in the *X*-ray spectra, ii, 458.

Broglie, *L. de*, and *J. L.* **Trillat**, physical interpretation of *X*-ray spectra of fatty acids, ii, 640.

Broglie, *M. de*, high-energy γ-rays and their photo-electric effect, ii, 347.

Broglie, *M. de*, and *J.* **Thibaud**, exceptionally intense absorption of a radiation by the emitting atom, ii, 165.

Brohm, *C.* See *J.* **Tröger.**

Broker, *W.* See *R. E.* **Oesper.**

Bronstein, *M.*, theory of the continuous *X*-ray spectrum, ii, 727.

quantum theory of the Laue effect, ii, 733.

Brook, *G. B.* See *D. M.* **Fairlie.**

Brooke, *W. L.*, essential oil of calantas wood, i, 418.
Brooks, *F. P.* See *A. S.* **Wheeler.**
Brooks, *M. M.*, permeability of living and dead cells. V. Effects of sodium hydrogen carbonate and ammonium chloride on the penetration of *Valonia* by tervalent and quinquevalent arsenic at various hydrogen-ion concentrations, i, 1004.
Broomé, *B. H.*, *X*-ray investigation of some mixed crystals of the systems (Na,Ag)Cl and K(Cl,Br), ii, 366.
Brophy, *D. H.*, determination of small amounts of boron in tungsten, ii, 901.
Brosche, *A.* See *F.* **Foerster.**
Brotz, *A.* See *E.* **Heuser.**
Broughall, *G. M.* See *E. G. R.* **Ardagh.**
Brown, *D. G.* See *W. M.* **Cumming.**
Brown, *E. B.* See *C. A.* **Nau.**
Brown, *F. E.*, distilling flask for corrosive liquids, ii, 897.
Brown, *F. L.*, and *J. W.* **Beams**, order of appearance of certain lines in the spark spectra of cadmium and magnesium, ii, 913.
Brown, *F. S.*, cryoscopic measurements with nitrobenzene. III. Equilibrium in nitrobenzene solution, ii, 296.
Brown, *F. S.*, and *C. R.* **Bury**, cryoscopic measurements with nitrobenzene. II. Variation of molecular depression with water content, ii, 32.
colloid systems in nitrobenzene, ii, 1055.
Brown, *G. G.*, *E. H.* **Leslie**, and *J. V.* **Hunn**, gaseous explosions. I. Initial temperature and rate of rise of pressure, ii, 682.
Brown, *H. C.* See *T. A.* **Henry.**
Brown, *J.*, vapour pressure of binary mixtures, ii, 377.
Brown, *J. B.*, and *A. K.* **Balls**, yeast metabolism. II. Carbon dioxide and alcohol, i, 470.
Brown, *J. B.* See also *A. K.* **Balls.**
Brown, *M. J.*, sugar content of the blood in normal and under-nourished children, and the effect of fat on the absorption of carbohydrate, i, 994.
Brown, *R. J.*, effect of some inorganic salts on the polarisation of raw sugar solutions, ii, 372.
Brown, *R. L.*, polymerisation and oxidation of indene in the vapour phase, i, 1258.
Browne, *A. W.* See *F.* **Wilcoxon.**
Brownlee, *A.*, methods of fitting the formula of Michaelis in relation to the effect of hydrogen-ion concentration on enzyme action to the data, with some discussion of the results, i, 1007.
Brownstein, *H. J.* See *C. D.* **Hurd.**
Bruckner, *B.*, and *W.* **Overbeck**, ultrafiltration under pressure, ii, 529.
Brudi, *E.* See *W.* **Küster.**
Brünnich, *J. C.*, electrometric titration, ii, 711.
Brugsch, *T.*, and *H.* **Horsters**, intermediate carbohydrate metabolism in the liver. VI. Insulin; intermediate sugar of the liver and musculature, i, 208.
intermediate carbohydrate metabolism in the liver. VIII. Phosphatase and phosphatese of hexosediphosphoric acid in the liver with regard to insulin, i, 483.
Brugsch, *T.*, *H.* **Horsters**, and *G.* **Shinoda**, intermediate carbohydrate metabolism in the liver. VII. Its gaseous exchange (normal, starving, insulin-treated, and depancreatised animals), i, 192.
Brugsch, *T.*, and *J.* **Rother**, significance of enterotropic uric acid for the physiology and pathology of uric acid metabolism, i, 860.
Bruhat, *G.*, and *M.* **Pauthenier**, dispersion of carbon disulphide in the ultra-violet, ii, 478.
carbon disulphide band at 320mμ, ii, 837.
Bruin, *T. L. de*, and *P.* **Zeeman**, connexion between the spectra of argon and ionised potassium, ii, 167.
Bruins, *H. R.* See *E.* **Cohen.**
Brukl, *A.*, preparation of metal tellurides from hydrogen telluride and solutions of salts, ii, 895.
Brukl, *A.* See also *L.* **Moser.**
Brummer, *E.*, and *S. von* **Náray-Szabó**, anodic purification of mercury, ii, 303.
Brun, *P.*, miscibility of mixtures of water, ethyl alcohol, and *iso*butyl alcohol, ii, 769.
Brunetti, *R.*, fine structure of the helium line 5876 Å., ii, 249.
Bruni, *G.*, solid solutions, ii, 380.
Bruni, *G.*, and *G. R.* **Levi**, solid solutions of compounds of elements of different valencies, ii, 281.
Brunken, *J.* See *A.* **Windaus.**
Brunner, *E.*, thermal decomposition of acetyl succinyl peroxide, i, 1236.
Brunner, *E.* See also *P.* **Ruggli.**
Brunner, *O.* See *E.* **Späth.**
Brus, *G.*, permanganic oxidation of nopinene, i, 47.
action of chlorine on α-pinene, i, 821.
Brutzkus, *M.*, method of producing chemical reactions, ii, 215.
realisation of chemical reactions in compressors, ii, 314.

Bruylants, *P.*, action of organo-magnesium compounds on nitriles; ethyl cyanoformate, i, 15.
isomerisation in olefinic compounds, i, 493.
Bruylants, *P.*, and *A.* **Christiaen**, thermochemistry of the butenonitriles, i, 797.
Bruylants, *P.*, *F.* **Lafortune**, and *L.* **Verbruggen**, determination of the atomic weight of selenium, ii, 174.
Bružs, *B.* See *M.* **Centnerszwer**, and *A. L.* **Marshall**.
Bubam, *W.* See *A.* **Gutbier**.
Buchanan, *C.* See *T. S.* **Patterson**.
Bucherer, *H. T.*, and *F.* **Stickel**, action of sulphites on aromatic hydroxy and amino compounds. XI. Action of phenylhydrazine-sodium hydrogen sulphite mixture on azo dyes, i, 1338.
Buchheim, *K.* See *W.* **Steinkopf**.
Buchwald, *E.*, oscillation-phenomena in diffraction spectra, ii, 1117.
Buchwaldt, *A.* See *G.* **Heller**.
Buck, *J. S.*, *W. H.* **Perkin**, *jun.*, and *T. S.* **Stevens**, synthesis of 2:3:10:11-bismethylenedioxyprotoberberine and 6:7:3′:4′-bismethylenedioxyprotopapaverine, i, 958.
Buck, *J. S.* See also *I. M.* **Heilbron**.
Buckley, *H. E.*, and *W. S.* **Vernon**, crystal structure of magnesium fluoride, ii, 484.
crystal structures of the sulphides of mercury, ii, 1037.
Buckley, *O. E.*, and *L. W.* **McKeehan**, effect of tension upon magnetisation and magnetic hysteresis in "permalloy," ii, 945.
Buckner, *G. D.*, *J. H.* **Martin**, and *A. M.* **Peter**, calcium metabolism in the laying hen. II., i, 190.
chemistry of the oviduct of the hen, i, 1347.
effect of a calcium carbonate supplement in the diet of hens on the weight, protein content, and calcium content on the white and yolk of their eggs, i, 1497.
mode of transference of calcium from the shell of the hen's egg to the embryo during incubation, i, 1497.
Budan. See *R.* **Kremann**.
Budde, *O.*, calcium fixation in animal tissues. XII., i, 718.
Budde, *O.*, and *E.* **Freudenberg**, measurement of calcium-ion concentration [in blood], i, 713.
Büchner, *K.* See *D.* **Vorländer**.
Bülow, *C.*, detection and determination of small amounts of acetone, ii, 1210.
Bülow, *C.*, and *K.* **Baur**, azo compounds with ethyl diacetylsuccinate and Bülow's synthesis of substituted pyrazoles, i, 1327.
Bülow, *C.*, and *W.* **Spengler**, arylazoacetylacetones and the products of their condensation and fission, i, 1102.
Bülow, *W.* See *A.* **Sonn**.
Bürker, *K.*, new hæmoglobinometer, i, 177.
Bürki, *F.*, anomalous rotatory dispersion, ii, 33.
Büttgenbach, *E.*, electroanalytical determination of cadmium in sulphuric acid solutions, ii, 439.
double acetates of copper and the alkali metals, i, 1035.
Bufano, *M.*, determination of dextrose in presence of sucrose in organic liquids, i, 453.
Buffett, *G. M.* See *T. J.* **Thompson**.
Buffington, *R. M.* See *W. M.* **Latimer**.
Buhlea, *C.* See *S.* **Fränkel**.
Buhtz, *E.*, process and apparatus for carrying out chemical reactions, ii, 427.
Buisson, *H.*, and *C.* **Jausseran**, spontaneous reversal of rays in the neon spectrum, iii, 333.
Bukschnewski, *J. D.*, determination of chlorine in benzaldehyde, ii, 1000.
Bulger, *H. A.* See *J. P.* **Peters**.
Bullock, *K.*, oleo-resin of Indian valerian root, i, 1294.
Bulmer, *F. M. R.*, *B. A.* **Eagles**, and *G.* **Hunter**, uric acid determinations in blood, i, 605.
Bumstead, *J. H.* See *A. R.* **Rich**.
Bundesmann, *H.* See *K. von* **Auwers**.
Bungartz, *E.*, spectra of oxygen and sulphur, ii, 609.
Bunting, *D.*, influence of lead and tin on the brittle ranges of brass, ii, 282.
Bunting, *R. W.* See *E. V.* **McCollum**.
Burd, *J. S.*, relation of biological processes to concentrations of cations in soils, i, 1527.
Burd, *J. S.* See also *J. C.* **Martin**.
Burdick, *W. L.*, some ammono-carbonic acids and their reactions in liquid ammonia, i, 1048.
Bureau, *J.*, displacement of some organic acids from their sodium salts as shown by electrical conductivity, ii, 792.
Burger, *H. C.* See *W. J. H.* **Moll**, and *L. S.* **Ornstein**.
Burger, *W.*, exchange of chlorine between the red blood corpuscle and the surrounding solution. III. Influence of the hydrogen-ion concentration on the exchange, i, 710.
Burgers, *W. G.* See *H. J.* **Backer**.

Burgess, *H.*, new halogen derivatives of camphor. IV. Action of hydroxylamine on α- and α′-chlorocamphor and bromocamphor. V. Action of sodium methoxide and ethoxide on αβ-dibromocamphor; formation of esters of α-bromocampholenic acid, i, 45.

Burgess, *H.*, and *T. M.* **Lowry**, studies of dynamic isomerism. XVI. The mutarotation of beryllium benzoylcamphor; formation of an additive compound with chloroform; the optical activity of beryllium, i, 46.

new halogen derivatives of camphor. VI. β-Bromocamphor-α-sulphonic acid. VII. Constitution of the Reychler series of camphorsulphonic acids; experiments on chlorosulphoxides, i, 415.

Burgess, *H.* See also *J. O.* **Cutter.**

Burgess, *P. S.*, yield and mineral content of crop plants as influenced by those preceding, i, 1519.

Burian, *O.*, constitution of the natural humic acids, i, 372.

Burichetti, *E.* See *U.* **Sborgi.**

Burk, *R. E.* See *C. N.* **Hinshelwood.**

Burkhardt, *G. N.*, and *A.* **Lapworth**, theories of polar and non-polar free affinities; reply to some recent criticisms and comparisons, ii, 937.

Burlot, *E.*, theoretical force and co-volume of explosives, ii, 558.

pressures developed in closed vessels by the combustion of explosives, ii, 1170.

experimental determination of the force and co-volume of explosives, ii, 1170.

Burmeister, *E.* See *W.* **Traube.**

Burnet, *F. M.*, hydrogen peroxide and bacterial growth, i, 1117.

effect of dyes on bacterial growth, i, 1117.

Burns, *K.*, red neon lines, ii, 1099.

Burr, *G. O.* See *H. M.* **Evans.**

Burrell, *R. C.*, and *T. G.* **Phillips**, determination of nitrate nitrogen in plants, i, 1367.

Burt, *A. W.* See *G. T.* **Morgan.**

Burt, *C. P.* See *H.* **Hibbert.**

Burt, *F. P.* See *D. H.* **Bangham**, and *J. T.* **Howarth.**

Burt, *R. C.*, constancy of total photocurrent from sodium with temperature change 20° to −190°, ii, 617.

sodium by electrolysis through glass, ii, 921.

Burtles, *R.*, and *F. L.* **Pyman**, 2-amino-4:5-dimethylglyoxaline, i, 1326.

Burtles, *R.*, *F. L.* **Pyman**, and *J.* **Roylance**, relation of pilocarpidine to pilocarpine; synthesis of 1:4- and 1:5-dimethylglyoxalines, i, 696.

Burton, *E. F.*, and *J. E.* **Currie**, mutual action of charged particles in liquid media, ii, 531.

Burton, *H.*, and *C. S.* **Gibson**, preparation of arsinic acids from the corresponding chloroarsines, i, 84.

preparation of 9-alkylcarbazoles, i, 154.

Burton, *J. Q.* See *J. M.* **McCandless.**

Burwell, *C. S.*, and *G. C.* **Robinson**, determination of oxygen and carbon dioxide in mixed venous human blood, i, 604.

Bury, *C. E.* See *E. R.* **Jones.**

Bury, *C. R.*, system, zinc sulphate–water, ii, 119.

Fulcher lines in the hydrogen spectrum, ii, 1113.

Bury, *C. R.* See also *F. S.* **Brown.**

Busch, *M.*, determination of organically combined halogen, ii, 823.

Busch, *M.*, and *R. von* **Beust**, isomeric hydrazones of glyoxylic acid. II. Remarkable, different behaviour of stereoisomerides, i, 400.

Busch, *M.*, *G.* **Friedenberger**, and *W.* **Tischbein**, isomerism of hydrazones; isomeric hydrazones of phenacylamines and the determination of their configuration, i, 40.

Busch, *W.* See *O.* **Ruff.**

Busse, *W.*, velocity of sound and ratio of specific heats of organic liquids, ii, 373.

law of photographic blackening for homogeneous *X*-rays, ii, 1080.

Buston, *H. W.* See *S. B.* **Schryver.**

Butkewitsch, *W.*, production of gluconic and citric acids from sucrose by moulds, i, 341.

moulds and bacteria which utilise quinic acid, i, 1511.

Butler, *C. L.*, *jun.*, and *R.* **Adams**, search in the diphenylmethane series for the isomerism characteristic of certain diphenyl derivatives, i, 1438.

Butler, *J. A. V.*, solubility, heat of solution, and lattice energy of salts, ii, 39.

seat of the electromotive force in the galvanic cell, ii, 42.

relation between deviations from Raoult's law and the partial heats of solution, ii, 539.

Butmi de Katzman, *V.* See *P.* **Petrenko-Kritschenko.**

Byk, *A.*, revised Trouton rule for the heat of vaporisation and the quantum theory, ii, 97.

Bylinkin, *I. G.* See *A. E.* **Tschitschibabin.**
Bylsma, *A. G.*, perfuming and flavouring substances in foods and condiments. I. Effect of ethyl acetate and other substances on the nitrogen excretion of normal dogs and those with greatly reduced thyroid glands, i, 1356.

C.

Cabannes, *J.*, and *J.* **Dufay,** measurement of the altitude of the layer of ozone in the atmosphere, ii, 998.
Cabannes, *J.*, and *J.* **Gauzit,** diffusion of light by methane and its gaseous homologues, ii, 1030.
Cabrera, *B.*, the constant Δ in the Weiss-Curie law, ii, 173.
rare earths and the magneton, ii, 358.
paramagnetism of the rare earths, ii, 618.
calculation of atomic radii from magnetic susceptibility, ii, 624.
magnetism and the structure of atoms and molecules, ii, 1107.
Cabrera, *B.*, and *A.* **Duperier,** thermal variation of magnetism of water and of some paramagnetic solutions, ii, 754.
Cadariu, *I.* See *I.* **Nitzescu.**
Cadness, *B. H. E.* See *H.* **Heap.**
Cady, *H. P.*, and *R.* **Taft,** electrolysis in liquid sulphur dioxide, ii, 1073.
oxidation and reduction, ii, 1073.
Caesar, *F.* See *D.* **Vorländer.**
Caglioti, *V.* See *F.* **Zambonini.**
Cahill, *P. J.* See *H.* **Ryan.**
Caille, *A.*, stability of cellulose esters, i, 371.
Caille, *E.*, and *E.* **Viel,** transformation of iodoantimonates of nitrogenated organic bases into crystalline iodomercurates, i, 68.
Cajori, *F. A.*, *C. V.* **Crouter,** and *R.* **Pemberton,** lactic acid in arthritis and rheumatoid conditions, i, 328.
Calcagni, *G.*, dichromates of ter- and sexa-valent metals, ii, 891.
Calcott, *W. S.*, *F. L.* **English,** and *F. B.* **Downing,** analysis of naphthalenesulphonic acids and naphthalene, ii, 73.
analysis of xanthate, ii, 606.
Calcott, *W. S.*, *F. L.* **English,** and *O. C.* **Wilbur,** analysis of acetic anhydride, ii, 1007.
Caldwell, *J. S.*, effects of seasonal conditions on the chemical composition of American grape juices, i, 1368.
Caldwell, *M. L.* See *H. C.* **Sherman.**
Calingaert, *G.*, organic compounds of lead, i, 798.
Callan, *T.*, detection and determination of small amounts of α-naphthol in β-naphthol, ii, 444.
Callow, *A. B.*, and *M. E.* **Robinson,** nitroprusside reaction of bacteria, i, 478.
Callow, *E. H.*, autolysis of the muscle of the cod fish, i, 469.
velocity of ice crystallisation through supercooled gelatin gels, ii, 777.
Callsen, *J.*, methiodides of αγ-didimethylaminopropan-β-ol, i, 1389.
Calvert, *E. G. B.*, determination of sugar in blood, i, 179.
Calvert, *S.* See *R. T.* **Dufford.**
Calvin, *D. B.* See *B. M.* **Hendrix.**
Cambi, *L.* [with *P. M.* **Voltolin**], reaction between arsenious anhydride and chlorine, ii, 148.
Cameron, *A. T.*, and *V. H. K.* **Moorhouse,** tetany of parathyroid deficiency and the calcium of the blood and cerebro-spinal fluid, i, 857.
Cameron, *D. H.*, laboratory pump, ii, 707.
Cameron, *W. H. B.*, possibility of reproducing the electrical conditions of the nitrogen afterglow, ii, 172.
Camis, *M.*, metabolism of phosphoric acid in the submaxillary gland, i, 191.
Camp, *A. F.* [determination of citric acid], ii, 246.
Campbell, *A. N.*, atomic volume of manganese, ii, 762.
Campbell, *A. N.* See also *A. J.* **Allmand.**
Campbell, *E. D.*, and *G. W.* **Whitney,** effect of changes in total carbon and in the condition of carbides on the specific resistance and on some magnetic properties of steel, ii, 274.
Campbell, *J. A.*, dissociation of oxyhæmoglobin in the tissues, i, 1481.
Campbell, *L. K.*, amino-acid content of the tubercle bacillus, i, 1511.
alanine and histidine metabolism of the tubercle bacillus, i, 1511.
Campbell, *R.*, and *J. W.* **Lunn,** chlorophaeite in dolerites near Edinburgh, ii, 1093.
Campus, *A.*, origin of lactose and lactosuria in cows, i, 327.
Canal, *H.* See *E.* **André.**
Canals, *E.*, and *R.* **Genevet,** distilled water in biological work, ii, 847.
Canals, *E.*, and *M.* **Gidon,** absorption of potassium iodide by the skin, i, 1116.
Canals, *E.* See also *A.* **Astruc.**

Cândea, dithymolisatin colouring matter, i, 298.
Candelin, *A. J.* See *A.* Scheunert.
Canneri, *G.*, double carbonates of guanidine with rare-earth metals, i, 524.
double acetates of rare-earth metals with organic bases, i, 525.
molybdovanadates. II., ii, 891.
Canneri, *G.*, and *L.* Fernandes, analytical separation of rare earths from uranium; alkali uranylsalicylates, ii, 71.
thermal analysis of the systems, thallous sulphide–arsenic trisulphide and thallous sulphide–lead sulphide, ii, 887.
complex sulphites and thiosulphates of the rare-earth metals, ii, 888.
Cantamessa, *G.* See *A.* Clementi.
Cantoni, *O.*, separation of the alkalis in silicate analysis, ii, 1001.
Capato, *E.* See *L.* Ruzicka.
Capodacqua, *A.* See *L.* Vecchiotti.
Cappelli, *G.*, lipase. II. Relationship of lipase to predisposition to human tuberculosis; action of lipase on Koch's bacillus, i, 725.
Capua, *di.* See Di Capua.
Cardot, *H.* See *A.* Blanchetière.
Cario, *G.*, and *O.* Oldenberg, electrical excitation of the band and line spectra of iodine, ii, 470.
Carius, *C.* See *P. A.* Thiessen.
Carlens, *O.* See *E. M. P.* Widmark.
Carli, *F. de*, reducibility of certain metallic halides by means of hydrogen, ii, 51.
reactivity in the solid state between acidic and basic metal oxides, ii, 670.
Carlsohn, *H.*, rare-gas nature of pseudo- and non-electrolytes as basis for the calculation of their m. p. and b. p., ii, 1044.
Carlsohn, *H.* See also *A.* Hantzsch.
Carlton, (*Miss*) *M.*, new peroxide of barium, ii, 1183.
Carlton, (*Miss*) *M.* See also *H. B.* Baker.
Carneiro, *V.* See *L.* Panisset.
Carnelley, *H. W.*, and *P. K.* Dutt, 2:5-iminodihydro-1:2:3-triazole. II., i, 165.
Caro, *L. de*, surface tension of gelatin solutions of different hydrogen-ion concentration, ii, 857.
Carobbi, *G.*, double nitrates of metals of the cerium group with copper and with cadmium, ii, 145, 222.
double chromates of the rare earths and alkali metals. I. Double chromates of lanthanum and potassium, ii, 315.
Carobbi, *G.*, synthetic praseodymiferous chlorovanadinite, ii, 582.
supposed isomorphism of uranyl compounds with those of isomorphogenous metals of the magnesium group, ii, 892.
Carobbi, *G.* See also *F.* Zambonini.
Carothers, *W. H.*, and *R.* Adams, platinum oxide as a catalyst in the reduction of organic compounds. VII. Effects of numerous substances on the platinum catalysis of the reduction of benzaldehyde, ii, 693.
Carr, *A. R.*, *R. E.* Townsend, and *W. L.* Badger, vapour pressures of glycerol–water and glycerol–water–sodium chloride solutions, ii, 767.
Carr, *A. R.* See also *E. H.* Leslie.
Carr, *M.* See *V.* Korenchevski.
Carré, *M. H.*, relation of pectose and pectin in apple tissue, i, 758.
Carrick, *C. W.*, and *S. M.* Hauge, presence of vitamin-*C* in livers of chickens fed on scorbutic diets, i, 617.
Carrick, *C. W.* See also *S. M.* Hauge.
Carrière, *E.*, and Arnaud, determination of the boiling and condensation curves of mixtures of hydrochloric acid and water under a pressure of 760 mm., ii, 102.
Carrière, *E.*, and *E.* Vilon, action of sulphuric acid on calcium oxalate, ii, 206.
Carrière, *J. F.*, behaviour of oil and oleic acid with water. IV.—VI., ii, 287.
Carroll, *B. H.*, *G. K.* Rollefson, and *J. H.* Mathews, ebullioscopic measurements in mixed solvents, ii, 858.
effect of a non-volatile solute on the partial pressures of liquid mixtures at the b. p., ii, 859.
Carroll, *J. A.*, series relations in the spectra of doubly ionised gallium and indium, ii, 1101.
Carroll, *M. F.* See *J. R.* Partington.
Carroll, *W. R.* See *E. B.* Fred.
Carson, *C. M.*, determination of aniline in aqueous solutions, ii, 447.
Carst, *A.*, continuous hydrogen spectrum, ii, 333.
Carter, *J. M.* See *H. J.* Lucas.
Carter, *S. R.*, and *F.* James, electrochemical aspects of the oxidising properties of sulphur dioxide, ii, 134.
Carter, *S. R.*, and *F. M.* Lea, diffusion potential and transport number of hydrochloric acid in concentrated solution, ii, 300.
influence of acid concentration on the oxidation-reduction potential of cuprous and cupric chlorides, ii, 403.

Carter, *S. R.* See also *G. T.* **Morgan.**
Carver, *E. K.*, and *H.* **Folts**, plasticity of cellulose in "cuprammonium hydroxide," ii, 662.
Carver, *E. K.*, and *F.* **Hovorka**, capillary rise of water in tubes of various metals, ii, 647.
Carver, *E. K.* See also *H.* **Crouch**, and *S. E.* **Sheppard.**
Cary, *A. P.*, and *E. K.* **Rideal**, behaviour of crystals and lenses of fats on the surface of water, ii, 388.
behaviour of crystals and lenses of fats on surface of water. I. Mechanism and rate of spreading, ii, 1046.
behaviour of crystals and lenses of fats on surface of water. II. Effect of temperature on the equilibrium pressure, ii, 1047.
behaviour of crystals and lenses of fats on surface of water. III. Effect of polar group on equilibrium pressure, ii, 1048.
Case, *F. H.*, derivatives of *p*-hydroxymethylbenzoic acid. I. Esters, i, 815.
Casey, *G. U.* See *J. R.* **Williams.**
Cash, *L. S.*, and *C. E.* **Fawsitt**, determination of cineole in essential oils by Cocking's process, ii, 75.
Caspar, *C.* See *V.* **Auger.**
Caspari, *W. A.*, system, sodium carbonate–sodium sulphate–water, ii, 123.
Caspers, *F.* See *P.* **Lipp.**
Cassel, *H.*, theory of metallic conductivity, ii, 942.
Cassella & Co., *L.*, preparation of a new arsenic compound of the aromatic series, i, 172.
preparation of condensation products of the indophenol type, i, 397.
new pharmaceutical products [nitro- and amino-3-chloro-4-hydroxyphenylarsinic acid], i, 1470.
arseno compounds, i, 1471.
Castoro, *N.*, the γ-galactan present in the seeds of *Cicer arietinum* and its molecular constitution, i, 1043.
constitution of lupeose, i, 1244.
Catalán, *M. A.*, spectrum of iron, ii, 167.
structure of cobalt spectrum, ii, 611.
structure of the spectrum of scandium. II., ii, 724.
Cathala, *J.*, mechanism of photosynthesis of hydrogen chloride in the visible spectrum, ii, 812.
Cattelain, *E.*, use of hydrazine sulphate in iodometry, ii, 1197.
Caulaert, *V.* See *L.* **Blum.**
Cauquil, (*Mlle.*) *G.*, thermochemical study of the sodium derivatives of *cyclo*hexanol, i, 657.
viscosity and surface tension during esterification, ii, 964.
Caven, *R. L.*, and *T. C.* **Mitchell**, equilibrium in systems of the type $Al_2(SO_4)_3$–M″SO_4–H_2O. I. Aluminium sulphate–copper sulphate–water and aluminium sulphate–manganous sulphate–water at 30°, ii, 396.
Cecchetti, *B.*, certain xanthates, i, 503.
Cecchetti, *B.* See also *G.* **Rossi.**
Centnerszwer, *M.*, and *B.* **Bružs**, stepwise dissociation of magnesium carbonate, ii, 206.
velocity of decomposition of solids. I. Dissociation of magnesium carbonate, ii, 685.
thermal decomposition of silver carbonate, ii, 803.
Centnerszwer, *M.*, *G.* **Falk**, and *A.* **Awerbuch**, dissociation of lead carbonate, ii, 400.
Centnerszwer, *M.*, and *C.* **Strenk**, preparation and properties of disulphur difluoride, ii, 701.
Cerecedo, *L. R.*, and *C. P.* **Sherwin**, comparative metabolism of aromatic acids. VII. Fate of *p*-chloro-, *p*-bromo-, and *p*-amino-acids, i, 100.
Cerezo, *J.* See *J.* **Pascual Vila.**
Cerighelli, *R.*, indole in the flowers of Spanish jasmine [*Jasminum grandiflorum*, L.], i, 621.
Cha, *C.*, incident and emergent velocities of photo-electrons emitted from thin platinum films, ii, 476.
Chaborski, *G.* See *G. G.* **Longinescu.**
Chabot, *G.*, volumetric determination of the reaction of a medium at true neutrality, ii, 899.
Chadwell, *H. M.* See *T. W.* **Richards.**
Chadwick, *J.* See (*Sir*) *E.* **Rutherford.**
Chakravarti, *D. N.*, and *N. R.* **Dhar**, fluorescence and chemical change, ii, 629.
Chakravarti, *G. C.*, colour of complex diazoles. I., i, 162.
dyes derived from oxalyldibenzyl ketone. I. Azine and azonium derivatives, i, 1330.
Chakravarti, *G. C.*, and *I. S.* **Gupta**, colour of complex diazoles [iminazoles]. II., i, 980.
Chakravarty, *J. N.* See *J. C.* **Ghosh.**
Chakravarty, *K. M.*, and *J. C.* **Ghosh**, catalytic formation of methane from carbon monoxide and hydrogen. I., ii, 1175.

Chakravarty, *K. M.*, and *J. C.* **Ghosh**, catalytic formation of methane from carbon monoxide and hydrogen. II. Production of fuel gases rich in methane, ii, 1175.
Chalkley, *L., jun.*, mercurisation of methylene-blue, i, 1108.
Challenger, *F.*, and *T. H.* **Bott**, interaction of thiocyanogen with unsaturated compounds, i, 936.
Challenger, *F., J. R. A.* **Jinks**, and *J.* **Haslam**, sulphur compounds of Kimmeridge shale oil. I., i, 282.
Challenger, *F.*, and *J. F.* **Wilkinson**, orientation of derivatives of triphenylphosphine oxide, i, 172.
Chamberlin, *D. S.*, and *D. M.* **Newitt**, apparatus for accurate analysis of small quantities of gas, ii, 710.
Chambers, *I. F.* See *E.* **Cherbuliez**.
Chambers, *R. F.*, and *P. C.* **Scherer**, benzyl-ψ-thiocarbamide salts of naphthalenesulphonic acids, i, 127.
Chambers, *W. H.*, and *H. J.* **Deuel**, *jun.*, animal calorimetry. XXX. Metabolism of glycerol in phloridzin diabetes, i, 1352.
Chambers, *W. H.* See also *H. J.* **Deuel**, *jun.*
Chamié, *C.* See *I.* **Curie**.
Chandler, *J.* See *A. W.* **Rowe**.
Chandrasena, *J. P. C., C. K.* **Ingold**, and *J. F.* **Thorpe**, structure of α-campholytic acid, i, 1275.
Channon, *H. J.*, cholesterol synthesis in the animal body, i, 1001.
Chapin, *R. M.*, does nicotine combine with calcium ions? i, 697.
Chapman, *A. W.*, imino-aryl ethers. III. Molecular rearrangement of *N*-phenylbenziminophenyl ether, i, 1400.
Chapman, *D. L.*, some conclusions from recent work on photochemistry, ii, 1078.
Chapman, *D. L., J. E.* **Ramsbottom**, and *C. G.* **Trotman**, union of hydrogen and oxygen in presence of silver and gold, ii, 310.
Chapman, *E.*, and *H.* **Stephen**, condensation of β-chloro- and β-ethylcarbonato-propionitriles with resorcinol, i, 669.
preparation of phthalamic acids and their conversion into anthranilic acids, i, 1151.
Chapman, *R. E.*, carbohydrate enzymes of some starch-free monocotyledons, i, 215.
Chapman, *S.*, and *A. E.* **Ludlam**, vibration of the carbonate ion, ii, 1025.
Chapman, *S.* See also *W. L.* **Bragg**.
Charaux, *C.*, datiscin, a glucoside obtained from *Datisca cannabina*, i, 823.
Charaux, *C.*, and *P.* **Delauney**, occurrence of loroglossoside (loroglossin) in *Listera ovata*, R. Br., and *Epipactis palustris*, Crantz, and its reactions, i, 874.
Charaux, *C.* See also *M.* **Bridel**.
Charles, (*Mlle.*). See *L.* **Randoin**.
Charlton, *J.*, buffer action of some Burma soils, i, 768.
Charonnat, *R.*, potassium chlororuthenites, ii, 586.
Charrier, *G.*, so-called *vic.*-2:*N*-aryltriazolephthalonic acids, i, 76.
Charrier, *G.*, and *A.* **Beretta**, action of nitrosobenzene on *o*-nitroaniline, i, 21.
preparation of diphenic acid, i, 34.
oxidation of *o*-quinones, i, 271.
nitroazobenzenes, i, 316.
Charrier, *G.*, and *G. B.* **Crippa** [with *V.* **Toia**, and *M.* **Bianchessi**], oxidation of arylazo-β-naphthylamines in acetic acid solution by means of hydrogen peroxide, i, 589.
Charrier, *G.*, and *M.* **Gallotti**, destruction of the αβ-naphthatriazole nucleus, i, 589.
Charrier, *G.*, and *M.* **Gallotti** [with *C.* **Vitale**], phenylene-2-aryltriazolylene-glycollic acids, i, 306.
Charrion, *A.*, catalytic action of alumina containing other substances, ii, 216.
Chassevent, *L.*, velocities of crystallisation of gypsum and preparation of a plaster of great resistance to compression, ii, 559.
Chattaway, *F. D., S. J.* **Ireland**, and *A. J.* **Walker**, colours produced by the action of sulphuric acid on some hydrazones, i, 1194.
Chattaway, *F. D.*, and *G. D.* **Parkes**, action of azides on toluquinone, i, 985.
Chattaway, *F. D.*, and *C. R. N.* **Strouts**, halogen-substituted 1-arylpyrazolones, i, 71.
Chattaway, *F. D.*, and *A. J.* **Walker**, compounds formed by the action of bromine on benzaldehydephenylhydrazone, i, 929.
action of halogens on *m*- and *p*-nitrobenzaldehydephenylhydrazones, i, 1193.
Chatterjee, *B. C.* See *R. L.* **Datta**.
Chatterji, *A. C.* See *N. R.* **Dhar**.
Chaturvedi, *R. K.*, serious difficulty in the determination of the number of vibrations radiated from a Bohr atom, ii, 926.
Chaudron, *G.* See *H.* **Forestier**, *J.* **Valentin**, and *X.* **Waché**.

Chaudun, (*Mlle.*) *A.* See *H.* **Colin.**
Chaussin, *J.*, soluble material and insoluble tissues during the development of wheat; influence of a complete mineral fertiliser, i, 623.
Cheadle, *F. M.*, insulin. I. Preparation and standardisation of insulin. II. Effect of p_H on activity of insulin subjected to high temperatures, i, 106.
Chelle, *L.*, and *M.* **Rangier**, form in which uric acid occurs in urines containing acid urates, i, 187.
forms in which uric acid is eliminated in the urine, i, 187.
Chemische Fabrik auf Aktien (vorm. *E.* Schering), preparation of homologues of 2-aminopyridine, i, 301.
preparation of alkyl homologues of pyridine, i, 431.
preparation of 2:6-diaminopyridine, i, 589.
preparation of *N*-2-pyridylpyrroles, i, 1329.
preparation of quinoline-4-aldehyde and its 2-aryl derivatives, i, 1452.
Chemische Fabrik Flora, piperonyl bromide, i, 1413.
Chemische Fabrik Griesheim-Elektron, preparation of dyes insoluble in water, i, 587, 599.
azo dyes, i, 598, 989.
Chemische Fabrik von *F.* Heyden, preparation of organic arsenic–antimony compounds, i, 85.
preparation of arsenic–antimony compounds, i, 86.
preparation of secondary and tertiary aromatic antimony compounds, i, 86.
preparation of monoarylantimony compounds, i, 86.
preparation of diarylantimony compounds, i, 86, 87.
preparation of complex compounds of aromatic stibinic acids, i, 87.
alkali salts of aromatic *N*-halogenosulphonamides, i, 380.
derivatives of *ar*-tetrahydro-β-naphthol, i, 1407.
Chemische Fabrik vorm. Sandoz, preparation of the alkaline-earth salts of alkylsulphonic acids, i, 1377.
Chemische Fabriken vorm. Weiler-ter Meer, derivatives of cinnamic acid, i, 1418.
Chemische Werke Grenzach, alkylamino esters of tropic and acyltropic acids, i, 31.
Chen, *K. K.*, and *C. F.* **Schmidt**, action of ephedrine, the active principle of the Chinese drug, Ma Huang, i, 194.
Chenault, *R. L.* See *P. D.* **Foote**, and *A. E.* **Ruark.**
Chenel, *L.* See *M.* **Marqueyrol.**
Cheramy, *P.*, colorimetric determination of solutions of novocaine, ii, 247.
Cherbuliez, *A.* See *J.* **Chevalier.**
Cherbuliez, *E.*, and *I. F.* **Chambers**, ring formation from asparagine; derivatives of aminosuccinimide, i, 1046.
Cherbuliez, *E.*, and *G.* **Sulzer**, derivatives of formaldehyde and succinimide, i, 1252.
Cherbuliez, *E.*, and *R.* **Wahl**, determination of amino-acids formed by hydrolysis of proteins. I. Determination in groups, ii, 1211.
Cherpillod, *F.* See *F.* **Kehrmann.**
Chertcoff, *M.* See *M. T.* **Bogert.**
Chesnut, *V. K.* See *F. B.* **Power.**
Chevalier, *J.*, and *A.* **Cherbuliez**, chloralose and parachloralose, i, 467.
Chevallier, *E.*, magnetic ferric oxide, ii, 639.
Chevenard, *P.*, dilatometric anomaly of α-solid solutions of copper and aluminium, ii, 768.
reversible anomaly of copper–nickel alloys in the paramagnetic region, ii, 851.
Cheymol, *J.* See *E.* **Gley**, and *H.* **Hérissey.**
Chibnall, *A. C.*, and *L. S.* **Nolan**, a protein from the leaves of the alfalfa plant; a protein from the leaves of *Zea mays*, i, 215.
Chick, *H.*, and *M.* **Tazelaar**, effect on the growth of rats receiving a diet deficient in fat-soluble vitamins of exposing their environment to the emanation from radium bromide, i, 211.
Chikano, *M.* See *Y.* **Kotake.**
Child, *W. C.*, and *H.* **Adkins**, condensation of aldehydes to esters by alkoxides, i, 632.
Childs, *W. H. J.*, peculiarity of some red neon lines, ii, 339.
Chinoin Fabrik Chemisch-pharmazeutischer Produkte, preparation of (iodo)-esters of carbamic acid and of acylated carbamic acids (allophanic acid, acetylcarbamic acid, etc.), i, 13.
Chipman, *J.*, solubility of benzoic acid in benzene and in toluene, ii, 30.
Chirvinski. See **Tschirvinski.**
Chlopin, *W.*, fractional crystallisation of radioactive substances, ii, 438.
Chodat, *F.*, cell permeability. I. Swelling of gelatin under the influence of carbamide, ii, 521.
Choucroun, (*Mlle.*). See *J.* **Perrin.**

Choufoer, *H. F.*, disaccharins, i, 896.
Chown, *H. B.* See *L. E.* **Holt**, *jun.*
Christen, *A.* See *F.* **Fichter.**
Christensen, *L. M.*, and *E. I.* **Fulmer**, adjustment of p_H of culture media under sterile conditions, i, 1216.
Christiaen, *A.*, action of organo-magnesium compounds on nitriles; α-aminonitriles, i, 23.
Christiaen, *A.* See also *P.* **Bruylants.**
Christiani-Kronwald, *A.* See *F.* **Feigl.**
Christiansen, *J. A.*, velocity of bi-molecular reactions in solutions, ii, 47.
burette for micro-gas analysis, ii, 593.
Christiansen, *J. A.* See also *G. von* **Hevesy.**
Christiansen, *W. G.*, nitration of *p*-carboxyphenoxyacetic acid, i, 817.
p-arsinobenzeneazophthaleins, i, 1192.
Christiansen, *W. G.*, and *A. J.* **Norton**, antimonyl tartrates of some organic bases, i, 654.
Christiansen, *W. G.*, *A. J.* **Norton**, and *J. B.* **Shohan**, sulphur content of arsphenamine [salvarsan] and its relation to the mode of synthesis and the toxicity, i, 1471.
Christie, (*Miss*) *R. K.* See *G. J.* **Fowler.**
Christmann, *F.* See *S.* **Goldschmidt.**
Chrometzka, *F.* See *E.* **Schmitz.**
Chrzaszcz, *T.*, determination of starch using malt, ii, 74.
Chrzaszczewska, (*Mlle.*) *A.*, the thiophens and intermediate products for their synthesis, i, 956.
Chrzaszczewska, (*Mlle.*) *A.*, and (*Mlle.*) *M.* **Biata**, influence of acetyl chloride on the nitration of acetanilide and dimethylaniline, i, 1058.
Chuckubutti, *B. N.*, colours shown by Nobili's rings, ii, 744.
Chudnoff, *M.* See *L.* **Bauman.**
Chudožilov, *L. K.*, preparation of symmetrical polynitro derivatives of the dinaphthyls by the action of finely-divided copper on halogenated nitronaphthalenes, i, 903.
Chudožilov, *L. K.* See also *V.* **Vesely.**
Cikrtová, *M.*, and *K.* **Sandera**, theory of the titration of boric acid, ii, 714.
Cittert, *P. H. van*, measurement of the fine structure of hydrogen lines with the Lummer–Gehrcke plate, ii, 909.
Ciusa, *R.*, some substances analogous with graphite, i, 1083.
Ciusa, *R.*, and *A.* **Galizzi**, constituents of lignites. III., i, 1045.
Ciusa, *R.*, and *E.* **Parisi**, aldoxime peroxides. III., i, 1070.
Claassen, *A.*, crystal structure of alkali monosulphides. I., ii, 845.
Claisen, *L.*, preparation of chromans, i, 277.
phenols alkylated in the nucleus, i, 1410.
Claisen, *L.* [with *F.* **Kremers**, *F.* **Roth**, and *E.* **Tietze**], *C*-alkylation (nucleus alkylation) of phenols, i, 656.
Claisen, *L.*, and *E.* **Tietze**, mechanism of the transformation of phenyl allyl ethers, i, 389.
Clapham, *H. W.* See *T. J.* **Nolan.**
Clare, *N. D.* See *J. W.* **Shipley.**
Clark, *A. L.*, definition of a perfect gas, ii, 495.
viscosity of ethyl ether near the critical point, ii, 499.
polarisation capacity and electrical double layers, ii, 673.
Clark, *C. H. D.* See *J. C.* **Philip.**
Clark, *E.*, application of sodium hyposulphite in qualitative organic analysis, ii, 332.
Clark, *E. P.*, and *J. B.* **Collip**, determination of calcium in blood serum by the Tisdall method, i, 713.
Clark, *E. P.* See also *J. B.* **Collip.**
Clark, *F. E.* See *J. W.* **Farren.**
Clark, *G. L.*, and *W.* **Duane**, relative intensities of fluorescent and scattered *X*-rays, ii, 336.
Clark, *G. L.*, *P. C.* **McGrath**, and *M. C.* **Johnson**, effect of *X*-rays on the platinum catalyst in the contact sulphuric acid reaction, ii, 1176.
Clark, *G. L.* See also *W. D.* **Harkins.**
Clark, *H.*, and *J. H.* **Northrop**, inactivation of trypsin by *X*-rays, i, 1361.
Clark, *L. M.*, benzthiazole series. III. Pseudo-bases of the 1-substituted benzthiazole quaternary salts, i, 841.
Clark, *M.*, recent studies on reversible oxidation-reduction in organic systems, ii, 673.
Clark, *W. M.*, *B.* **Cohen**, and *H. D.* **Gibbs**, oxidation-reduction. VIII. Methylene-blue, ii, 1164.
Clark, *W. M.*, and *A. T.* **Merrill**, production of gelatinase by *Proteus*, i, 1511.
Clark, *W. M.* See also *B.* **Cohen.**
Clarke, *B. L.*, swelling. I. Swelling of agar-agar gels as a function of water content before swelling, ii, 863.
Clarke, *B. L.* See also *J.* **Kendall**, and *D. T.* **MacDougal.**
Clarke, *F. W.*, composition of the river and lake waters of the United States, ii, 323.
Clarke, *F. W.*, and *H. S.* **Washington**, composition of the earth's crust, ii, 63.

Clarke, *G. R.*, and *C. G. T.* **Morison**, losses of ammonia from soil by volatilisation, i, 491.
Classen, *A.*, and *G.* **Strauch**, atomic weight of bismuth, ii, 175.
Clausen, *S. W.*, excretion of organic acids after pneumonia, i, 1491.
Clay, *J.*, helium in earth gases of petrol sources, ii, 1195.
Claydon, *D.* See *H. G.* **Barbour**.
Clemens, *F.* See *J.* **Meyer**.
Clementi, *A.*, and *G.* **Cantamessa**, enzymic deamination of asparagine, i, 200.
Clemo, *G. R.* See **British Dyestuffs Corporation, Ltd.**
Clerici, *E.*, fusion mixture for isopycnometric analysis, ii, 594.
Clews, *F. H.*, interaction of sodium chloride and alumina, ii, 577.
Clibbens, *D. A.*, and *A.* **Geake**, chemical analysis of cotton. II. Determination of copper number, ii, 906.
Clibbens, *D. A.* See also *C.* **Birtwell**.
Clifford, *P. H.*, and *M. E.* **Probert**, constituents of the wax of American (Mississippi Delta) cotton, i, 879.
Clifford, *W. M.*, effect of halogen salts on salivary digestion, i, 738.
Close, *H. W.* See *H. S.* **Taylor**.
Clough, *R. W.* See *C. R.* **Fellers**.
Clutterbuck, *P. W.*, γ-hydroxystearic acid, i, 5.
Clutterbuck, *P. W.*, and *H. S.* **Raper**, oxidation of the ammonium salts of normal saturated fatty acids and its biological significance, i, 882.
Cobb, *J. W.* See *H. S.* **Houldsworth**.
Cobenzl, *A.*, preparation of mauveine and various bases, i, 436.
Coblens, *M.*, and *J. K.* **Bernstein**, titanous chloride and nitric acid, ii, 804.
Coblentz, *W. W.*, and *H. R.* **Fulton**, radiometric investigation of the germicidal action of ultra-violet radiation, i, 616.
Coehn, *A.*, streams of gas bubbles directed by electrolysis, ii, 1165.
Coehn, *A.*, and *G.* **Jung**, influence of aqueous vapour pressure and wavelength on the photochemical formation of hydrogen chloride, ii, 142.
Coffey, *S.*, mercuration of aromatic substances. I. Toluene, i, 844.
Coffignier, *C.*, solutions of lead resinates. I., i, 1294.
Cofman, *V.*, electrical dispersion of liquids, ii, 1060.
Coghill, *R. D.*, hydantoins. XLII. Method of synthesising 1:5-diarylhydantoins: 1:5-di(*p*-hydroxyphenyl)-hydantoin, i, 583.
Coghill, *R. D.*, and *T. B.* **Johnson**, hydantoins. XLI. Synthesis of hydantoins containing phenolic groups in the glyoxaline nucleus, i, 582.
Coghill, *R. D.* See also *T. B.* **Johnson**.
Cohen, *B.*, *H. D.* **Gibbs**, and *W. M.* **Clark**, oxidation-reduction. VI. Indophenols; (A) dibromo-substitution products of phenolindophenol; (B) substituted indophenols of the *o*-type; (C) miscellaneous, i, 25.
Cohen, *B.* See also *W. M.* **Clark**.
Cohen, *E.*, metastability of matter and physical constants, ii, 1138.
Cohen, *E.*, and *J. C. van der* **Bosch**, piezochemical studies. XXVIII. Solubility determination at high pressures by means of conductivity determination, ii, 283.
Cohen, *E.*, and *H. L.* **Bredée**, heats of solution of enantiotropic modifications (of ammonium nitrate) at the transition point, ii, 976.
Cohen, *E.*, and *H. R.* **Bruins**, precision method for the determination of diffusion coefficients in any solvent. II., ii, 28.
piezochemical studies. XXVII. Relation between diffusion-velocity, viscosity, and external pressure, ii, 280.
influence of pressure on velocity of diffusion of metals in mercury, ii, 648.
potentiometric measurement of velocities of diffusion of metals in mercury, ii, 648.
Cohen, *E.*, and *W. D.* **Helderman**, metastability of elements and compounds as a result of enantiotropy and monotropy. VIII., ii, 23.
Cohen, *E.*, *W. D.* **Helderman**, and *A. L. T.* **Moesveld**, true specific heats of salt solutions (cadmium iodide, ammonium nitrate, and zinc sulphate), ii, 126.
calorimeter for the electrical adiabatic determination of heats of solution, ii, 151.
Cohen, *E.*, and *C. W. G.* **Hetterschij**, solubility curves of zinc sulphate, ii, 652.
Cohen, *E.*, *W. A. T. de* **Meester**, and *A. L. T.* **Moesveld**, apparatus for the accurate determination of solubilities, ii, 151.
piezochemical studies. XXVI. Influence of pressure on solubility in the system, naphthalene–tetrachloroethane, ii, 190.
influence of pressure on the solubility of substances. V. The system, naphthalene–tetrachloroethane, ii, 852.

Cohen, *E.*, and *A. L. T.* **Moesveld**, metastability of elements and compounds as a result of enantiotropy and monotropy, ii, 374, 950.
equilibrium in the system, zinc sulphate-water, ii, 652.
Cohen, *E.*, *A. L. T.* **Moesveld**, and *W. D.* **Helderman**, electrical, adiadatic calorimeter, and its use in the determination of heats of solution, ii, 402.
Cohen, *H.*, determination of uric acid by Benedict's method, i, 184.
Cohen, *I.*, occurrence of diastase in the cerebrospinal fluid, i, 721.
Cohen, *J. B.* See *E. J.* **Wayne**.
Cohen, *W. D.* See *J.* **Böeseken**.
Cohn, *E. J.*, *J. L.* **Hendry**, and *A. M.* **Prentiss**, physical chemistry of proteins. V. Molecular weights of proteins. I. Minimal molecular weights of certain proteins, ii, 641.
Colacicchi, *U.* See *G.* **Plancher**.
Colani, *A.*, acid uranyl acetate, i, 5.
uranyl oxalate, i, 1235.
action of sodium carbonate on phosphates, ii, 1001.
Colbert, *J. C.* See *L. C.* **Raiford**.
Colby, *W. F.*, use of half-quantum numbers in interpretation of hydrogen chloride absorption bands, ii, 1114.
Coles, *H. W.* See *L. A.* **Congdon**.
Colin, *H.*, origin of lævulosans in plants, i, 618.
formation, distribution, and circulation of inulin in the stem of the artichoke, i, 620.
Colin, *H.*, and (*Mlle.*) *A.* **Chaudun**, constant of hydrolysis of sucrose, i, 233.
Colin, *H.*, and *A.* **Grandsire**, mineral matter in green and in chlorotic leaves, i, 1123.
Collander, *R.*, permeability of the copper ferrocyanide membrane to acids, and the action of protoplasm as an ultrafilter, ii, 201.
Collard, *E.*, *jun.*, keeping properties of tincture of iodine, ii, 1168.
keeping properties of standard sodium thiosulphate solution, ii, 1168.
Collazo, *J. A.*, *M.* **Händel**, and *P.* **Rubino**, insulin. II., i, 343.
Collazo, *J. A.*, and *I.* **Lewicki**, effect of insulin on the lactic acid in the blood, i, 870.
lactic acid metabolism in diabetes and the effect of insulin, i, 1364.
Collazo, *J. A.*, and *J.* **Supniewski**, effect of insulin and other substances on lactic acid metabolism, i, 342.
Collazo, *J. A.* See also *W.* **Arnoldi**.
Collenberg, *O.*, and *B.* **Andersen**, electrolytic oxidation of double cyanides of quadrivalent molybdenum, ii, 1165.
Collenberg, *O.*, and *J.* **Backer**, electrolytic reduction of tungstic acid in hydrochloric acid solution, ii, 571.
Collenberg, *O.*, and *K.* **Wilson**, electrolytic reduction of tungstic acid in presence of oxalic acid, ii, 1166.
Colles, *W. M.*, and *C. S.* **Gibson**, α- and β-naphthalenesulphonylalanines, i, 137.
Collie, *J. N.*, reactions of triethylphosphine, i, 797.
Collie, *J. N.*, and *G.* **Bishop**, nitro- and amino-ethoxylutidine, i, 974.
Collinet, *M.* See *A.* **Perot**.
Collingwood, *B. J.*, method of transport of oxidised carbon from the tissues to the blood, i, 451.
Collins, *A. M.* See *W. A.* **Jacobs**.
Collins, *E. M.* See *A. W. C.* **Menzies**.
Collins, *G. E.*, swelling of cotton cellulose. III. Cotton hairs in solutions of lithium, rubidium, and cæsium hydroxides, ii, 781.
Collins, *G. E.*, and *A. M.* **Williams**, swelling of cotton cellulose. II. Cotton hairs in solutions of potassium hydroxide, ii, 781.
Collins, *H.*, structure of chromium, ii, 18.
structure of barium, ii, 623.
structure of strontium, ii, 733.
active hydrogen, ii, 842.
structure of zinc, ii, 926.
structure of magnesium, ii, 1023.
structure of cadmium, ii, 1112.
Collins, *W. D.*, *H. V.* **Farr**, *J.* **Rosin**, *G. C.* **Spencer**, and *E.* **Wichers**, recommended specifications for analytical reagent chemicals, ii, 899.
Collip, *J. B.*, internal secretion of the parathyroid glands, i, 1364.
Collip, *J. B.*, and *E. P.* **Clark**, physiological action of parathyroid hormone, i, 1017.
Collip, *J. B.*, *E. P.* **Clark**, and *J. W.* **Scott**, extraction of a parathyroid hormone; effect of parathyroid hormone on normal animals, i, 754.
Collip, *J. B.* See also *E. P.* **Clark**.
Colson, *A.*, conditions of maximum solubility: gypsum, ii, 37.
displacement of the maximum solubility and the existence of solubility constants, ii, 121.

Comber, *N. M.*, rôle of the electro-negative ions in the reactions between soils and electrolytes, i, 219.
Combes, *R.*, descent of nitrogenous substances in leaves towards the trunk during autumnal fading, i, 1023.
does light directly effect the decomposition of chlorophyll in leaves in autumn? i, 1120.
Comella, *G.*, quantitative variations of homogeneous mixtures of two salts and a new indirect method of quantitative analysis, ii, 714.
Comley, *M. A.* See *C. E.* **Wood**.
Compagnie Nationale de Matières Colorantes et de Produits Chimiques, preparation of perylene, i, 21.
Compton, *A.* See *G.* **Bertrand**.
Compton, *A. H.*, and *J. A.* **Bearden**, effect of a surrounding box on the spectrum of scattered *X*-rays, ii, 867.
Compton, *A. H.*, and *R. L.* **Doan**, *X*-ray spectra from a ruled reflection grating, ii, 1105.
Compton, *A. H.*, and *A. W.* **Simon**, measurements of β-rays associated with scattered *X*-rays, ii, 347.
directed quanta of scattered *X*-rays, ii, 1034.
Compton, *A. H.*, and *Y. H.* **Woo**, wavelength of molybdenum $K\alpha$ rays scattered by light elements, ii, 1128.
Compton, *A. H.* See also *O. K.* **DeFoe**.
Compton, *K. T.*, production of atomic nitrogen and its arc spectrum, ii, 910.
Compton, *K. T.*, and *C.* **Eckart**, diffusion of electrons against an electric field in the non-oscillatory abnormal low-voltage arc, ii, 253.
Compton, *K. T.*, *L. A.* **Turner**, and *W. H.* **McCurdy**, striated glow discharge in mercury vapour, ii, 86.
Compton, *K. T.*, and *C. C. van* **Voorhis**, probability of ionisation of gas molecules by electron impacts, ii, 1106.
Compton, *K. T.*, and *C. T.* **Zahn**, electric moment of gaseous hydrogen chloride and hydrogen bromide molecules, ii, 1118.
Compton, *K. T.* See also *W. H.* **McCurdy**, and *L. A.* **Turner**.
Conant, *J. B.*, and *L. F.* **Fieser**, methæmoglobin, i, 455.
determination of methæmoglobin in the presence of its cleavage products, i, 456.
Conant, *J. B.*, and *R. E.* **Hussey**, relation between the structure of organic halides and the speeds of their reaction with inorganic iodides. II. Alkyl chlorides, i, 493.
Conant, *J. B.*, *W. R.* **Kirner**, and *R. E.* **Hussey**, relation between the structure of organic halides and the speeds of their reaction with inorganic iodides. III. Influence of unsaturated groups, i, 494.
alternating polarity in chain compounds, i, 803.
Conant, *J. B.*, and *R. E.* **Lutz**, unsaturated 1:4-diketones. I. Halogen derivatives of dibenzoylethylene and related substances, i, 681.
Conant, *J. B.*, and *A. W.* **Sloan**, dissociation into free radicals of substituted dixanthyls. I. Dibenzyl- and dibutyl-dixanthyl, i, 955.
Conant, *J. B.*, *L. F.* **Small**, and *B. S.* **Taylor**, electrochemical relation of free radicals to halochromic salts, ii, 874.
Condorelli, *L.*, combined sugar in blood; methods for micro-determination; conditions in normal individuals; glycolysis and combined sugar, i, 714.
Congdon, *L. A.*, *W. B.* **Crabtree**, *H. W.* **Coles**, *L. L.* **Smith**, and *M. L.* **Vehalgo**, critical studies on methods of analysis. XIV. Chlorine, ii, 65.
Congdon, *L. A.*, *A. B.* **Guss**, and *F. A.* **Winter**, critical studies on methods of analysis. XVI. Zinc, ii, 1002.
Congdon, *L. A.*, and *G.* **Vanderhook**, critical studies on methods of analysis. XV. Magnesium, ii, 601.
Conklin, *O. E.*, microturbidimeter, ii, 708.
Connell, *S. J. B.*, colorimetric determination of lycopin, i, 214.
Conolly, *E. J. V.*, homologues of 2:2′-diquinolyl, i, 1329.
Constable, *F. H.*, catalytic action of copper. VI. Reproducibility of the catalyst, and of the periodic change in its activity, and the activation of the catalyst by alternate oxidation and reduction, ii, 311.
catalytic action of copper. VII. Effect of pressure on the rate of dehydrogenation of alcohols, ii, 311.
mechanism of catalytic decomposition, ii, 804.
effect of poisonous substances and mixed vapours on catalytic activity, ii, 881.
effect of diluents on the initial stages of catalytic action, ii, 983.
Constable, *F. H.* See also *W. G.* **Palmer**.
Constantino, *A.*, occurrence of sugars in muscle juice, i, 720.
Contardi, *A.*, phosphoric derivatives of the inositol of *Hevea brasiliensis*, i, 277.

Conway, *A. W.*, quantum explanation of the Zeeman effect, ii, 830.
Cook, *D. H.*, temperature coefficients of enzymic activity and heat destruction of pancreatic and malt amylases, i, 1358.
Cook, *G.* See *L. J.* **Bircher**.
Cook, *J. W.* See *E. de B.* **Barnett**.
Cook, *K. G.* See *W. C.* **Rose**.
Cook, *W. A.* See *R. E.* **Oesper**.
Cooke, *W. H.*, *I. M.* **Heilbron**, and *G. H.* **Walker**, *meso*-thioanthracene derivatives. II. Dianthranyl disulphide and dianthranyl tetrasulphide, i, 1410.
Coombs, *H. I.*, and *T. S.* **Hele**, mercapturic acid synthesis in the dog, i, 1496.
Cooper, *E. A.*, action of paraldehyde on proteins and lipins, i, 91.
Cooper, *E. A.*, and *S. D.* **Nicholas**, solubility of proteins and proteoses in aldehydes and other organic solvents, ii, 955.
Cooper, *E. A.*, *D. L.* **Woodhouse**, and *G. E.* **Forstner**, conditions affecting bactericidal power, i, 749.
Cooper, *E. A.* See also *G. T.* **Morgan**.
Cooper, *N. C.*, f. p. of *p*-dichlorobenzene, i, 800.
Cooper, *R. A.*, platinum and palladium dimethylglyoximes, ii, 827.
Cooper, *S. E.* See *M. L.* **Nichols**.
Coops, *J.* See *P. E.* **Verkade**.
Coops, *J.*, *jun.* See *P. E.* **Verkade**.
Copaux, *H.*, and *C.* **Matignon**, various states of beryllium oxide, ii, 1192.
Copaux, *H.*, *H.* **Perperot**, and *R.* **Hocart**, production of active hydrogen, ii, 587.
Coper, *K.* See *H.* **Zocher**.
Coppens, *A.*, influence of mercury on the sulphonation of anthraquinone, i, 1432.
Coppens, *A.* See also *J. P.* **Wibaut**.
Coquillat, *A.*, Tromsdorff reagent for nitrites, ii, 328.
Corbet, *G.* See *A.* **Boutaric**.
Corbett, *C. S.*, leverrierite as a schist-forming mineral, ii, 997.
Corbitt, *H. B.* See *H. E.* **Dubin**, and *C. N.* **Myers**.
Corby, *F. J.* See *G. T.* **Morgan**.
Cordier, *G.* See *E.* **Ducloux**.
Corey, *R. B.*, and *A. W.* **Laubengayer** [with *L. M.* **Dennis**], germanium. VIII. Physical properties of monogermane, ii, 493.
Cori, *C. F.*, insulin and liver glycogen, i, 753.
effect of insulin and adrenaline on lactic acid content of blood and tissues, i, 753.
Cori, *C. F.*, and *G. T.* **Cori**, carbohydrate metabolism of tumours. I. Free dextrose, lactic acid, and glycogen content of malignant tumours, i, 999.
carbohydrate metabolism of tumours. II. Changes in sugar, lactic acid, and carbon dioxide combining power of blood passing through a tumour, i, 1492.
Cori, *G. T.* See *C. F.* **Cori**.
Cork, *J. M.*, short wave *X*-ray spectrograph and some *K*-series emission wave-lengths, ii, 250.
Corley, *R. C.* See *W. C.* **Rose**.
Cornubert, *R.* See *A.* **Haller**.
Cornwall, *L. H.*, and *C. N.* **Myers**, neurosyphilis. III. Relative arsenic content of the spinal fluid, brain, and spinal cord of rabbits after intravenous injection of silver salvarsan, i, 611.
Corran, *J. W.*, and *W. C. McC.* **Lewis**, hydrogen-ion concentration of the whole blood of normal males and of cancer patients measured by means of the quinhydrone electrode, i, 188.
lecithin and cholesterol in relation to the physical nature of cell membranes, i, 198.
Correa, *L. M.* See *A. H.* **Roffo**.
Cosma, *J.* See *I. I.* **Nitzescu**.
Cosmovici, *N. L.*, action of hydrogen ions on the clotting of milk, i, 608.
rôle of acidity in the shrinkage of the clot [in milk], i, 608.
Costa, *D.*, absorptive power of cellulose nitrate for gases, ii, 956.
Costa, *J. L.*, exact determination of the atomic mass of the lithium isotope 6, ii, 619.
mass spectra of light elements, ii, 1021.
Coste, *F.* See *P.* **Pagniez**.
Costeanu, *N. D.*, action of iodine on benzene, i, 238.
Coster, *D.*, energy levels of *X*-ray spectra of chemical elements, ii, 458.
Coster, *D.*, and *Y.* **Nishina**, quantitative chemical analysis by means of *X*-ray spectrum, ii, 324.
Cotton-Feytis, (*Mlle.*) *E.*, paramagnetic salts, ii, 945.
Couch, *H. R.* See *T. L.* **Davis**.
Couch, *J. F.*, new lupine alkaloid, spathulatine, isolated from *Lupinus spathulatus* (Rydb.), i, 61.
Grant's test for sparteine, ii, 448.
Conder, *A.*, action of ammonia on cyanamide, i, 525.
Coupin, *H.*, peroxydases in dried seeds, i, 615.

Courjon, *R.* See *A.* **Lumière.**
Courtot, *C.*, and *A.* **Dondelinger**, α-halides of indane, i, 654.
optical study of indanyl bases, ii, 274.
Courtot, *C.*, and *R.* **Geoffroy**, [so-called] 2:7:9:9-tetrahydroxyfluorene, i, 926.
Courtot, *C.*, and *P.* **Petitcolas**, synthesis of fluorenylamines, i, 247.
Coutts, *J. R. H.*, law of distribution of particles in colloidal suspension; specific volume of a gamboge suspension, ii, 290.
Couture, *E.* See *L.* **Hugounenq.**
Couturier, *F.*, and *S.* **Perraud**, properties of urea in the soil, i, 765.
Couturier, *H.* See *A.* **Lumière.**
Coward, *H. F.*, *L.* **Spencer**, and *F. C.* **Wood**, sorption by cotton, ii, 507.
Coward, *H. F.*, *F. C.* **Wood**, and *F. L.* **Barrett**, tendering of cotton fabric by acids, i, 643.
Coward, *K. H.*, synthesis of vitamin-*A* by a fresh-water alga, *Chlorella* (sp. ?), i, 750.
persistence of vitamin-*A* in plant-tissues, i, 1017.
Coward, *K. H.* See also *J. C.* **Drummond.**
Cox, *D. C.*, differential electro-titration, ii, 999.
Cox, *H. E.*, determination of small quantities of arsenic and its occurrence in urine and in fish, ii, 157.
Cox, *R. E. S.*, chemical constant of chlorine, ii, 645.
Crabtree, *W. B.* See *L. A.* **Congdon.**
Cragoe, *C. S.* See *N. S.* **Osborne.**
Craik, *J.*, and *A. K.* **Macbeth**, glucosides. III. Synthesis of "thioindican," i, 1296.
Craik, *J.* See also *A. K.* **Macbeth.**
Craven, *R.*, and *W. A. T.* **Duncan**, laboratory preparation of *p*-benzoquinone, i, 938.
Crawford, *A. B.* See *F. J.* **Wilson.**
Creighton, *H. J. M.*, and *W. H.* **Ogden**, disintegration of carbon anodes in nitric acid, ii, 1068.
Crespi, *M.*, and *R. W.* **Lunt**, decomposition of carbon monoxide in the corona due to alternating electric fields. I., ii, 1178.
Crespi, *M.* See also *E.* **Moles.**
Cretcher, *L. H.*, *J. A.* **Koch**, and *W. H.* **Pittenger**, further syntheses with ββ′-dichlorodiethyl ether, i, 627.
Cretcher, *L. H.*, and *W. H.* **Pittenger**, syntheses with ββ-dichlorodiethyl ether, i, 228.
glycol esters of certain aromatic acids, i, 1415.
Crew, *H.*, vacuum-arc spectrum of titanium, ii, 335.
Crew, *M. C.*, *H. E.* **Steinert**, and *B. S.* **Hopkins**, solubility of yttrium salts, ii, 190.
Crippa, *G. B.* See *G.* **Charrier.**
Crommelin, *C. A.* See *E.* **Mathias.**
Crooks, *W. E.* See *E. B. R.* **Prideaux.**
Cross, *W.*, photographic method for absorption spectra in the ultra-violet, ii, 351.
Crouch, *H.*, and *E. K.* **Carver**, effect of nitrogen and carbon dioxide dilutions on explosion limits of acetone and methyl alcohol and their mixtures, ii, 682.
Crouch, *J. F.*, lupine studies. IV. Isolation of *d*-lupanine from *Lupinus Kingii* (S. Watson), i, 1447.
Crouter, *C. Y.* See *F. A.* **Cajori.**
Crowe, *J. H.*, and *A. H.* **Newey**, combustion of carbon monoxide mixtures, ii, 875.
Crowe, *M.*, precision determination of the electrical conductivities of concentrated aqueous solutions of calcium chloride, ii, 541.
Crowe, *W. H.*, amino-4-pyridones, i, 1319.
Crowther, *E. M.*, soil reaction. III. Determination of the hydrogen-ion concentration of soil suspensions by means of the hydrogen electrode, i, 875.
soil reaction. IV. Soil reaction of continuously manured plots at Rothamsted and Woburn, i, 875.
soil reaction. V. Depth distribution of reaction, and flocculation in continuously manured soils, i, 875.
availability of organic nitrogen compounds in pot experiments, i, 1371.
effect of removing the soluble humus from a soil on its productiveness, i, 1372.
Crowther, *E. M.*, and *W. S.* **Martin**, soil reaction. VI. Interaction of acid soils, calcium carbonate, and water in relation to the determination of "lime requirements," i, 876.
Crowther, *E. M.* See also *A. N.* **Puri.**
Crowther, *J. A.*, and *R. J.* **Stephenson**, some electrode phenomena in electrolysis, ii, 1167.
Croze, *F.*, line spectrum of nitrogen, ii, 77.
line spectra of nitrogen and ionised oxygen, ii, 166.
line spectra of ionised oxygen, ii, 250.
Crozier, *W. J.*, possibility of identifying chemical processes in living matter, i, 101.
biological oxidations as function of temperature, i, 102.
Crump, *L. M.* See *D. W.* **Cutler**

Cruto, *A.* See *C.* Serono.
Csapó, *J.*, determination of sugar in the cerebrospinal fluid, i, 721.
influence of neutral salts on the combination of gelatin with acids, ii, 1157.
Csapó, *J.*, and *J.* Faubl, calcium content of serum protein fractions, i, 96.
Csapó, *J.*, and *D. von* Klobusitzky, influence of hydrogen-ion concentration on the precipitation of serum proteins by salts. I., i, 178.
blood clotting and the Hofmeister series, i, 717.
Csapó, *J.* See also *A.* Bosanyi.
Császár, *E.*, the statistical distribution function in the theory of radiation and atomic heat, ii, 733.
Csonka, *F. A.* See *D. B.* Jones.
Cuenca, *B. S.* See *C. J.* Diaz.
Cullen, *G. E.*, and *E.* Biilmann, use of quinhydrone electrode for determination of p_H of serum, i, 1201.
Cumming, *W. M.*, hydroferrocyanides and hydroferricyanides of organic bases. IV., i, 122.
Cumming, *W. M.*, and *D. G.* Brown, hydroferrocyanides and hydroferricyanides of alkaloids. I., i, 572.
Cummings, *E. O.* See *J. F.* Norris.
Cunliffe, *P. W.*, action of light on dyes applied to cotton fabrics; summary of the literature, ii, 812.
Cunliffe, *P. W.* See also *A. J.* Allmand.
Cupr, *V.*, absorption of hydrogen chloride in concentrated sulphuric acid, ii, 655.
Curie, (*Mlle.*) *I.*, homogeneity of initial velocities of α-particles from polonium, ii, 348.
variations of range, initial velocity, and ionising power of the α-particles from polonium, ii, 834.
Curie, (*Mlle.*) *I.*, and *C.* Chamié, radioactive constant of niton, ii, 8.
Curie, (*Mlle.*) *I.*, and *J.* D'Espine, magnetic spectrum of β-particles from radium-*E*, ii, 732.
Curie, (*Mlle.*) *I.*, and *N.* Yamada, distribution of length of α-particles of polonium in oxygen and nitrogen, ii, 175.
long-range particles emitted by polonium, ii, 621.
Curie, (*Mme.*) *Marie*, determination of radium in uranium minerals containing tantalum, niobium, and titanium, ii, 241.
constancy of the rate of transformation of radium emanation at different concentrations, ii, 463.
Curie, (*Mme.*) *Marie*, and *D. K.* Yovanovitch, increase of the heating effect of radium preparations due to growth of polonium, ii, 464.
Curie, *Maurice*, photo-electric and phosphorogenic effect, ii, 355.
Currie, *A. N.*, determination of small quantities of copper in tissues, i, 183.
Currie, *J. A.* See *D. L.* Hammick.
Currie, *J. E.* See *E. F.* Burton.
Curtis, *W. E.*, Fulcher hydrogen bands, ii, 351.
Curtis, *W. E.*, and *W.* Jevons, Zeeman effect on the helium bands, ii, 1103.
Curtis, *W. E.*, and *R. G.* Long, structure of the band spectrum of helium. III. The doublet bands, ii, 722.
Curtiss, *L. F.*, direct determination of distribution of intensity in the natural β-ray spectrum of radium-*B* and -*C*, ii, 622.
Curtius, *F.* See *A.* Kossel.
Curtman, *L. J.*, *C.* Margulies, and *W.* Plechner, removal of phosphates in systematic qualitative analysis, ii, 68.
Cusmano, *G.*, reaction between 2:6-dibromo*cyclo*hexanones and alkali, i, 818.
synthetic catalysts, ii, 690.
Cusmano, *G.*, and *G.* Massa, relations between diketocineole and buchucamphor. VI., i, 686.
Cutler, *D. W.*, and *L. M.* Crump, influence of washing on the rate of reproduction of *Colpidium colpoda*, i, 1012.
Cutter, *J. O.*, *H.* Burgess, and *T. M.* Lowry, rotatory dispersive power of organic compounds. XVI. Halogen derivatives of camphor; optical superposition in the camphor series, ii, 743.
Cutter, *J. O.* See also *T. M.* Lowry.
Cuy, *E. J.*, electrical conductivity of metallic solid solutions, ii, 378.
Czerny, *M.*, measurements of the rotation spectrum of hydrogen chloride in the long-wave ultra-red, ii, 1024.
Czerny, *O.*, nature of the colophony extracted from the firs of Bucovina, i, 253.
Czerwinski, *J.* See *K.* Jellinek.
Czochralski, *J.*, structure of metals and its physical investigation, ii, 186.
modified reflexion in metallography, ii, 487.
radio technique in metallurgy, ii, 642.

D.

Daecke, *H.*, statistical investigations on the sub-electron, ii, 258, 349.
Dällenbach, *W.*, generalisation of the Townsend theory of spark potentials, ii, 740.
Daeves, *K.*, iron–carbon diagram and the most important constituents of plain carbon steels, ii, 401.
Dahl, *O.* See *G.* **Tammann**.
Dahll, *P.* See *H.* **Goldschmidt**.
Dahmen, *W.*, spark spectrum of potassium, ii, 167.
Dains, *F. B.*, *R. Q.* **Brewster**, *I. L.* **Malm**, *A. W.* **Miller**, *R. V.* **Maneval**, and *J. A.* **Sultzaberger**, substituted thiocarbamides. V. Synthesis of thiocarbamides from aminoethanols, and of thiazolidine derivatives, i, 1063.
Dam, *H.*, iodine value of coprosterol, i, 856.
determination of the iodine number of cholesterol, ii, 444.
Damerell, *V. R.* See *W. L.* **Semon**.
D'Amico, *E.* See *G.* **Romeo**.
Damiens, *A.*, tellurium suboxide, ii, 316.
allotropy of mercuric iodide, ii, 490.
artificial magnesium silicate, ii, 812.
Danckwortt, *P. W.*, and *E.* **Pfau**, fate of hydrocyanic acid in the animal organism; new method of detecting thiocyanates in organic material, i, 196.
proteolytic enzyme in the pods of *Vicia faba*, L., i, 202.
Danehl, *J.* See *J.* **Tröger**.
Daniel, *W.* See *K. von* **Auwers**.
Daniels, *F.* See *J. K.* **Hunt**, and *J. W.* **Williams**.
Daniels, *S.*, cast alloys of aluminium containing small amounts of magnesium, ii, 103.
Danilov, *A. N.*, pigment formation by fungi, i, 1013.
Danner, *P. S.*, barium and strontium amalgam electrodes, ii, 42.
preparation of very pure barium and strontium, ii, 62.
Dannerth, *C. A.* See *H. C.* **Parker**.
D'Ans, *J.*, and *A.* **Jäger**, sodium hydroxide and cellulose, i, 1387.
Darmois, *E.*, optical activity; copper salts of malic acid, ii, 15.
action of boric acid on the rotatory power of malic acid and malates, ii, 357.
molecular dissymmetry and optical activity, ii, 1119.
Darmois, *E.*, and *A.* **Honnelaitre**, ammonium dimolybdomalate, ii, 184.
D'Arsonval, and **Bordas**, colloids and mineral waters, ii, 291.
Darwin, *C. G.*, optical constants of matter, ii, 2.
resonance radiation and the correspondence principle, ii, 169.
Daschavsky, *P. G.* See *T. B.* **Johnson**.
Datta, *R. L.*, and *B. C.* **Chatterjee**, halogenation. XII. Derivatives of carbamic esters; chlorine as a simultaneous oxidising and chlorinating agent. II., i, 891.
Datta, *S.*, regularities in band spectra, ii, 86.
Datta, *S. K.* See *C. V.* **Raman**.
Dauphinee, *J. A.* See *A.* **Hunter**.
Daure, *P.*, determination of Avogadro's number from the light diffused by ethyl chloride, ii, 753.
Dauvillier, *A.*, new experiments with Crookes' tube, ii, 1116.
Dauvillier, *A.* See also *L. de* **Broglie**.
Davey, *W. P.*, lattice constants of metals, ii, 747.
plasticity of single crystals, ii, 1039.
decomposition of hydrogen peroxide, ii, 1181.
Davey, *W. P.* See also *L.* **Navias**.
David, *L.*, reactions of some opium alkaloids, ii, 1010.
David, *W. T.*, effect of infra-red radiation on the rate of combustion of inflammable gaseous mixtures, ii, 980.
Davidsohn, *H.*, vitamin studies; water-soluble growth-promoting factor. I. Determination of the factor promoting growth in bacteria, i, 108.
Davidson, *A. W.*, solutions in 100% sulphuric acid; solvolysis and double decomposition reactions, ii, 505.
Davidson, *B. M.*, intoxication. III. Action of ethylene. IV. Action of propylene. V. Action of ethyl chloride. VI. Action of methyl ether, i, 1503.
Davidson, *D.*, hydantoins. XLIV. Pyvuril and dipyruvic triureide, i, 583.
hydantoins. XLVI. Nitropyruvic ureide, i, 975.
Davidson, *D.*, and *O.* **Baudisch**, oxidation of *iso*barbituric acid, i, 1188.
Davidson, *D.*, and *T. B.* **Johnson**, hydantoins. XLV. Dipyruvic ureide, i, 584.
Davidson, *D.* See also *O.* **Baudisch**.
Davidson, *L. F.* See *T. T.* **Baker**.
Davies, *C. W.*, conductivity of electrolytes, ii, 541.

Davies, *C. W.*, conductivity of electrolytes. II. Mobility of the hydrogen ion at 25°, ii, 871.
conductivity of electrolytes. III. Correlation of strong and weak electrolytes, ii, 871.
Davies, *E. L.*, and *G. H.* **Livens**, kinetic theory of metallic conduction, ii, 630.
Davies, *G. H. B.* See *W. G.* **Whitman**.
Davies, *G. R.* See *G. T.* **Morgan**.
Davies, *P. G.* See *M. P.* **Applebey**.
Davis, *B.*, dependence of the intensity of the Compton effect on the atomic number, ii, 747.
critical potentials and the refractive indices of elements and compounds, ii, 933.
Davis, *D. S.*, pressure–temperature charts for organic vapours, i, 1033.
Davis, *D. S.* See also *W. G.* **Whitman**.
Davis, *R. C.* See *R. H.* **Major**.
Davis, *T. L.*, mechanism of reactions in the carbamide series, i, 375.
Davis, *T. L.*, and *A. J. J.* **Abrams**, dehydration of ammonium nitrate, ii, 581.
Davis, *T. L.*, *A. A.* **Ashdown**, and *H. R.* **Couch**, two forms of nitroguanidine, i, 644.
Davisson, *C.*, Schottky's method of determining the distribution of velocities among thermionic electrons, ii, 730.
Davisson, *C.*, and *L. H.* **Germer**, thermionic work function of oxide-coated platinum, ii, 81.
Dawson, *E. R.* See *B. S.* **Platt**.
Dawson, *L. E.*, technique for measuring the hydrogen-ion concentration of distilled water and unbuffered solutions not in equilibrium with the carbon dioxide of the air, ii, 680.
electrode vessel for liquids heavier and lighter than the liquid junction potential eliminator, ii, 978.
Dayhuff, *W. C.*, and *D. R.* **Hoagland**, electrical charge on a clay colloid as influenced by hydrogen-ion concentration and by different salts, i, 219.
De, *S. C.* See *P.* **Guha**.
Dean, *A. L.*, *R.* **Wrenshall**, and *G.* **Fujimoto**, synthesis of the anhydride of hydroxymercuri-ethoxychaulmoogric acid and ethyl acetoxymercuri-ethoxychaulmoograte, i, 545.
leprosy. XXXVIII. Catalytic reduction of chaulmoogric and hydnocarpic acids, i, 1414.
Dean, *A. L.* See also *R.* **Wrenshall**.
Dean, *G.*, atomic weight of carbon and silver, ii, 255.
Dean, *H. F.*, and *M.* **Nierenstein**, constitution of catechin. VIII. α-3:5:3′:4′-Pentahydroxy-4-benzyl-1:2-dihydrocoumarone, i, 280.
attempts to synthesise myricetin, i, 951.
Dean, *P. M.*, and *E.* **Newcomer**, determination of chlorides by calorimetric titration; titration of mixtures of cyanide and halides, ii, 597.
Dearden, *W. H.* See *F. C.* **Thompson**.
Debucquet, *L.*, arsenyl tartrates of pyridine, quinoline, and some alkaloids, i, 973.
arsenical emetics; emetics of pyridine, quinoline, and some alkaloids, i, 1090.
Debye, *P.*, and *J.* **McAulay**, electric field of ions and neutral salt action, ii, 171.
Debye, *P.*, and *L.* **Pauling**, inter-ionic attraction theory of ionised solutes. IV. Influence of variation of dielectric constant on the limiting law for small concentrations, ii, 970.
Decans, *V.*, and *J.* **Dufour**, electrolytic reduction of benzoic acid at the b. p., i, 1272.
Decarrière, *E.*, catalytic oxidation of ammonia by air in contact with platinum–palladium alloys, ii, 565.
Decarrière, *E.* See also *P.* **Pascal**.
Dede, *L.*, and *T.* **Walther**, preparation of colloidal elements by photochemical decomposition of their gaseous hydrides. I. Preparation of colloidal arsenic, ii, 197.
Deel, *H.*, and (*Mme.*) *H.* **Deel**, influence of hydrogen-ion concentration of soil on formation and composition of peppermint oil, i, 622.
Deel, (*Mme.*) *H.* See *H.* **Deel**.
DeFoe, *O. K.*, and *A. H.* **Compton**, density of rock salt and calcite, ii, 646.
DeFoe, *O. K.*, and *W. W.* **Nipper**, total intensity of scattered *X*-radiation, ii, 336.
DeFoe, *O. K.* See also *G. E. M.* **Jauncey**.
Dehe, *H.* See *B.* **Helferich**.
Dehn, *O. von*, separate determination of potassium and sodium in urine, i, 855.
Dehnert, *F.*, and *W.* **König**, action of strong bases on cotton cellulose. I. and II., i, 369.
Deiss, *E.*, arsenates of tervalent manganese. I., ii, 893.
Déjardin, *G.* See *L.* **Bloch**.
Deker, *M.* See *E.* **Wilke-Dörfurt**.
Delaby, *R.*, and *J. M.* **Dumoulin**, isomerism of vinylalkylcarbinols and ethyl alkyl ketones, i, 632.

Delaby, *R.*, and *G.* **Morel**, preparation of methylalkylglycerols, i, 773.
Delacre, *M.*, *photo*dypnopinacolins, i, 681.
Delaplace, *R.*, extension of the law of Gay-Lussac to superficial solutions, ii, 772.
Delauney, *E.*, new method of quantitative analysis by means of *X*-rays, ii, 822.
Delauney, *P.*, glucosides of several species of indigenous orchids, i, 487.
Delauney, *P.* See also *C.* **Charaux**.
Delaval, *H.* See *E.* **Kayser**.
Delaville, *L.* See *L.* **Blum**.
Delaville, *M.*, and *C. M.* **Jones**, determination of uric acid in blood plasma, i, 1201.
determination of uric acid in blood, i, 1344.
Delaville, *M.* See also *L.* **Blum**.
Delbanco, *A.* See *J. N.* **Brönsted**.
Délépine, *M.*, structural relations between pinenes and the terpineols or limonenes derived from them, i, 564.
Delf, *E. M.*, influence of storage on the antiscurvy value of fruits and vegetable juices, i, 484.
Dellacher, *J.* See *R.* **Kremann**.
Deloraine, *E. M.*, new alloy of iron and nickel of high permeability, ii, 639.
Demjanovski, *S.*, application of electrical conductivity to quantitative analysis in biochemical practice. I. Titration of certain inorganic salts with sodium hydroxide, i, 1113.
Demolon, *A.*, siliceous matter in quaternary clays, ii, 1195.
Demoussy, *E.*, displacement of acids by diffusion, ii, 654.
Demoussy, *E.* See also *G.* **André**.
Dempster, *A. J.*, life of metastable helium, ii, 171.
passage of slow canal rays through hydrogen, ii, 1020.
Demuth, *F.*, milk and gastric lipase, i, 103.
phosphate metabolism. I. Hexosephosphatases in human organs and body fluids, i, 1497.
Deneke, *H.* See *F.* **Krauss**.
Denigès, *G.*, Thomas' naphthol reaction for free and combined pentoses, i, 790.
general application of the alloxantin reaction for ferric iron, ii, 441.
detection and determination of cobalt by spectroscopy and colorimetry, ii, 826.
induced crystallisation in microchemistry, ii, 906.
Denina, *E.*, introduction to a general theory of electromotive force, ii, 41.
Dennis, *L. M.*, drying tube for phosphorus pentoxide, ii, 428.
Dennis, *L. M.*, and *F. E.* **Hance**, germanium. IX. Germanium tetraethyl; preparation and purification of zinc diethyl; analysis by combustion of a liquid containing carbon and hydrogen, i, 798.
Dennis, *L. M.*, and *A. W.* **Laubengayer**, germanium. XI. Germanium glasses, ii, 888.
Dennis, *L. M.* See also *R. B.* **Corey**, *E. B.* **Johnson**, and *D. L.* **Tabern**.
Dennler, *W. S.* See *A.* **McKenzie**.
Densch, *A.*, nature and significance of soil acidity, i, 221.
copper sulphate as fertiliser, i, 766.
effect of soluble silicates on crop yields and on the utilisation of phosphates, i, 767.
Densch, *A.*, and **Hunnius**, experiments with copper sulphate [on plants], i, 489.
Densch, *A.*, and **Pfaff**, determination of nutritive requirements [of soil] by Mitscherlich's method and some remarks on Neubauer's method, i, 1371.
Derieux, *J. B.* [electric charges carried by individual microscopic particles], ii, 832.
Derx, *H. G.*, oxidative cleavage of fats by fungi, i, 1119.
Desai, *R. D.*, iodine as a catalyst in reactions involving elimination of hydrogen halides, i, 887.
Desch, *C. H.*, theory of crystallisation in rock magmas, ii, 788.
Desgrez, *A.*, *H.* **Bierry**, and *L.* **Lescœur**, blood-corpuscles and the alkali reserve, i, 604.
Desgrez, *A.*, *H.* **Bierry**, and *F.* **Rathery**, inorganic phosphates and insulin hypoglycæmia, i, 1016.
Desgrez, *A.*, and *R.* **Vivario**, determination of carbon in organic substances, ii, 436.
Deshusses, *J.* See *L.* **Deshusses**.
Deshusses, *L.*, and *J.* **Deshusses**, physico-chemical analysis, by conductivity, of vegetable ash. I. Determination of phosphoric acid, ii, 67.
Deslandres, *H.*, structure and distribution of band spectra, ii, 626, 736, 930, 1023, 1114.
D'Espine, *J.*, magnetic spectrum of high-velocity β-particles from radium-$B+C$, ii, 622.

D'Espine, *J.* See also (*Mlle.*) *I.* **Curie**, and *D. K.* **Yovanovitch.**
Desvergnes, *L.*, detection of nitroaminophenols in urine, i, 328.
physical properties of nitro compounds, i, 1056; ii, 490.
determination of the composition of phenol nitration products, ii, 447.
gravimetric determination of trinitrophenol and a mixture of picric acid and trinitrocresol, ii, 447.
determination of picric acid in the presence of other nitro compounds, ii, 607.
Deuel, *H. J., jun.*, and *W. H.* **Chambers**, rate of excretion of ingested sugars in phloridzin diabetes, i, 1352.
Deuel, *H. J., jun.* See also *W. H.* **Chambers.**
Deuticke, *H. J.*, significance of ions in muscular function. VII. Effect of various organic anions on the lactacidogen changes, i, 729.
Deutsch, *D.*, effect of dielectrics on the stability of colloids, ii, 525.
Dewael, *A.*, abnormal reaction of propylene chlorohydrin, i, 14.
Dewael, *A.*, and *A.* **Weekering**, primary γ- and δ-methylhexanols, i, 3.
Dewey, *J.*, transference numbers of sodium and potassium chlorides and of their mixtures, ii, 873.
Dey, *A. N.*, and *N. R.* **Dhar**, induced oxidation and its mechanism explained on the basis of the formation of ions during chemical reactions, ii, 692.
Dey, *B. B.*, and *K. K.* **Row**, reactivity of the methylene group in coumarin-4-acetic acids and their esters. I. and II., i, 149, 953.
Dhar, *N. R.*, vitamin deficiency and pernicious anæmia, i, 1221.
temperature-coefficients of thermal and photochemical reactions, ii, 135.
activation of atoms and molecules and mechanism of chemical change, ii, 214.
action of nitric acid on metals, ii, 315.
negative catalysis of oxidation reactions, ii, 690.
Dhar, *N. R.*, and *A. C.* **Chatterji**, theory of Liesegang ring formation, ii, 865, 959.
Dhar, *N. R.*, and *B. K.* **Mukerji**, life period of activated molecules in thermal and photochemical reactions, ii, 809.
Dhar, *N. R.*, and *B. K.* **Mukerji**, Einstein's law of photochemical equivalence, ii, 1075.
mechanism of photochemical reactions, ii, 1079.
Dhar, *N. R.*, and *R. P.* **Sanyal**, photosynthesis in tropical sunlight, ii, 884.
Dhar, *N. R.* See also *D. N.* **Chakravarti**, *A. N.* **Dey**, *S.* **Ghosh**, *N. M.* **Mittra**, *K. B.* **Mukerji**, *C. C.* **Palit**, and *R. P.* **Sanyal.**
Dhéré, *C.*, electrodialysis, i, 199.
Dhéré, *C.*, *A.* **Schneider**, and *T. van der* **Bom**, fluorescence of metallic compounds of hæmatoporphyrin, ii, 88.
D'Huart, adsorption of water vapour and some other vapours by the surface of glass, ii, 657.
Diamant, *N.* See *S.* **Fränkel.**
Diaz, *C. J.*, and *B. S.* **Cuenca**, microdetermination of blood-sugar, i, 453.
Di Capua, *C.*, ternary system, lead–cadmium–thallium, ii, 787.
hardness of ternary alloys of lead, bismuth, and cadmium, ii, 1051.
hardness of ternary alloys of lead, bismuth, and tin, ii, 1051.
Dickens, *F.*, *E. C.* **Dodds**, and *S.* **Wright**, preparation and standardisation of the ovarian hormone, i, 1513.
Dickinson, *J.*, electrification of gases by surface combustion, ii, 740.
Dickinson, *R. G.*, and *J. B.* **Friauf**, crystal structure of tetragonal lead monoxide, ii, 18.
Dickson, *B. R.* See *F. N.* **Allan.**
Dickson, *J. G.* See *S. H.* **Eckerson.**
Dickson, *J. V. E.*, liberation of hydrogen from carbon compounds, i, 1033.
Diechmann, *G. H.* See *P.* **Karrer.**
Dieke, *G. H.*, structure of the so-called ultra-violet bands of water vapour, ii, 180, 927.
intensities in the many-lined spectrum of hydrogen, ii, 450.
bands in the secondary spectrum of hydrogen, ii, 625.
intensities in band spectra, ii, 626, 836.
Fulcher hydrogen bands, ii. 737.
Diekmann, *J. J.* See *J. P.* **Wibaut.**
Diels, *O.*, *J. H.* **Blom**, and *W.* **Koll**, formation of *endo*methylenepiperidazine from *cyclo*pentadiene and azo-esters, and its conversion into 1:3-diamino*cyclo*pentane, i, 976.

Diels, *O.*, and *W.* **Gädke**, dehydrogenation of cholesterol, i, 1062.
Diels, *O.*, and *W.* **Koll**, cuprohalide molecular compounds of azo compounds, i, 988.
Dienes, *O. von*, hydrogen persulphide, ii, 228.
Diepolder, *E.* See *O.* **Fischer.**
Diesbach, *H. de*, and *K.* **Strebel**, dibenzoylxylenes and dinaphthanthradiquinones. III., i, 1435.
Diesbach, *H. de*, and *G.* **Zurbriggen**, derivatives of cumidic and pyromellitic acids, i, 1427.
Dietrich, *W.*, influence of experimental conditions on the decomposition of benzoyl peroxide, i, 544.
Dietrichson, *G.* See *L. J.* **Bircher.**
Dietzel, *R.*, and *S.* **Galanos**, optical researches on sulphurous acid and its alkali salts, especially potassium and ammonium pyrosulphites, ii, 1115.
Dietzel, *R.*, and *R.* **Krug**, chemical equilibrium between lactic acid and its anhydrides in aqueous solution, i, 1036.
Dietzel, *R.*, and *J.* **Naton**, halochromism of fulgides. II., i, 1067.
Dietzel, *R.*, and *F.* **Schlemmer**, hypochlorous acid and the alkali hypochlorites, ii, 892.
Dijck, *W. J. D. van*, Becquerel effect on copper oxide electrodes, ii, 1083.
Dijkstra, *D. W.* See *F. M.* **Jaeger.**
Dill, *D. B.*, composition of crude gluten, i, 622.
proximate composition of certain Pacific Coast fish, i, 855.
Dill, *D. B.*, and *C. L.* **Alsberg**, preparation, solubility, and specific rotation of wheat gliadin, i, 1478.
Dilthey, *P.* See *F.* **Fischer.**
Dilthey, *W.*, triphenylmethane dyes, i, 650.
diketonates of metalloids. VI. Action of tin and zirconium tetrachlorides on β-diketones, i, 1473.
Dilthey, *W.* [with *A.* **Schaefer**], arylated pyridines. VI. *N*-Alkylquinopyridans, i, 153.
Dilthey, *W.*, and *E.* **Floret**, arylated pyrylium compounds and their relations to the benzopyrylium compounds. XIV., i, 55.
Dilthey, *W.*, and *W.* **Radmacher**, isomeric chalkones [phenyl styryl ketones], i, 408.
pyrylium compounds. XV. Arylated pyridines. VII. *m*-Substituted triphenylpyrylium compounds, i, 1441.
Dilthey, *W.*, and *C.* **Thelen**, 3-methoxy-2-phenylquinoline-4-carboxylic acid; [3-methoxyatophan], i, 1317.
Dimitrov, *M.*, test for chlorine in the presence of bromine, iodine, etc., ii, 326.
iodometric titrations, ii, 598.
Dimmett, *P. S.* See *W. C.* **Rose.**
Dimroth, *O.*, influence of solvent on the equilibrium of isomerides, ii, 36.
Dinanath, *T.* See *G. J.* **Fowler.**
Dingemanse, *E.*, micro-determination of blood-sugar, i, 323.
Dingemanse, *E.*, and *E.* **Laqueur**, adsorption of poisons by charcoal. II., i, 1500.
Dirac, *P. A. M.*, conditions for statistical equilibrium between atoms, electrons, and radiation, ii, 6.
Dirken, *M. N. J.*, multiple gas analysis apparatus, ii, 154.
Dirks, *B.*, preparation of 4-acetamidocoumaranone, i, 148.
Dirsch, *R.* See *S.* **Goldschmidt.**
Dirska, *G.* See *J.* **Meyer.**
Ditman, *N. E.*, electromagnetic nature of colloidal, enzyme, and catalytic action and its significance, ii, 51.
Dittler, *E.*, manganese-bearing river pebbles, ii, 322.
new mineral analyses, ii, 323.
analytical-synthetic researches on zincite, ii, 1184.
Dittmer, *A. F.* See *I.* **Langmuir.**
Dittrich, *J.*, calcium content of bile, i, 325.
Dixon, *A. L.* See *W. H.* **Rodebush.**
Dixon, *H. B.*, ignition of carbon disulphide vapour and its phosphorescent flame, ii, 633.
Dixon, *M.*, xanthine oxydase. V. Function of catalase, i, 1010.
Dixon, *M.*, and *S.* **Thurlow**, xanthine oxydase. VI. A cell oxidation system independent of iron, i, 1213.
Dixon, *M.* See also *F. G.* **Hopkins.**
Doan, *F. J.* See *H. E* **Bierman.**
Doan, *R. L.* See *A. H.* **Compton.**
Dobrescu-Cluy, *J. M.*, dynamics of assimilation of potassium [by plants] from mineral silicates, i, 1223.
Dobrowsky, *A.* See *E.* **Späth.**
Dodds, *E. C.*, *W.* **Lawson**, and *J. C.* **Mottram**, metabolic differences, following *X*-radiation, between normal rats and rats immune to Jensen's rat sarcoma, i, 1492.
Dodds, *E. C.* See also *F.* **Dickens.**
Doelter, *C.*, importance of colloid chemistry in mineralogy and geology, ii, 514.

Döpel, *R.*, electromagnetic analysis of positive rays, ii, 168.
selective photo-electric effect on strontium, ii, 832.
Doerner, *H. A.*, and *W. M.* Hoskins, co-precipitation of radium and barium sulphates, ii, 381.
Dognon, *A.*, influence of wave-length on the coagulation of a colloidal solution by *X*-rays, ii, 665.
Dohme, *A. R. L.* See Sharp & Dohme.
Dokan, *S.*, action of alkalis on Konyaku colloid, ii, 967.
Dokan, *S.* See also *L.* Michaelis.
Dolde, *A.* See *K. A.* Hofmann.
Doleschall, *F.* See *N.* Frank.
Dominik, *W.*, potassium ferrocyanide from sodium ferrocyanide and potassium chloride, i, 526.
Dominikiewicz, *M.*, structure of the benzene nucleus, i, 15.
structure of fluoran and phthalophenone derivatives, i, 53.
catalytic reduction of thymol to menthol, i, 146.
structure of kaolin; theory of the structure of silicates, ii, 1036.
the structure of ultramarine, ii, 1131.
Domogalla, *B. P.*, *C.* Juday, and *W. H.* Peterson, forms of nitrogen in lake waters, i, 765.
Domogalla, *B. P.* See also *W. H.* Peterson.
Donat, *H.* See *E.* Wichert.
Donath, *W. F.*, changes in the percentage of vitamin-*A* and in the nature of albumin during the germination of seeds of *Phaseolus radiatus*, L. (katjang idjo), i, 483.
Dondelinger, *A.* See *M.* Bourgeaud, and *C.* Courtot.
Donder, *T. de*, affinity, ii, 539.
calculation of specific affinity, ii, 790.
Donker, *H. J. L.* See *A. J.* Kluyver.
Donnan, *F. G.*, influence of J. Willard Gibbs on the science of physical chemistry, ii, 395.
Doolan, *J. J.*, conditions of precipitation, by electrolytes, of selenium hydrosol and other hydrosols, ii, 293.
Doolan, *J. J.*, and *J. R.* Partington, vapour pressure of tellurium, ii, 278.
Dorabialska, (*Mlle.*) *A.*, thermochemical researches on the oximes. III. Stereoisomeric dioximes, ii, 208.
thermochemical researches on the oximes. IV. Acetaldoxime, ii, 1140.
Doreas, *M. J.* See *W. J. V.* Osterhout.
Dorenfeldt, (*Mme.*). See (*Mlle.*) *E.* Gleditsch.
Dorgelo, *H. B.*, intensity measurements in the ultra-violet, ii, 335.
intensity relations of triplet components of the alkaline earths and spark doublets of calcium, ii, 724.
distribution of energy over the lines of the main series of neon in a column discharge, ii, 1099.
Dorier, *P. C.* See *L.* Bert.
Dorrell, *G. W.*, catalysis by alumina of the reaction between ethyl alcohol and ammonia, ii, 1174.
Dorrer, *E.* See *H.* Wieland.
Doser, *A.* See *K.* Freudenberg.
Dosios, *C.*, and *T.* Tsatsas, nitro derivatives of diphenyl ethylene ether, i, 655.
Dougal, *J. W.*, chlorohydrocarbons as toxic agents, i, 334.
Doughty, *H. W.*, reaction of dichloroacetic acid with aromatic amines, i, 805.
Mohr's method for determination of silver and halogens in other than neutral solutions, ii, 238.
Doughty, *H. W.*, and *A. P.* Black, preparation and properties of dichloroacetic acid, i, 628.
Douglas, *G. W.* See *W. R.* Atkin.
Douker, *H. J. L.* See *A. J.* Kluyver.
Dowding, *E. S.*, regional and seasonal distribution of potassium in plant tissues, i, 871.
Dowling, *P. H.*, contact *E.M.F.* between the solid and liquid phases of the same metal and between the outgassed surfaces of two dissimilar metals, ii, 796.
Downey, *W. E.* See *H. J.* Emeléus.
Downing, *F. B.* See *W. S.* Calcott.
Dox, *A. W.*, phenylethylethylbarbituric acid and relative derivatives, i, 300.
tetra-alkylsuccinimides and their pharmacological action, i, 796.
Dox, *A. W.* See also *A.* Thomas.
Dozier, *C. C.* See *E.* Wagner.
Draganescu, *S.*, and *A.* Lissievici-Draganescu, enzymes of cerebrospinal fluid in pathological conditions, i, 611.
Dragendorff, *O.* See *H.* Wieland.
Drane, *H. D. H.*, spiral springs of quartz, ii, 995.
Draves, *C. Z.*, and *H. V.* Tartar, instability of phthalate solutions towards the hydrogen electrode, ii, 695.
Drazil, *H.* See *R.* Kremann.
Dreisch, *T.*, influence of the CH-group on the absorption of certain organic compounds below 3μ, ii, 178.
absorptive power of liquids and their vapours for infra-red radiation of wave-length less than 3μ, ii, 627.

Dresbach, *M.*, and *H. R.* **Hosmer**, polarisation of metals used as electrodes, ii, 1063.
Dresel, *K.*, and *H.* **Rothmann**, microdetermination of blood-sugar, i, 714.
Dresel, *K.*, and *E.* **Wollheim**, electrolytic migrations in the blood and tissues caused by adrenaline, i, 616.
Drew, *H. D. K.* See *G. T.* **Morgan**.
Dreyfuss, *H.*, blood-sugar reduction tables for Bang's "new method" calculated for 50 to 130 mg. of blood, i, 94.
Driggs, *F. H.*, and *B. S.* **Hopkins**, rare earths. XVI. Purification and atomic weight of holmium, ii, 463.
Drouillon, *F.*, study of the ternary mixture: water–ethyl alcohol–*n*-butyl alcohol, ii, 651.
Druce, *J. G. F.*, organic compounds of tin; stannonic acids and some of their derivatives, i, 798.
organic chloro-stannites and -stannates. VII. Some miscellaneous compounds, i, 1096.
solid hydrides of arsenic and antimony, ii, 700.
search for the element 93. I. Examination of crude manganese compounds and isolation of element of atomic number 75, ii, 1124.
Druce, *J. G. F.* See also *F. H.* **Loring**, and *E. J.* **Weeks**.
Drucker, *C.*, and *H.* **Weissbach**, critical miscibility and elevation of b. p., ii, 953.
Drucker, *C.* See also *W. U.* **Behrens**.
Drumm, *J. J.*, *N. G. J.* **O'Reilly**, and *H.* **Ryan**, *aa*- and *aγ*-isomerides of 2:4:6:3′:4′-pentamethoxydiphenylpropane, i, 1268.
Drummond, *J. C.*, *O.* **Rosenheim**, and *K. H.* **Coward**, relation of sterols to vitamin-*A*, i, 617.
Drummond, *J. C.*, and *T. A.* **Webster**, ultra-violet radiations and antirachitic substances, ii, 630.
Drummond, *J. C.* See also *A. S.* **Parkes**, and *O.* **Rosenheim**.
Drury, *D. R.*, total bile. VII. Calcium content, i, 325.
Druschinin, *D. W.* See *E. W.* **Bobko**.
Drzewina, *A.*, and *G.* **Bohn**, production of acid by cytolysis, i, 1512.
Drzimal, *H.*, occurrence of salicyluric acid in the urine after administration of salicylic acid, i, 99.
Dschu, *G. L.* See *K.* **Feist**.
Duane, *W.* See *S. K.* **Allison**, (*Miss*) *A. H.* **Armstrong**, and *G. L.* **Clark**.
Dubief, *J.*, variation of viscosity of fluids as a function of volume, ii, 498.
Dubien, *M.* See *V.* **Grignard**.
Dubin, *H. E.*, *H. B.* **Corbitt**, and *L.* **Freedman**, relationship between chemical structure and physiological action; effect of *l*-adrenaline and derivatives on blood-sugar, i, 1502.
Dubin, *H. E.*, and *C.* **Funk**, cod-liver oil. I. Effect of hydrogenation on the vitamin content. II. Concentrate manifesting both antirachitic and antiophthalmic properties, i, 1120.
Duboin, *A.*, application to chromium of a general method for synthesis of fluorides and silicates, ii, 994.
Dubois, *C.*, and *M.* **Polonovski**, influence of adrenaline on the concentration of carbamide in the blood, i, 481.
Dubois, *R.* See *R.* **Fosse**.
Dubon, *A.*, silicate compounds of cadmium, ii, 221.
Dubrisay, *R.*, capillary chemical phenomena, ii, 961.
Duchon, *F.*, action of silica in increasing the yield [of plants] in sand cultures with insufficient phosphoric acid, i, 767.
Duck, *A. E.* See *G. T.* **Morgan**.
Duckers, *G. E.* See *I. D.* **Garard**.
Duckett, *J.*, and *W. H.* **Patterson**, influence of a third substance on the critical solution temperature of phenol and water, ii, 381.
Duckett, *J.* See also *W. H.* **Patterson**.
Duclaux, *J.*, and *J.* **Errera**, mechanism of ultrafiltration, ii, 530.
measurement of viscosity, ii, 1048.
Ducloux, *E.*, and *G.* **Cordier**, action of pancreatic extract of *Acanthias vulgaris* (dog-fish) compared with that of beef insulin, i, 1364.
Dudley, *H. W.*, *M. C.* **Rosenheim**, and *O.* **Rosenheim**, chemical constitution of spermine. I. Isolation of spermine from animal tissues and preparation of its salts, i, 294.
Dünner, *L.*, and *M.* **Mecklenburg**, clinical experiments with phloridzin, i, 1500.
Dützmann, *A.* See *E.* **Merck**.
Dufay, *J.* See *J.* **Cabannes**.
Duffendack, *O. S.*, excitation of the secondary spectrum of hydrogen by electron impacts, ii, 333.
energy levels in band spectra, ii, 1114.
Duffendack, *O. S.*, and *H.* **Huthsteiner**, low-voltage arcs in phosphorus vapour, ii, 452.
Duffendack, *O. S.* See also *E. F.* **Barker**.
Duffieux, *M.*, origin of band spectra, ii, 1023.

Dufford, *R. T.*, *D.* **Nightingale**, *S.* **Calvert**, spectra of luminescence of Grignard compounds, ii, 89.
luminescence of Grignard compounds; spectra and brightness, ii, 474.
Dufour, *A.*, wave-length of maximum energy in the sound spectrum of an explosion, ii, 183.
Dufour, *J.* See *V.* **Decans**.
Dufraisse, *C.*, and *H.* **Moureu**, $\alpha\gamma$-diphenylpropane-$\alpha\beta$-dione (phenylbenzylglyoxal), i, 937.
Dufraisse, *C.*, and *J. E.* **Viel**, α-chlorostyrene, i, 1138.
Dufraisse, *C.* See also *C.* **Moureu**.
Duin, *C. F. van*, alternating polarity in chain compounds, i, 802.
Dumanski, *A.*, stability of arsenious sulphide hydrosol and velocity of colloidal particles moving under the influence of gravity, ii, 290.
Dumoulin, *J. M.* See *R.* **Delaby**.
Dunbar, *R. T.*, *J*-phenomena and the quantum theory of scattering of *X*-radiation, ii, 455.
Duncan, *E. E.* See *H. J.* **Stander**.
Duncan, *W. A. T.* See *R.* **Craven**.
Dunker, *E.* See *J.* **Tröger**.
Dunn, *E. R.* See *C.* **Voegtlin**.
Dunn, *M. S.*, liberation of carbon dioxide, ammonia, and amino-nitrogen from casein by acid hydrolysis, i, 1477.
Duparc, *L.*, *P.* **Wenger**, and *G.* **Graz**, solubility of calcium fluoride in acetic acid, ii, 652.
Duparc, *L.*, *P.* **Wenger**, and *C.* **Urfer**, gaseous catalysis by means of metals of the platinum group, ii, 1177.
Duperier, *A.*, thermo-magnetic studies of certain solutions, ii, 173.
Duperier, *A.* See also *B.* **Cabrera**.
Dupont, *J.*, and *L.* **Labaune**, determination of citronellal in citronella oil, ii, 75.
Durand, *J. F.*, and *S.* **Houghton**, reduction of nitro compounds by calcium hydride, i, 646.
Durand, *J. F.*, and *R.* **Naves**, action of hydrogen peroxide on magnesium arylamines, i, 535.
action of ethyl hypochlorite on mixed organo magnesium compounds and on magnesium-amines, i, 1054.
hypochlorous esters and the problem of the polarity of valencies, i, 1230.
Durand, *J. T.*, and *E.* **Rougé**, cryoscopy of diphenyl ether, ii, 759.
D'Urso, *S.* See *G.* **Minunni**.
Duschinsky, *R.* See *E.* **Späth**.
Duseberg, *T.*, absorption of fluorescent light by the emitting substance, ii, 262.
Dusen, *M. S. Van*, platinum-resistance thermometry at low temperatures, ii, 590.
Dushman, *S.*, *H. N.* **Rowe**, *J.* **Ewald**, and *C. A.* **Kidner**, electron emission from tungsten, molybdenum, and tantalum, ii, 845.
Dushman, *S.* See also *M. R.* **Andrews**.
Dussol, *M.*, electrolytic preparation of hexabromoethane, i, 350.
electrochemical preparation of di-iodoacetylene and "di-iodoform" [tetraiodoethylene], i, 350.
Dustman, *R. B.*, absorption of mineral elements by plants, i, 1123.
Dutt, *P. C.* See *A. C.* **Sircar**.
Dutt, *P. K.* See *H. W.* **Carnelley**.
Dutt, *S.*, general synthesis of α-unsaturated acids from malonic acids, i, 882.
constitution of Indian kamala. I., i, 1296.
Dutt, *S.*, and *J. F.* **Thorpe**, ring-chain tautomerism. XI. The fluoresceins and rhodamines, i, 140.
Duus, *H. C.* See *J. N.* **Brönsted**.
Duval, *M.*, ionic reaction of the blood of certain invertebrates, i, 325.
Dyckerhoff, *K.* See *H.* **Staudinger**.
Dyer, *H. A.* See *C.* **Voegtlin**.
Dyer, *J. W. W.* See *N. K.* **Adam**.
Dymond, *E. G.*, measurement of critical potentials of gases, ii, 6, 253.
double impacts by electrons in helium, ii, 617.
Dyniewicz, *H. A.* See *H. A.* **Oberhelman**.
Dziewoński, *K.*, *J.* **Schoenówna**, and *E.* **Waldmann**, derivatives of 2-methylnaphthalene, i, 1056.
Dziewoński, *K.*, and *J.* **Suszko**, hydrogenation of decacyclene (triaphthylenebenzene), i, 242.
fluorocyclene, i, 649.

E.

Eadie, *G. S.*, *J. J. R.* **Macleod**, and *E. C.* **Noble**, action of insulin, i, 1512.
Eagles, *B. A.* See *F. M. R.* **Bulmer**, and *V. J.* **Harding**.
Eastcott, *E. V.*, formation of bios in infusions, i, 1017.
Eastman, *E. D.*, theory of certain electrometric and conductometric titrations, ii, 594.
Eaton, *F. J.* See *G.* **Barger**.
Ebaugh, *W. C.* See *F. G.* **Keenen**, and *H. F.* **Smith**.

Ebel, *F.* See *R.* **Kuhn**.
Ebeling, *I.*, metallic reflexions. I. and II., ii, 643.
Ebermann, *N. F.* See *W. A.* **Patrick**.
Ebert, *L.*, dissociation constants of dibasic carboxylic acids and the normal potential of the quinhydrone electrode in absolute methyl alcohol, i, 230.
dielectric polarisation in pure compounds and mixtures, ii, 14.
exact magnitude of the electric moment of dipolar molecules, and the chemical significance of orientation polarisation, ii, 262.
velocity of addition of hydrogen chloride to quinone in methyl alcohol, ii, 408, 556.
Echave, *D.*, analysis of adrenaline, ii, 248.
Echstein, *H. C.*, fatty acids in subcutaneous fat of man, i, 1203.
Eck, *P. N. van*, determination of blood in fæces, i, 187.
Eckart, *C.*, post-arc conductivity and metastable helium, ii, 1104.
Eckart, *C.* See also *K. T.* **Compton**.
Ecker, *E. E.*, and *J. L.* **Morris**, factors influencing the destruction of uric acid by *Aerobacter aerogenes*, i, 1113.
Ecker, *E. E.* See also *J. L.* **Morris**.
Eckerson, *S. H.*, and *J. G.* **Dickson**, influence of soil temperature and moisture on the chemical composition of wheat and maize, i, 217.
Eckert, *A.*, oxidation in light, i, 413.
dianthraquinonyl, i, 414.
chlorination of helianthrone, i, 414.
Eckert, *F.*, constitution of glass, ii, 1145.
Eckl, *K.* See *O.* **Lemmermann**.
Eckstein, *H. C.*, synthesis of lecithin in the animal organism, i, 458.
Ectors, *E.*, action of organo-magnesium compounds on nitriles; benzonitrile, i, 138.
Eddington, *A. S.*, derivation of Planck's law from Einstein's equation, ii, 1022.
Eddy, *W. H.*, *R. W.* **Kerr**, and *R. R.* **Williams**, isolation from autolysed yeast of a crystalline substance melting at 223°, having the properties of a bios, i, 342.
Edee, *R. H.* See *T. J.* **Thompson**.
Eder, *J. M.*, solarisation of the photographic plate, ii, 986.
Eder, *R.*, and *F.* **Hauser**, derivatives of β-methylanthraquinone. V. Frangula emodin, emodic acid, and their derivatives, i, 562.
Eder, *R.*, and *F.* **Hauser**, derivatives of β-methylanthraquinone. VI. Naturally-occurring monomethyl ether of Frangula emodin, i, 563.
[composition of] chrysarobin, i, 948, 1160.
Ederer, *S.*, influence of vitamin-*A* and of vitamin-*B* on unbalanced dietaries, i, 869.
action of piperidine on calcium deposition, i, 869.
Edgar, *G.*, and *H. E.* **Shiver**, equilibrium between creatine and creatinine in aqueous solution; effect of hydrogen ion, ii, 533.
Edlbacher, *S.*, nitrogen distribution in the hydroxyproteic acid fraction of urine, i, 855.
Edlbacher, *S.*, and *P.* **Bonem**, arginase, i, 863.
Edlbacher, *S.*, and *H.* **Röthler**, arginase. II. Quantitative determination of arginase in animal organs. III. Arginine exchange and sexuality, i, 1505.
Eds, *F. de*, fate of hexamethylenetetramine in the body, i, 461.
determination of formic acid in blood and urine, i, 713.
Edwards, *C. A.*, and *L. B.* **Pfeil**, tensile properties of single iron crystals and the influence of crystal size upon the tensile properties of iron, ii, 946.
Edwards, *G. A.*, *W. H.* **Perkin**, *jun.*, and *F. W.* **Stoyle**, new synthesis of the meconines, i, 404.
Edwards, *P. R.*, surface tensions of aqueous solutions of various organic compounds, ii, 387.
Eegriwe, *E.*, detection of sulphur dioxide, nitrogen dioxide, and some acids, ii, 156.
Effront, *J.*, absorbent power of agar-agar, ii, 201.
Efimoff, *W. W.*, colorimetric determination of oxygen, i, 481.
Efremov, *N.*, latent heat of fusion of camphor, ii, 1140.
camphor and nitrophenols, ii, 1160.
Ege, *R.*, influence of temperature and reaction on the destruction and activity of pepsin, i, 743.
Egerton, *A. C.*, vapour pressures of monatomic substances, ii, 25.
numerical values of chemical constants and frequencies of elements, ii, 277.
Egg, *C.* See *V.* **Kohlschütter**.
Egger, *T.* See *E.* **Briner**.
Eggert, *J.*, Landolt's reaction. IV., ii, 52.

Eggert, *J.*, and *W.* **Noddack**, silver halide emulsions and the law of photochemical equivalence, ii, 573.
photochemistry of silver compounds, ii, 573.
Eggert, *J.*, and *L.* **Pfeffermann**, Landolt's reaction. III., ii, 407.
Eggert, *J.*, and *J.* **Reitstötter**, photographic action of methylene-blue as an adsorption effect, ii, 509.
Eggleton, *P.*, and *L.* **Gross**, blood-sugar levels of rats fed with complete diets and diets deficient in vitamin-*B*, i, 1220.
Eguchi, *M.*, the permanent electret, ii, 462.
Ehler, *O.* See *C. E.* **Mange**.
Ehrenberg, *R.*, tryptic digestion with dilute enzyme solutions. I. and II., i, 103, 202.
Ehrenhaft, *F.*, electrical behaviour of radioactive colloidal particles of the order of 10^{-5} cm. as observed separately in a gas, ii, 465.
Ehrenstein, *M.* See *F.* **Straus**.
Ehrlich, *F.*, and *K.* **Rehorst**, *d*-glycuronic acid, i, 1379.
Eibner, *A.*, and *E.* **Munzing**, oil film or "oxyne." I., i, 1036.
Eibner, *A.*, and *F.* **Pallauf**, acceleration of the drying of fatty oils by driers, i, 777.
Eibner, *A.*, and *G.* **Ried**, oil films or "oxyns." II. Autoxidation during the drying of a fatty oil; Walton process linoxyn, i, 1377.
Eichelberger, *L.* See *E. M.* **Terry**.
Eichholtz, *F.*, interaction of colloidal fats and lipoids, i, 199.
Eichholtz, *F.*, and *E. H.* **Starling**, action of inorganic salts on the secretion of the isolated kidney, i, 860.
Eickel, *W.* See *A.* **Windaus**.
Eidinov, *A.* See *T. A.* **Webster**.
Eilert, *A.*, electrolytic deposition of calcium from solutions of calcium hydroxide in water, and calculation of the normal potential of calcium, ii, 547.
Einstein, *A.*, quantum theory of the monatomic perfect gas, ii, 495.
quantum theory of the ideal gas, ii, 624.
Eisele, *I.*, effect of pressure on refractive index of organic liquids, ii, 264.
Eisenkolb, *F.*, passivity of nickel, ii, 1165.
Eisenkolb, *F.* See also *V.* **Rothmund**.
Eisenlohr, *F.*, and *L.* **Schulz**, molecular coefficients of refraction, i, 17.
Eisenman, *A. J.* See *J. P.* **Peters**.
Eisler, *M.*, behaviour of precipitin and agglutinin adsorbed on charcoal or kaolin to their antigen, i, 96.
Eistert, *B.* See *F.* **Arndt**.
Eitel, *W.*, silicates, ii, 580.
Ekhard, *W.* See *F.* **Straus**.
Ekkert, *L.*, colour reactions of eserine, ii, 247.
colour reaction of *tert.*-amyl alcohol, ii, 1006.
colour reaction for lactic acid, ii, 1007.
diphenylamine reaction [for nitrates], ii, 1093.
colour reactions of nitrous and nitric acids, ii, 1200.
Elam, *C. F.*, orientation of crystals in metal test-pieces subjected to small strains followed by heat treatment, ii, 945.
orientation of crystals produced by heating strained iron, ii, 946.
tensile tests of an aluminium–zinc alloy, ii, 954.
Elam, *C. F.* See also *G. I.* **Taylor**.
Elbs, *K.*, phenyltriazoles, i, 163.
Elbs, *K.*, and *M.* **Gaumer**, electrochemical reduction of nitrobenzylanilines in weakly alkaline solution, i, 167.
Elbs, *K.*, *H.* **Nacken**, and *H.* **Hofmann**, dianilino-*p*-azoxystilbene, i, 168.
Eldred, *D. N.* See *M.* **Walker**.
Eldridge, *J. A.*, excitation function of the mercury spectrum, ii, 1102.
Whittaker's atomic model, ii, 1112.
Elion, *L.*, replacement of the benzoyl group by the nitro group, i, 44.
action of nitric acid on derivatives of benzophenone, i, 262.
Elion, *L.*, and *C.* **Janssen**, *jun.*, diazotisation and nitration of 3:5-dibromo-*o*-anisidine, i, 389.
Eller, *W.*, constitution of natural humic acids, i, 372.
Eller, *W.* [with *G.* **Helmrich**, *D.* **Klemm**, *E.* **Haubold**, and *A.* **Schöppach**], humic acids. VII. Properties and reactions of humic acids and humins, i, 521.
Eller, *W.*, and *V.* **Lorenz**, action of sulphuryl chloride on aminophenols, i, 537.
Ellestad, *R. B.* See *P. H. M.-P.* **Brinton**.
Ellett, *A.*, polarisation of sodium resonance radiation in magnetic fields, ii, 628.
Ellinger, *P.* [iron the oxygen-carrying component of the respiratory enzyme], i, 1342.

Ellinghaus, *J.*, investigation of tryptic digests by Folin's colorimetric method for determination of amino-acids, i, 865.

Elliott, *G. A.*, and *I.* **Masson**, thermal separation in gaseous mixtures, ii, 763.

Ellis, *C. D.*, high energy groups in the magnetic spectrum of the radium-*C* β-rays, ii, 9.

Ellis, *C. D.*, and *W. A.* **Wooster**, heating effect of γ-rays from radium-*B* and radium-*C*, ii, 622, 923.

Ellis, *J. W.*, emission and absorption bands of carbon dioxide in the infra-red, ii, 1115.

Ellis, *O. C. de C.*, influence of nitrogen dilution on the speed of flame, ii, 135.

Ellis, *O. C. de C.*, and *H.* **Robinson**, flame analysis, ii, 590.

Ellis, *O. C. de C.*, and *R. V.* **Wheeler**, movement of flame in closed vessels, ii, 554.

Ellis, *O. W.*, intermetallic reactions in a lead-base bearing metal, ii, 282.

Ellman, *S.*, volumetric determination of mercuric iodide, mercuric chloride, and some other mercury compounds, ii, 1205.

Ellsworth, *H. V.*, radioactive minerals as geological age indicators, ii, 593.

Elöd, *E.*, theory of mordanting. II., ii, 531.

Elvehjem, *C. A.* See *E. B.* **Hart**.

Embden, *G.*, determination of lactic acid in animal organs. II., i, 719.

Embden, *G.*, and *H.* **Hentschel**, action of fluorine ions on the activity and lactacidogen metabolism of frog muscle, i, 727.

Embden, *G.*, *M.* **Kahlert**, and *Hermann* **Lange**, effect of sodium chloride and sodium bromide on the synthesis of lactacidogen by calcium ions, i, 728.

Embden, *G.*, and *M.* **Zimmermann**, lactacidogen. IV., i, 729.

Emeléus, *H. J.*, glow of phosphorus, ii, 354.

spectroscopic study of the combustion of phosphorus trioxide and of hydrogen phosphide, ii, 740.

Emeléus, *H. J.*, and *W. E.* **Downey**, spectroscopic study of the luminescent oxidation of phosphorus, ii, 89.

Emeléus, *K. G.*, number of β-particles from radium-*E*, ii, 8.

Emeléus, *K. G.* See also *E. V.* **Appleton**.

Emelianova, *N. V.*, dropping mercury cathode. VII. Nickel and cobalt, ii, 676.

Emmerich, *W.* See *H.* **Ley**.

Emmert, *B.*, *G.* **Jungck**, and *H.* **Häffner** [with *R.* **Kuhn**], quinhydrone-like compounds of dihydro-4:4′-dipyridyl, i, 72.

Emmert, *B.*, and *N.* **Roh** [with *M.* **Koberne**], new group of organic molecular compounds, i, 587.

Emmett, *P. H.* See *A. F.* **Benton**, and *L.* **Pauling**.

Emmrich, *C.*, and *Hermann* **Lange**, effect of calcium and some of its antagonists on the lactacidogen changes in minced muscle, i, 728.

Endo, *H.*, measurement of the change in volume in metals during solidification, ii, 281.

measurement of the change in volume in alloys during solidification, ii, 281.

Endoh, *C.*, behaviour of tribromoethyl alcohol in the animal body, i, 332.

mixed Cannizzaro reaction. III., i, 1428.

Endres, *R.* See *S.* **Goldschmidt**.

Engel, *O.* See *J. von* **Braun**.

Engel, *W.* See *E.* **Herzfeld**.

Engelhardt, *W.* See *A.* **Bach**.

Engels, *H.* See *K.* **Freudenberg**.

Engfeldt, *N. O.*, value of the sodium nitroprusside test for the detection and determination of the total acetone in urine and certain other body fluids, i, 1490.

Engledon, *F. L.* See *H. E.* **Woodman**.

Engler, *L.* See *E.* **Fromm**.

Englis, *D. T.*, and *C.* **Hale**, occurrence of free pentoses in plants; effect of extraction of the sugars with ammoniacal alcohol, i, 618.

English, *F. L.* See *W. S.* **Calcott**.

English, *S.*, effect of composition on the viscosity of glass. III. Some four-component glasses, ii, 954.

Enklaar, *C. J.*, labile prussic acid (*iso*-hydrocyanic acid), i, 1394.

Enlund, *B. D.*, structure of quenched carbon steels, ii, 486.

Enos, *G. M.*, fundamental factors in corrosion, ii, 1068.

Ensslin, *H.* See *M.* **Bergmann**.

Ephraim, *F.*, cobaltammines with more than six molecules of ammonia, ii, 992.

Ephraim, *F.*, and *W.* **Flügel**, cobalt-ammines of the nitrogen sulphonic acids and sulphatocobaltammines, ii, 61.

Ephraim, *F.*, and *A.* **Pfister**, salts of aromatic sulphonic acids and their solubilities [in water], i, 896.

salts of certain aromatic carboxylic acids and their solubility, i, 1148.

Epifanova, (*Mme.*) *T.* See *E.* **Khotinska.**
Epstein, *A. A.*, action of pepsin on insulin, i, 1513.
Epstein, *C.* See *A.* **Fodor.**
Epstein, *P. S.*, simultaneous jumping of two electrons in Bohr's model, ii, 1.
Epstein, *Z. A.*, electrical conductivity of an element and its place in the periodic system, ii, 623.
Erben, *F.*, compounds of quinine and copper, i, 573.
Erben, *F. X.*, and *N.* **Schniderschitsch** [with *W.* **Vio**], derivative of cupreine containing arsenic, i, 707.
Erdmann, *W.* See *T.* **Sabalitschka.**
Erdtman, *H.* See *H. von* **Euler.**
Eriksen, *H. A.*, nature of the ions in air and in carbon dioxide, ii, 6.
mobility of actinium active deposit ions, ii, 79.
mobility of argon and hydrogen ions in air, ii, 1107.
Eriksson, *E.* See *H. von* **Euler**, and *K.* **Sjöberg.**
Ernest, *A.*, universal commutator for potentiometric measurements by the compensation method, ii, 236.
Ernst, *Z.*, extra-hepatic production of bile pigments in surviving organs. II. Surviving spleen, kidney, and lung, i, 732.
Ernst, *Z.*, and *J.* **Förster**, extra-hepatic production of bile pigments in surviving organs. III. Surviving spleen of dogs poisoned with phenylhydrazine. IV. Surviving spleen of dogs treated with collargol or colloidal iron, i, 732.
accelerating action of carbohydrates on the oxidation of acetoacetic acid, ii, 684.
Ernst, *Z.*, and *B.* **Szappanyos**, extra-hepatic production of bile pigments in surviving organs. I. Surviving spleen, i, 732.
Erp, *H. van*, simplified preparation of certain organic compounds. II. Chloro-*p*-benzoquinone, i, 685.
Errera, *J.*, solid state from the electrical point of view; dispersion in the Hertzian region, ii, 362.
Errera, *J.*, and *V.* **Henri**, ultra-violet absorption spectra of dichloroethylenes, ii, 738.
optical properties of ethylenic isomerides, ii, 1137.
Errera, *J.* See also *J.* **Duclaux.**
Escher, *H. H.*, isolation of natural crystalline lecithin, i, 1232.
Escourrou, *R.* See *V.* **Grignard.**
Esp, *V.* See *C. N.* **Riiber.**
Essinger, *R.*, and *P.* **György**, colorimetric determination of the inorganic phosphorus of serum, i, 178.
Estermann, *J.*, influence of density and geometrical dimensions of a molecular stream on the formation of deposits, ii, 962.
formation of metallic deposits by molecular radiation, ii, 1053.
Estill, *H. W.* See *A. A.* **Noyes.**
Ets, *H. N.*, chemical changes in the blood produced by drugs. III. Phloridzin, i, 734.
Ettisch, *G.*, and *H.* **Runge**, sensitisation of Congo-red by globulin, ii, 864.
Ettisch, *G.* See also *H.* **Freundlich.**
Eucken, *A.*, heats of dissociation of the oxygen and nitrogen molecules, ii, 207.
Eucken, *A.*, and *F.* **Fried**, entropy of condensed gases at the absolute zero, ii, 97.
Eucken, *A.*, *E.* **Karwat**, and *F.* **Fried**, constant *i* of the thermodynamic vapour-pressure equation for polyatomic molecules, ii, 98.
Euler, *H. von*, affinities existing between substrate and enzyme and their specificity, i, 863.
Euler, *H. von*, and *H.* **Erdtman**, irisin and the enzymic hydrolysis of polyfructosides, i, 1369.
Euler, *H. von*, and *E.* **Eriksson**, growth factors. V., i, 1220.
Euler, *H. von*, and *R.* **Johansson**, comparative determination of phosphate-, calcium-, and magnesium-content of the tibia of rats and guinea-pigs, i, 1489.
Euler, *H. von*, and *K.* **Josephson**, invertase, i, 1008.
Euler, *H. von*, and *T.* **Lövgren**, capacity of fresh yeast to ferment galactose after preliminary treatment with this sugar and the constancy of this property, i, 1214.
kinetics of the oxidation-reduction reaction of formaldehyde, ii, 981.
Euler, *H. von*, and *K.* **Myrbäck**, fermentation co-enzyme (co-zymase) of yeast. VI. Further isolation experiments, i, 105.
acceleration of the fermentative activity of fresh yeast by the biocatalyst *z*, i, 745.
phosphate and calcium content of blood of guinea-pigs and rats with varying vitamins-*C* and-*A* administration, i, 1515.
Euler, *H. von*, *K.* **Myrbäck**, and *S.* **Karlsson**, enzymic degradation and synthesis of carbohydrate. I. Phosphate exchanges and glycogen cleavage in muscle and in yeast, i, 744.

Euler, *H. von*, *K.* **Myrbäck**, and *R.* **Nilsson**, enzymic degradation and synthesis of carbohydrates. I., i, 866.
Euler, *H. von*, and *R.* **Nilsson**, fermentation of galactose by yeast after previous treatment with this sugar, i, 866.
dextrose and lævulose in alkaline and phosphate-containing solutions, i, 1042.
co-zymase. VII., i, 1361.
hexoses taking part in carbohydrate metabolism, i, 1496.
Euler, *H. von*, and *A.* **Ölander**, catalytic decomposition of acetoacetic acid by strong acids and bases, ii, 1069.
Euler, *H. von*, *A.* **Ölander**, and *E.* **Rudberg**, theory of catalysis. I. Kinetics of mutarotation, ii, 876.
Euler, *H. von*, and *E.* **Rudberg**, "reaction-influencing" ions in light and dark reactions, ii, 135.
influence of salts on solubility, ii, 207.
solubility of ampholytes, ii, 853.
Euler, *H. von*, and *V.* **Sandberg**, nitrogenous equilibrium of the yeast cell, i, 1213.
Euler, *H. von*, and *O.* **Swartz**, connexion between the water-soluble growth factors and activators of the degradation of sugar; a thermostable biocatalyst in yeast, i, 209.
Euler, *H. von*, and *G.* **Westling**, dried yeast. II., i, 203.
Euler, *H. von*, and *H.* **Widell**, growth factors. IV. Influence of excess of *lD* [fat-soluble growth-promoting factor] on the growth of rats, i, 869.
Euler, *H. von*, *H.* **Widell**, and *E.* **Eriksson**, growth factors. III., i, 869.
Eusslin, *N.* See *M.* **Bergmann**.
Evans, *B. S.*, separation and determination of tin in alloys, ii, 826.
colorimetric determination of cobalt in the presence of nickel, ii, 904.
Evans, *D. C.* See *A. S.* **Russell**.
Evans, *H. M.*, and *G. O.* **Burr**, antisterility vitamin fat-soluble-*E*, i, 1022.
Evans, *R.* See *J. E.* **Humphries**.
Evans, *U. R.*, action of salt solutions on iron and steel in the presence of oxygen, ii, 140.
colours due to thin films on metals, ii, 288.
water-line corrosion of iron and steel, with special reference to the action of the so-called "inhibitors" of corrosion, ii, 687.
oxygen distribution as a factor in the corrosion of metals, ii, 688.
Everitt, *B.* See *K.* **Myrbäck**.
Evers, *F.*, cataphoresis of metal sols in organic dispersion media, ii, 668.
Evers, *N.* See *C. W.* **Maplethorpe**.
Ewald, *J.* See *S.* **Dushman**.
Ewald, *W.*, and *M.* **Pólányi**, strength and elastic limits of natural rock-salt, ii, 371.
Ewbank, *E. K.* See *N. V.* **Sidgwick**.
Ewing, *D. T.*, and *H. W.* **Schmidt**, electrolytic preparation of potassium bromate with carbon electrodes, ii, 551.
Ewing, *D. T.*, and *H. A.* **Shadduck**, composition of a constant-boiling solution of hydrogen bromide in water, ii, 859.
Ewing, *W. W.*, preparation of electrolytic mercurous chloride in saturated potassium chloride for use in the calomel electrode, ii, 571.
Eymer, *L.*, action of chromic acid on indigotin, i, 1174.
reducing action of sodium hyposulphite in alcoholic solution, ii, 532.
Eynon, *L.* See *J. H.* **Lane**.

F.

Fabre, *R.*, nature and variations of the aldehyde contained in the blood, i, 324, 852.
extraction of alkaloids or various organic compounds contained in organs, i, 719.
hæmatoporphyrin, ii, 1116.
spectrophotometric determination of fluorescent bodies in solution, ii, 1212.
Fabre, *R.*, and *P.* **Fredet**, localisation and excretion of alkylated barbituric acids, i, 1504.
Fabre, *R.*, and *R.* **Frossard**, influence of the reaction of the medium on digestion by papain, i, 863.
Fabre, *R.*, and *E.* **Parinaud**, dissociation of salts of narcotine and optimum conditions for its extraction, i, 962.
Fabre, *R.* See also *E.* **Bayle**, and *P.* **Fredet**.
Fabry, *C.*, atmospheric ozone as absorbing material for radiations, ii, 627.
Facer, *J. E.* See *S. G. P.* **Plant**.
Färber, *E.* See *H.* **Stobbe**.
Fage, *W. E.* See *E. A.* **Owen**.
Fairbrother, *F.*, electro-endosmosis. II., ii, 129.
Fairbrother, *F.*, and *H.* **Mastin**, electro-endosmosis. I. and III., ii, 47, 302.
Fairlie, *D. M.*, and *G. B.* **Brook**, determination of sodium in aluminium, ii, 241.

Fairweather, *D. A.*, electrolysis of salts of alkyloxy-acids, i, 631.
electrosynthesis of *n*-duotriacontanedicarboxylic acid, i, 1236.
Faivret, *T.* See *A.* **Wahl**.
Fajans, *K.*, melting and heat of vaporisation of graphite, ii, 277.
properties of chemical compounds and atomic structure, ii, 623.
Faldino, *M.* See *G. R.* **Levi**.
Falk, *G.* See *M.* **Centnerszwer**.
Falk, *K. G.*, *H. M.* **Noyes**, and *K.* **Sugiura**, enzyme action. XXX. Lipolytic action of tissues of different animals, i, 471.
enzyme action. XXXIII. Lipase actions of extracts of the whole rat at different ages, i, 1360.
Falk, *K. G.* See also *H. M.* **Noyes**.
Falke, *E.* See *F.* **Kehrmann**.
Falkenhagen, *H.*, Paschen–Back effect in hydrogen, ii, 79.
Famulener, *L. W.* See *R.* **Kautsky**.
Fanselow, *J. R.* See *E. O.* **Kraemer**.
Fantl, *P.* See *E.* **Urbach**.
Farnsworth, *M.*, hydration of anhydrite, ii, 980.
Farbenfabriken vorm. *F.* Bayer & Co., preparation of aromatic amines by reduction of the corresponding nitro compounds, i, 132.
preparation of pyrazolone derivatives, i, 301.
preparation of derivatives of basic hydroxyalkyl ethers, i, 374.
monoazo dyes, i, 598.
preparation of polymethine dyes, i, 839.
dyes of the pyrone series, i, 955.
alkylamine esters of aromatic amino-acids, i, 1419.
ether derivatives of ring-substituted mercury aromatic hydroxy-acids, i, 1473.
Farbwerke vorm. Meister, Lucius, & Brüning, preparation of *CC*-substituted succinimides, i, 376.
preparation of derivatives of hydroxyanthranilic acid, i, 400.
preparation of acridine derivatives, i, 429.
preparation of plastic material from cellulose esters, i, 544.
monoazo dyes, i, 598.
preparation of acetic anhydride, i, 1233.
esters of aromatic alkyloxy- and alkylamino-carboxylic acids, containing iodine in the aliphatic side-chain, i, 1423.
preparation of 2-naphthol-4-carboxylic acid, i, 1426.
Farbwerke vorm. Meister, Lucius, & Brüning, dimethylaminoethylimide of camphoric acid, i, 1437.
Fargher, *R. G.*, and *L.* **Higginbotham**, constituents of the wax of Egyptian sakellaridis cotton, i, 879.
Fargher, *R. G.*, and *M. E.* **Probert**, alcohols present in the wax of American cotton, i, 879.
Farnsworth, *H. E.*, electronic bombardment of metal surfaces, ii, 169.
Farnsworth, *M.* See *G. L.* **Wendt**.
Farr, *H. V.* See *W. D.* **Collins**.
Farren, *J. W.*, and *H. R.* **Fife** [with *F. E.* **Clark**, and *C. E.* **Garland**], chloro-ethers. II. Preparation of some new chloro-ethers and alkoxymethyl esters, i, 1230.
Farrer, *E.* See *H.* **Stobbe**.
Farrow, *F. D.*, and *G. M.* **Lowe**, flow of starch paste through capillary tubes ii, 509.
Farrow, *F. D.*, and *S. M.* **Neale**, measurement of the viscosity of solutions of cotton in aqueous cuprammonium hydroxide and its significance as a test of textile quality, ii, 773.
Farrow, *F. D.*, and *E.* **Swan**, absorption of water by dried films of boiled starch, ii, 506.
Farrow, *M. D.*, and *C. K.* **Ingold**, tautomerism depending on the mobility of a hydroxyl group. I. Open-chain triad systems, i, 155.
Fasold, *H.* See *A.* **Hahn**.
Fassbender, *M.*, negative nitrogen band spectrum, ii, 350.
Faubl, *J.* See *J.* **Csapó**.
Faulkner, *I. J.*, and *T. M.* **Lowry**, dynamic isomerism. XVII. Mutarotation of aluminium benzoylcamphor, ii, 632.
Faurholt, *C.*, aqueous solutions of carbon dioxide and carbonic acid, ii, 295.
aqueous solutions of carbamates and carbonates, ii, 396.
Faust, *O.*, binary liquid mixtures, ii, 29.
Faust, *T. H.*, and *T.* **Spängler**, determination of chlorine in benzaldehyde and cinnamaldehyde, ii, 1000.
Fawsitt, *C. E.* See *L. S.* **Cash**.
Fazi, *Remo de*, indones. VI. Methods of preparation of indones, i, 263.
indones. VII. Constitution and synthesis of truxones, i, 269.
Fazi, *Remo de.* See also *Romolo de* **Fazi**.
Fazi, *Romolo de*, and *Remo de* **Fazi**, action of ultra-violet rays on alcoholic fermentation and on yeast, i, 475.

Fearon, *W.*, molecular weight of glycogen, i, 12.
Fedorov, *W. S.* See *K.* **Shaposchnikov.**
Feenstra, *T. P.* See *H.* **Zwaardemaker.**
Fehér, *D.*, and *I.* **Vági**, action of nitrites on the growth of plants. II., i, 488.
Fehér, *D.*, and *S.* **Vági**, action of sodium carbonate on germination and growth in plants, i, 1023.
Fehse, *W.* See *H.* **Alterthum.**
Feick, *R.*, colour of colloidal silver and mercury, ii, 1152.
Feigl, *F.*, qualitative microanalysis. II., ii, 435.
capillary-chemical reaction in spot-tests, ii, 509.
Feigl, *F.* [with *F. L.* **Lederer**], relation between atomic grouping and specific affinity. I., i, 170.
Feigl, *F.* [with *F.* **Pavelka** and *R.* **Schacherl**], co-ordination studies on the analytical behaviour of heavy metal sulphides, ii, 70.
Feigl, *F.*, and *A.* **Christiani-Kronwald**, use of oxalenediuramidoxime in the detection and determination of nickel, ii, 330.
Feigl, *F.*, and *R.* **Kobiliansky**, intermediate compounds formed during the esterification of oxalic acid with phenols, i, 1235.
Feigl, *F.*, and *G.* **Krauss**, complex-chemical methods for the volumetric determination of acidity, basicity, and aluminium content of aluminium solutions, ii, 329.
Feigl, *F.*, and *H.* **Ordelt**, use of pyrogallol in the gravimetric determination of bismuth and its separation from lead, ii, 442.
Feigl, *F.*, and *A.* **Sucharipa**, amides of mercurous salts, ii, 1184.
Feist, *K.*, and *H.* **Bestehorn**, oakwood tannin; preparation and purification of tannins. II., i, 566.
Feist, *K.*, and *G. L.* **Dschu**, alkaloids of the calumba root. III., i, 830.
Fejér, *A. von*, and *G.* **Heténvi**, metabolism in diseases of the liver. I. Carbohydrate metabolism in liver disease, i, 725.
Feldmann, *A.*, catalytic reduction by means of nickel and hydrogen, i, 1263.
Feldtmann, *G. A.* See *C. G.* **Schwalbe.**
Felix, *F.* See *H.* **Staudinger.**
Felix, *K.*, synthesis of the histones of the thymus gland, i, 1203.
Felix, *K.*, and *H.* **Rothler**, behaviour of ornithine, lysine, and putrescine in the surviving liver, i, 859.
Fellenberg, *T. von*, occurrence of iodine in nature. II. Determination of minute quantities of iodine, i, 329.
occurrence of iodine in nature. VI. Relation between the incidence of goitre and the iodine content of the environment, i, 329.
occurrence of iodine in nature. III. Iodine determinations on foodstuffs, manures, and Swiss mineral waters, i, 347.
occurrence of iodine in nature. IV. Evolution of elementary iodine from sea water, ii, 306.
occurrence of iodine in nature. V. Iodine content of air, ii, 316.
occurrence of iodine in nature. VII. Iodine content of rocks, geological formations, and minerals, and conditions for the accumulation of iodine in earths, ii, 321.
Fellenberg, *T. von*, and *H.* **Geilinger**, occurrence of iodine in nature. IX. Iodine liberation and accumulation by micro-organisms, i, 339.
Fellenberg, *T. von*, *H.* **Geilinger**, and *K.* **Schweizer**, occurrence of iodine in nature. VIII. Evolution of elementary iodine from earths, ii, 321.
Feller, *A.* See *K.* **Schaum.**
Fellers, *C. R.*, and *R. W.* **Clough**, determination of indole and skatole in bacterial cultures, i, 1015.
Fells, *H. A.*, and *J. B.* **Firth**, preparation and properties of silicic acid gel, ii, 390.
Felsher, *A. R.* See *C. C.* **Wang.**
Felton, *L. D.*, oxydase activity and isolation of pure cultures of bacteria, i, 1509.
indicator for testing the reducing power of bacteria, i, 1509.
Fenwick, *F.* See *R. G. van* **Name.**
Ferguson, *A.*, and *I.* **Vogel**, calculation of the equivalent conductivity of strong electrolytes at infinite dilution. I. Aqueous solutions, ii, 1163.
Ferguson, *A. L.*, and *G. van* **Zyl**, transfer resistance, ii, 547.
Ferguson, *J.*, dissociation pressures of hydrated double selenates, ii, 1063.
Ferguson, *J. B.*, light filter in interferometry, ii, 839.
magnetic form of ferrous oxide, ii, 846.
Ferguson, *J. B.*, and *W. S.* **Funnell**, vapour pressures of solutions of phenol and water at 75°, ii, 501.
Ferguson, *J. B.*, and *W. B.* **Hope**, heats of formation of phenol–water solutions at 75°, ii, 492.
Ferguson, *W. C.* See *A.* **McMillan.**

Fermi, *E.*, intensity of multiple lines, ii, 340.
relation between the constants of the infra-red bands of triatomic molecules, ii, 471.
Fermi, *E.*, and *F.* **Rasetti**, effect of an alternating magnetic field on the polarisation of the resonance radiation of mercury vapour, ii, 473, 839.
Fernandes, *L.*, co-ordination valency of two hydroxyl groups in the ortho position. I. Complexes of pyrocatechol and pyrogallol with acids of the molybdenum group, i, 912, 1061.
separation of thorium from zirconium and from the tervalent rare-earth metals, ii, 426.
isomorphism of zirconium sulphate and quadrivalent cerium sulphate, ii, 748.
isomorphism of quadrivalent uranium and zirconium compounds, ii, 1133.
Fernandes, *L.* See also *G.* **Canneri**.
Fernández, *O.*, ethylenic peroxides; oxygenase of the Bach–Chodat system, i, 769.
Fernbach, *A.*, and *S.* **Nicolau**, effect of nitrates on yeast, i, 477.
Ferrari, *A.*, crystal structure and isomorphism of the fluorides of lithium and magnesium, ii, 845.
X-ray analysis of the crystal structure of lead dioxide, ii, 1125.
Ferro, *M. R.*, bio-reduction, i, 340.
Fetzer, *W. R.*, device for estimating corrosion, ii, 996.
Feulgen, *R.*, and *K.* **Voit**, groups responsible for the nucleal reaction and nucleal coloration. II. Preparation of hydroxymethylfurfuraldehyde, i, 1477.
Fichter, *F.*, and *A.* **Christen**, electrochemical oxidation of anethole and *iso*eugenol, i, 813.
Fichter, *F.*, and *W.* **Kern**, formation of carbamide from ammonium hydrogen carbonate solution at the body temperature, i, 796.
Fichter, *F.*, and *P.* **Lotter**, electrochemical oxidation of iodobenzene, *o*-iodotoluene, and *p*-iodotoluene, i, 1055.
Fichter, *F.*, and *J.* **Meyer**, electrochemical oxidation of homologues of benzene. I. *m*-Xylene, i, 881.
electrochemical oxidation of homologues of benzene. II. Cymene, i, 800.
Fichter, *F.*, and *P.* **Müller**, chemical and electrochemical oxidation of *as*-*m*-xylidine and its mono- and di-methyl derivatives, i, 805.
Fichter, *F.*, and *F.* **Reichart**, "weighting" of silk with stannic chloride, ii, 193.
Fichter, *F.*, and *E.* **Stocker**, electrochemical oxidation of benzenesulphonic acid, toluene-*o*-sulphonic acid, and benzene-*p*-disulphonic acid, and the per-acids formed in the process, i, 239.
Fiegel, *A.* See *P.* **Rona**.
Fieger, *E. A.* See *C. O.* **Rost**.
Field, *E.* See *A.* **Henwood**.
Field, *H.*, *jun.* See *A. V.* **Bock**.
Field, (*Miss*) *M. J.*, *W. E.* **Garner**, and *C. C.* **Smith**, ionisation of aromatic nitro compounds in liquid ammonia. I., ii, 792.
Fieser, *L. F.*, absorbent for oxygen in gas analysis, ii, 238.
Fieser, *L. F.* See also *J. B.* **Conant**.
Fife, *H. R.* See *J. W.* **Farren**.
Fikentscher, *H.* See *K.* **Freudenberg**.
Filippi, *E.* See *E.* **Mameli**.
Filonenko, *E. P.* See *S. V.* **Lebedev**.
Finck, *J. L.*, and *R. M.* **Wilhelm**, variation with pressure of the boiling points of naphthalene, benzophenone, and anthracene, ii, 759.
Finger, *H.*, and *R.* **Gaul**, action of methyl cyanoformate on organomagnesium compounds, i, 1431.
Finger, *H.*, and *F.* **Kraft**, indigoid dyes of the pyridine series, i, 73.
Fink, *A.* See *M.* **Kohn**.
Fink, *D. E.*, metabolism during embryonic and metamorphic development of insects, i, 726.
Fink, *D. E.* See *J. H.* **Bodine**.
Fink, *H.* See *Hans* **Fischer**.
Finkelstein, *W.*, decomposition potentials of non-aqueous solutions, ii, 546.
Finken, *H.* See *E.* **Ott**.
Finlay, *H. J.* See *F. H.* **McDowall**.
Finzi, *C.*, alkylation by esters of toluene-*p*-sulphonic acid, i, 648.
derivatives of 1-naphthylamine-8-sulphonic acid, i, 654.
dinitro- and triamino-naphthalenes, i, 701.
Fiore, *O. de.* See *F.* **Zambonini**.
Firth, *J. B.*, and *F. S.* **Watson**, catalytic decomposition of hydrogen peroxide solution by animal charcoal; the production of highly active charcoals, ii, 310.
sorption of iodine and catalytic decomposition of hydrogen peroxide solution by "norit" charcoals, ii, 880.

Firth, *J. B.* See also *H. A.* **Fells.**
Fischbach, *W.* See *F.* **Mayer.**
Fischbeck, *K.*, electrochemical reduction of solid electrodes, ii, 1166.
Fischenich, *M.*, and *M.* **Pólányi**, cause of conductivity of casein solutions, ii, 662.
Fischer, *A.* See *O.* **Fürth.**
Fischer, *A. H.* See *H.* **Freundlich.**
Fischer, *Ernst.* See *D.* **Vörlander.**
Fischer, *Eugen.* See *N.* **Troensegaard.**
Fischer, *F.*, *H.* **Tropsch**, and *P.* **Dilthey**, reduction of carbon monoxide to methane with metal catalysts, ii, 982.
Fischer, *H.* See *E.* **Berl.**
Fischer, *Hans*, and *H.* **Beller**, synthesis of a tetrapyrrylethylene and of some 2:3-dimethylpyrrole derivatives, i, 1333.
Fischer, *Hans*, and *H.* **Fink**, synthesis of coproporphyrin by yeast and influencing factors, i, 105.
synthesis of coproporphyrin by yeast and influencing factors. II. Analysis of crystalline copper coproporphyrin from fresh yeast and the increase of porphyrins by the addition of substances, i, 866.
Fischer, *Hans*, and *M.* **Heyse**, tripyrrylmethanes. II., i, 76.
Fischer, *Hans*, and *J.* **Hilger**, natural porphyrins. XII. Ætioporphyrin from urinoporphyrin, i, 307.
Fischer, *Hans*, and *H.* **Hilmer**, phylloerythrin. II., i, 855.
Fischer, *Hans*, and *F.* **Lindner**, natural porphyrins. XIV. Ooporphyrin and its conversion into hæmin ester, i, 992.
natural porphyrins. XVI. Kämmerer's porphyrin, i, 997.
Fischer, *Hans*, and *J.* **Klarer**, synthesis of xanthopyrrolecarboxylic acid; synthesis of the acid scission products of blood pigment. III., i, 577.
Fischer, *Hans*, and *R.* **Müller**, natural porphyrins. XIII. Conversion of hæmoporphyrin into mesoporphyrin and its degradation to ætioporphyrin, i, 845.
natural porphyrins. XV. Tetramethylhæmatoporphyrin ester and its conversion into ooporphyrin ester, i, 846.
Fischer, *Hans*, and *C.* **Nenitzescu**, action of formaldehyde and substituted alcohols on pyrrole derivatives and a new synthesis of *iso*phonopyrrolecarboxylic acid, i, 834.
Fischer, *Hans*, and *G.* **Niemann**, bile pigments. IX., i, 1198.
Fischer, *Hans*. See also *A.* **Stock.**
Fischer, *M. H.*, the colloid-chemical theory of water fixation in the organism, ii, 36.
Fischer, *O.*, *E.* **Diepolder**, and *E.* **Wölfel**, substituted 4-aminoquinolines, i, 438.
Fischer, *O.*, *Alfred* **Müller**, and *A.* **Vilsmeier**, action of phosphoryl chloride on aceto-methyl- and -ethyl-anilide; synthesis of 4-chloro*iso*quinocyanines, i, 439.
Fischer, *P.*, hydrogen overvoltage on alloys, ii, 44.
electrolytic preparation of hydrogen sulphide and sulphides, ii, 807.
electrolytic preparation of selenides and iodides, ii, 808.
Fischer, *W. M.*, supersaturated solutions. I. Mechanism of separation of salts from supersaturated solutions and the formation of rhythmic precipitates in gels, ii, 853.
Fischer-Treuenfeld, *A. von.* See *O.* **Mumm.**
Fischl, *V.* See *H.* **John.**
Fischler, *F.*, and *F.* **Ottensooser**, hypoglycæmia; identity of intoxication due to dextrose starvation with the hypoglycæmic reaction, i, 715.
Fischli, *A.* See *P.* **Ruggli.**
Fisher, *D. J.*, crystallography of methyldiphenylmethyldichloroamine, ii, 942.
Fisher, *N. F.*, and *E. B.* **McKinley**, presence of toxic and insulin-like substances in oranges, grape fruit, and lemons, i, 1016.
Fisk, *C. H.*, and *S. S.* **Sokhey**, excretion of ammonia and fixed base after administration of acid, i, 723.
Fitz, *W.* See *P.* **Pfeiffer.**
Flaschenträger, *B.*, micro-determination of hydroxyl groups, ii, 999.
Fleming, *N.* See *E. A.* **Owen.**
Flemming, *W.* See *F.* **Arndt.**
Fletcher, *F. A.* See *R. R.* **Read.**
Fleury, *P.*, laccase and the laws of enzyme action, i, 471.
laccase. IV. Action of sodium chloride; influence of the reaction of the medium, i, 614.
laccase. V. Action of hydrocyanic acid, i, 1360.
Fleury, *P.*, and *H.* **Levaltier**, determination of nitrogen by Kjeldahl's method and its modifications, ii, 66, 434.
Fleury, *P.*, and *P.* **Tavernier**, reducing action of dextrose on copper salts in alkaline and acid solution, ii, 605.
Fleysher, *M. H.*, electrometric titration of antimony and tin by potassium dichromate, ii, 243.

Fleysher, *M. H.* See also *H. S.* **Harned.**
Flörov, *K. W.*, S-shaped adsorption curve, ii, 657.
Flössner, *O.*, echinococcal fluid. II., i, 329.
Flössner, *O.*, and *F.* **Kutscher**, *Petromyzon fluviatilis*, L. I. Detection of adenine, xanthine, methylguanidine, leucine, tyrosine, fatty acids of the $C_nH_{2n}O_2$ series, and lactic acid. II. Detection of neosine, the chief extractive of *Petromyzon*, and of betaine, choline, and crangitine, i, 327.
chemical investigation of the sturgeon (*Acipenser sturio*), i, 720.
Florence, *G.* See *L.* **Hugounenq.**
Florentin, *D.* See *M.* **Marqueyrol.**
Floret, *E.* See *W.* **Dilthey.**
Flügel, *W.* See *F.* **Ephraim.**
Foa, *E.*, specific heat of liquids according to the theory of corresponding states, ii, 1138.
Fock, *E.*, and *S. A.* **Holbøll**, distribution of blood-sugar between corpuscles and plasma; studies on carbohydrate metabolism, i, 1486.
Focken, *C. M.* See *S. P.* **McCallum.**
Fodor, *A.*, *A.* **Bernfeld**, and *R.* **Schönfeld**, nature of the peptide-cleaving enzyme of yeast macerates, i, 1215.
Fodor, *A.*, and *C.* **Epstein**, kinetics of the cleavage of peptides by yeast enzymes, i, 1214.
Fodor, *A.*, and *A.* **Reifenberg**, nature of the process of germination; determination of proteins by means of adsorption applied to the decomposition of proteins in germinating pea seeds, i, 756.
fermentation of dried tobacco. I. Methods for separating nicotine and ammonia. II. Enzymic production of volatile products from nicotine under the influence of tobacco-leaf extracts, i, 1519.
Fodor, *A.*, and *A.* **Rosenberg**, separation methods by means of specific adsorption, ii, 1060.
Fodor, *A.*, and *R.* **Schönfeld**, adsorption of the phosphoproteins of yeast by various adsorbents and the elution of the adsorbates, ii, 857.
Foerster, *F.*, formation and decomposition of polythionates, ii, 148, 229, 701.
Foerster, *F.*, *A.* **Brosche**, and *C.* **Norberg-Schulz**, sodium and potassium salts of sulphurous acid, ii, 120.
Foerster, *F.*, and *K.* **Kubel**, sulphurous acid and its salts. II. Decomposition of sulphites at red heat, ii, 120.
Förster, *J.* See *Z.* **Ernst**, and *N.* **Frank.**
Foex, *G.*, various magnetic states of an ion, ii, 345.
Foex, *G.*, and *L.* **Royer**, diamagnetism of nematic substances, ii, 755.
Fogg, *H. C.* See *M. D.* **Williams.**
Folberth, *W.* See *A.* **Löwenhein.**
Folts, *H.* See *E. K.* **Carver.**
Foote, *H. W.*, system, sodium nitrate–sodium sulphate–water and the minerals darapskite and nitroglauberite, ii, 786.
Foote, *P. D.*, nitrogen and uranium, ii, 18.
spectroscopy and Bohr's theory of atomic structure, ii, 624.
Foote, *P. D.*, *W. F.* **Meggers**, and *R. L.* **Chenault**, visible radiation from solid targets, ii, 80.
Foote, *P. D.*, and *F. L.* **Mohler**, photoelectric ionisation of cæsium vapour, ii, 919.
Foote, *P. D.*, *T.* **Takamine**, and *R. L.* **Chenault**, excitation of forbidden spectral lines, ii, 166, 916.
Foran, *H. P.*, preparation of halogen-substituted ethers, i, 774.
contraction of ethyl alcohol on dilution, ii, 101.
Forbes, *G. S.*, and *G. R.* **Harrison**, constricted mercury arc as a source of light for photochemical work, ii, 1194.
Forcrand, *de*, xenon hydrate, ii, 812.
Ford, (*Miss*) *G. W.* See *D.* **Hanson.**
Fordyce, *J. A.*, *L.* **Rosen**, and *C. N.* **Myers**, syphilis. IX. Arsenic content of the blood after intravenous injection of neosalvarsan. X. Arsenic in human milk after intravenous injection of salvarsan. XI. Partition of arsenic in serum and clot after intravenous administration of salvarsan, neosalvarsan, and silver salvarsan. XII. Arsenic content of the blood after intravenous injection of tryparsamide. XIII. Arsenic content of the cerebrospinal fluid after intravenous injection of hypertonic saline solutions and neosalvarsan. XIV. Localisation and fate of salvarsan, neosalvarsan, silver salvarsan, and tryparsamide in the viscera after intravenous administration in rats, i, 189.
syphilis. XV. Excretion of arsenic through the kidney after intravenous administration of salvarsan, neosalvarsan, silver salvarsan, and tryparsamide, i, 611.

Foresti, *B.*, catalysis by the action of subdivided metals. III. Heat of adsorption of hydrogen on nickel, ii, 692.
Foresti, *B.* See also *M.* **Padoa.**
Forestier, *H.*, and *G.* **Chaudron**, transformation points of solid solutions of alumina or chromic oxide in ferric oxide, ii, 534.
magnetic transformation points in the system, ferric oxide–magnesia, ii, 1159.
Forrer, *R.*, artificial magnetic anisotropy of nickel, ii, 486, 639.
Forrest, *J.*, magnetic quality in crystals, ii, 1133.
Forrester, *G. C.* See *M.* **Gomberg.**
Forster, *J.* See *Z.* **Ernst.**
Forster, *M. O.*, and *K. A. N.* **Rao**, *d*-mannitol from *Gardenia turgida*, i, 1295.
Forster, *M. O.*, and *P. P.* **Shukla**, camphane series. XL. Constitution of Manasse's hydroxycamphor, i, 1161.
Forster, *R. B.*, and *C. M.* **Keyworth**, arylamine salts of the naphthalenesulphonic acids. II. Salts of α- and β-naphthalenesulphonic acids, i, 126.
Forster, *T. A.* See *I. M.* **Heilbron.**
Forstmann, *W.* See *A.* **Lottermoser.**
Forstner, *G. E.* See *E. A.* **Cooper.**
Forsyth, *R.*, *C. I.* **Kelly**, and *F. L.* **Pyman**, *iso*quinoline derivatives. IX. Preparation and reduction of *iso*quinoline and its derivatives, i, 1167.
Forsyth, *W. G.*, and *F. L.* **Pyman**, tautomerism of amidines. V. Methylation of glyoxalines by diazomethane; bromination of 4(or 5)-phenylglyoxaline, i, 699.
Fosse, *R.*, *P.* **Hagene**, and *R.* **Dubois**, analysis of cyanamide in its calcium compound, ii, 76.
Fosse, *R.*, and *A.* **Hieulle**, identification of glyoxylic acid by reaction with hydrazine and xanthhydrol to form dixanthylhydrazone–glyoxylic acid, i, 1130.
colour reaction, supposed specific for formaldehyde, produced by glyoxylic acid, ii, 162.
Foster, *D. L.*, relation between the pancreas and the carbohydrate metabolism of muscle. II. Antiglyoxalase and glyoxalase, i, 1495.
Foster, *J. S.*, Stark effect patterns in helium, ii, 831.
new combination series in the helium spectrum, ii, 1099.
Fouard, *E.*, collodion ultra-filtration membrane for physico-chemical analysis of solutions, ii, 324.
Found, *C. G.* See *I.* **Langmuir.**
Fourneau, *E.* See **Les Établissements Poulenc Frères**, and *A.* **Girard.**
Fournier, *G.*, absorption of β-rays by matter, ii, 176, 622.
half-value period of radium-*E*, ii, 1110.
Fournier, *L.*, and *A.* **Schwartz**, curative action of basic bismuth 3-acetamido-4-hydroxyphenylarsinate in syphilis, i, 1006.
Fowler, *A.*, structure of spectrum of ionised nitrogen, ii, 250.
spectrum of silicon at successive stages of ionisation, ii, 452.
Fowler, *G. J.*, and (*Miss*) *R. K.* **Christie**, symbiosis of seeds and bacteria, i, 344.
Fowler, *G. J.*, and *T.* **Dinanath**, biogenesis of Mahua oil, i, 346.
Fowler, *G. J.*, and *M. A.* **Malandkar**, examination of some gum enzymes, i, 1437.
Fowler, *G. J.*, and *V.* **Subramanyan**, acetone-producing organisms, i, 1216.
Fowler, *R. H.*, statistical theory of dissociation and ionisation by collision, with applications to the capture and loss of electrons by α-particles, ii, 7.
application of the correspondence principle to the theory of line-intensities in band spectra, ii, 623.
stopping power of hydrogen atoms for α-particles, ii, 834.
summation rules for the intensities of spectral lines, ii, 1104.
Fox, *E. L.* See *F. G.* **Benedict.**
Fox, *F. W.*, and *J. A.* **Gardner**, origin and destiny of cholesterol in the animal organism. XIV. Cholesterol metabolism in normal breast-fed infants, i, 859.
Fox, *F. W.* See also *J. A.* **Gardner.**
Fränkel, *S.*, and *C.* **Buhlea**, *apo*quinine, i, 573.
Fränkel, *S.*, and *N.* **Diamant**, aminoquinotoxine, i, 574.
Fränkel, *S.*, and *O.* **Karpfen**, lipoids. XX. Hypocerebric acid (Hypohirnsäure), a new triaminomonophosphatomonosulphatide from human brain, i, 720.
Fränkel, *S.*, *C.* **Tritt**, *M.* **Mehrer**, and *O.* **Herschmann**, aminoquinine, i, 573.
Fraenkel, *W.*, and *W.* **Goez**, kinetic studies on solid metals. Decomposition of the compound Al_2Zn_3, ii, 314.
space velocity of transformation of the modifications of sulphur, ii, 557.

Francesconi, *L.*, *M.* **Manfredi**, and *R.* **Astengo**, genesis of ethereal oils in plants, i, 759.

Francis, *A. G.*, and *A. T.* **Parsons**, determination of oxides of nitrogen (except nitrous oxide) in small concentration in the products of combustion of coal gas and in air, ii, 713.

Francis, *A. W.*, directive influence of substituents in the benzene ring. III. Active agent in aqueous bromination, i, 1261.

directive influence of substituents in the benzene ring. IV. Partial bromination of derivatives of aniline, i, 1399.

Francis, *A. W.*, and *A. J.* **Hill**, directive influence of substituents in the benzene ring. I. Chemical determination of the meta-isomeride in some disubstituted derivatives of benzene, ii, 163.

Francis, *A. W.*, *A. J.* **Hill**, and *J.* **Johnston**, directive influence of substituents in the benzene ring. II. Relative rates of bromination of certain *o*-, *m*-, and *p*-isomerides, i, 1141.

Francis, *W.*, and *R. V.* **Wheeler**, oxidation of banded bituminous coal at low temperatures; composition of coal, i, 373.

resolution of coal by oxidation, i, 644.

properties and constitution of coal ulmins; composition of coal, i, 1389.

Franck, *J.*, atomic and molecular collisions and their chemical significance, ii, 836.

elementary processes of photochemical reactions, ii, 1077.

Franck, *J.* See also *P. M. S.* **Blackett**, and *M.* **Born**.

Francke, (*Fr.*) *C.*, variation of dielectric constant with pressure for organic liquids at pressures up to 800 atmospheres, ii, 741.

François, *M.*, and *C.* **Lormand**, determination of tartaric acid by precipitation as calcium tartrate, ii, 75.

François, *M.*, and *L.* **Seguin**, amorphous quinine iodobismuthate, i. 1084.

François, (*Mlle.*) *T.* See *E.* **André**.

François-Dainville. See *F.* **Bordas**.

Frank, *L.*, property–composition curves of binary liquid mixtures, ii, 188, 648.

Frank, *N.*, and *F.* **Doleschall**, determination of diastase in fæces, i, 461.

Frank, *N.*, and *J.* **Förster**, glycogen content of liver. I. Behaviour of the blood-sugar and liver glycogen after administration of morphine, i, 1503.

Frank, *O.*, theory and construction of lever manometers, ii, 995.

Frank, *W.* See *H.* **Wieland**.

Franklin, *R. G.*, *R. E. W.* **Maddison**, and *L.* **Reeve**, experimental technique of photochemistry. II. Determination of energy distribution and total energy in radiation from quartz mercury lamps, ii, 809.

Franssen, *A.*, action of organo-magnesium compounds on naphthaquinones. I. Action of magnesium phenyl bromide on *α*-naphthaquinone, i, 1146.

Franzen, *G.*, nature of the substances which cause the production of "protective enzymes" in the organism, i, 1007.

Franzen, *H.*, and *F.* **Schmitt**, formation of citric acid from ketipinic acid [diketoadipic acid], i, 231.

Fraps, *G. S.*, effect of cropping on the active potash of the soil. i, 1523.

Frazer, *J. C. W.*, and *C. E.* **Grieder**, heats of oxidation of carbon monoxide and of hydrogen by manganese dioxide at 0°, ii, 1064.

Frazer, *J. C. W.* See also *A.* **Grollman**.

Frazer, *J. E.*, and *H. B.* **Hartley**, conductivity of uni-univalent salts in methyl alcohol, ii, 1163.

Fred, *E. B.*, and *W. H.* **Peterson**, nitrogen in algæ, i, 1122.

Fred, *E. B.*, *W. H.* **Peterson**, and *W. R.* **Carroll**, occurrence of a red-pigment-producing organism in maize mash of the acetone–butyl alcohol fermentation, i, 1013.

Fred, *E. B.*, *W. H.* **Peterson**, and *H. R.* **Stiles**, biochemistry of the granulated lactic acid bacteria from cereals, i, 1014.

Fred, *E. B.* See also *W. H.* **Peterson**, and *H. R.* **Stiles**.

Frederick, *R. C.*, preparation of Nessler's solution, ii, 435.

Frederick, *R. C.*, and *E. R.* **Webster**, spectroscope lighting unit, ii, 588.

Fredet, *P.*, and *R.* **Fabre**, localisation in the organism of alkyl derivatives of barbituric acid, i, 467.

Fredet, *P.* See also *R.* **Fabre**.

Freedman, *L.* See *H. E.* **Dubin**.

Freeman, *B.* See *J. M.* **Nelson**.

Freeth, *F. A.*, deduction of the type of a two-component system by means of the addition of a third component, ii, 669.

Frejka, *J.*, and *F.* **Balaš**, abietic acid, i, 669, 1422.

Frejka, *J.*, and *J.* **Vitha**, bromonovocaine, i, 663, 1416.

Frenc, *M.*, theory of extraction, ii, 506.
French, *H. E.* See *F. N.* **Peters**, *jun.*
Frenkel, *J.*, theory of adsorption and allied phenomena, ii, 194.
motion of a free electron in the field of plane electro-magnetic waves, ii, 477.
theory of metals, ii, 479.
Frenzel, *C.*, calculation of the work of chemical changes involving variable concentrations, ii, 119.
Frêrejacque, *M.*, structure of phenylhydrazones of dextrose, i, 635.
Frese, *E.* See *K. von* **Auwers**.
Fresno, *C. del*, electronic theory of valency and the electrolytic oxidation of formaldehyde, ii, 267.
potentiometric standardisation of potassium permanganate solution with sodium oxalate, ii, 602, 904.
potentiometric indication in the action of halogens on ferrocyanides, ii, 1192.
Freudenberg, *E.* See *O.* **Budde**.
Freudenberg, *K.*, and *F.* **Blümmel**, tannins and similar substances. XVII. Hamameli tannin. III., i, 51.
Freudenberg, *K.*, and *A.* **Doser**, acetone sugars. V. Synthesis of aminohexoses from galactose, i, 366.
Freudenberg, *K.*, and *H.* **Fikentscher**, the 3:4-dimethoxyphenylpyrazoline obtained from catechin, i, 69.
Freudenberg, *K.*, *H.* **Fikentscher**, and *M.* **Harder**, tannins and similar substances. XVIII. Catechin, i, 419.
Freudenberg, *K.*, *H.* **Fikentscher**, *M.* **Harder**, and *Otto* **Schmidt**, tannins and similar substances. XX. Conversion of cyanidin into catechin, i, 1165.
Freudenberg, *K.*, *H.* **Fikentscher**, and *W.* **Wehner**, tannins and similar substances. XIX. Constitution of catechin, i, 692.
Freudenberg, *K.*, *H. von* **Hochstetter**, and *H.* **Engels**, derivatives of maltose and dextrose, i, 635.
Freudenberg, *K.*, and *O.* **Huber**, steric series. V. Transformation of *d*-lactic acid into *l*-alanine, i, 229.
Freudenberg, *K.*, and *L.* **Markert**, steric series. VI. Configuration of mandelic acid, i, 1275.
Freudenberg, *K.*, and *W.* **Stoll**, isomeric *C*-substituted pyrazolines, i, 70.
Freudenberg, *K.*, and *E.* **Weber**, microdeterminations of acetyl groups, ii, 446.
Freudenberg, *K.*, and *A.* **Wolf**, acetone sugars. VI. Constitution of diacetonemannose [mannose di*iso*propylidene ether], i, 367.
Freudenberg, *K.* See also *A.* **Wohl**.
Freund, *E.*, and *A.* **Sittenberger-Kraft**, hydroxyproteic acid fraction of urine, i, 723.
Freund, *E.* See also *R.* **Weiss**.
Freundler, *P.*, and (*Mlle.*) *Y.* **Laurent**, photochemical properties of stannous iodide, ii, 22.
properties of stannous iodide, ii, 1085.
Freundlich, *H.*, sols with non-spherical particles, ii, 1153.
Freundlich, *H.*, and *S. K.* **Basu**, influence of agitation on the coagulation of hydrophobic sols, ii, 522.
Freundlich, *H.*, and *G.* **Ettisch**, electrokinetic and thermodynamic potentials, ii, 873.
Freundlich, *H.*, and *A. H.* **Fischer**, kinetics of the oxidation of thiocarbamide by charcoal, ii, 307.
Freundlich, *H.*, and *H. J.* **Kores**, viscosity and elasticity of soap solutions, ii, 663.
Freundlich, *H.*, and *L. F.* **Loeb**, electrodialysis, i, 96.
Freundlich, *H.*, and *W.* **Malchow**, iron carbonyls, ii, 231.
Freundlich, *H.*, and *F.* **Moor**, action of silver sol on arsenious sulphide sol, ii, 198.
Freundlich, *H.*, and *F.* **Oppenheimer**, rate of crystallisation of undercooled aqueous sols, ii, 203.
Freundlich, *H.*, and *A.* **Rosenthal**, kinetics of the sol–gel transformation of concentrated ferric oxide sols, ii, 967.
Freundlich, *H.*, and *E.* **Schalek**, viscosity and elasticity of colloidal solutions, ii, 112.
Freundlich, *H.*, *F.* **Stapelfeldt**, and *H.* **Zocher**, vanadium pentoxide sol. I. Streaming anisotropy, ii, 199.
vanadium pentoxide sol. II. The vortex cross, ii, 200.
Freundlich, *H.*, and *H. P.* **Zeh**, influence of valency on coagulation and cataphoresis, ii, 115.
Frey, *A.*, birefringency in colloids, ii, 200.
Frey, *F. E.* See *W. P.* **Yant**.
Frey, *L.* See *S.* **Kostytschev**.
Friauf, *J. B.* See *R. G.* **Dickinson**.
Fricke, *H.*, Compton's theory of *X*-ray scattering, ii, 941.
Fricke, *H.*, and *O.* **Glasser**, secondary electrons produced by hard *X*-rays in light elements, ii, 16.
Fricke, *H.*, and *S.* **Morse**, electrical conductivity of disperse systems. I. Cream, i, 608.

Fricke, *K.*, chemical constituents of the leaves of certain deciduous trees, i, 764.
Fricke, *R.*, hydration of molecules and ions, ii, 36.
viscosity of rubidium hydroxide solutions, ii, 389.
two crystal forms of zinc hydroxide, ii, 484.
activity of the hydroxyl ion in concentrated lyes on the basis of electrode and liquid potential measurements, ii, 539.
influence of finely porous materials at the liquid boundaries on liquid potential, ii, 544.
ageing of metallic hydroxides, ii, 578.
separation of gallium from aluminium and iron, ii, 717.
method for investigating diffusion in gels, ii, 965.
Fricke, *R.*, and *W.* **Blencke**, gallium, ii, 417.
Fricke, *R.*, and *L.* **Hauestadt**, complex compounds of beryllium. II., ii, 886.
Fricke, *R.*, and *C.* **Rohmann**, differences of potential at the boundaries of solutions, ii, 41.
Fricke, *R.*, and *F.* **Ruschhaupt**, complex compounds of beryllium. I., ii, 886.
molecular compounds of halogen–metal acids and acid amines, ii, 894.
Fricke, *R.*, and *G.* **Spilker**, preparation of *o*-ethylthiophenol by hydrogenation of thionaphthen, i, 249.
[non-catalytic] reduction of thionaphthen, i, 1311.
Fricke, *R.*, and *O.* **Windhausen**, ageing of metal hydroxides, and the system, chromium hydroxide–chromite–sodium hydroxide, ii, 35.
Fricke, *R.* See also *L.* **Havestadt**.
Fried, *E.*, and *W.* **Pauli**, general colloid chemistry. XIII. Analysis and constitution of silver sols. III., ii, 390.
Fried, *F.* See *A.* **Eucken**.
Friedel, *E.*, smectic compounds and *X*-rays, ii, 186.
Friedel, *G.*, ethyl anisylidene-*p*-aminocinnamate, i, 664.
symmetry between growth and diminution in size of crystals, ii, 271.
fatty acids, ii, 272.
Friedenberger, *G.* See *M.* **Busch**.
Frieden, *J.* See *E.* **Fromm**.
Friedländer, *P.* See *M.* **Marqueyrol**.
Friederich, *E.*, properties of simple compounds and types of the solid state, ii, 374.
Friederich, *E.*, and *L.* **Sittig**, preparation and properties of nitrides, ii, 419.
preparation and properties of carbides, ii, 705.
m. p. of inorganic compounds and of elements, ii, 848.
high-melting lower oxides, ii, 889.
Friederich, *P.* See *K.* **Schaum**.
Friedländer, *P.*, indigoid dyes of the naphthalene series, i, 956.
Friedli, *H.*, ultra-violet absorption spectra of hæmoglobin derivatives; chemical constitution of blood pigments, ii, 179.
Friedmann, *L.* See *B. M.* **Margosches**.
Friedrich, *F.* See *A.* **Lottermoser**.
Frieling, *L.* See *C.* **Weygand**.
Friend, *J. N.*, determination of dissolved oxygen, ii, 326.
periodic sphere and position of the rare-earth metals, ii, 363.
Friend, *J. N.*, and *J. S.* **Tidmus**, influence of emulsoids on the rate of dissolution of zinc in solutions of lead, nickel, and copper salts, ii, 306.
Fries, *F. A.* See *B.* **Helferich**.
Fries, *K.* [with *K.* **Bartens**, *E.* **Pusch**, and *K.* **Saftien**], oxindigo [3:3′-diketo-$\Delta^{2:2'}$-dicoumaran], i, 567.
Fries, *K.*, and *K.* **Billig**, derivatives of 2:3-diamino-1:4-naphthaquinone, i, 938.
Fries, *K.*, and *M.* **Nöhren**, *bz*-hydroxycoumarone compounds, i, 954.
Friese, *H.* See *H.* **Scheibler**.
Frischer, *M.* See *B. M.* **Margosches**.
Frith, *A. B.* See *M.* **Rabinovitch**.
Fritz, *G.*, resorption of bismuth in relation to bismuth intoxication, i, 334.
Fritz, *G.*, and *B.* **Paul**, a simple method for taking samples of blood in the Hagedorn–Jensen blood-sugar determination, i, 1486.
Fritzmann, *E.* See *L.* **Tschugaev**.
Frivold, *A.*, anomalous behaviour of strong electrolytes, ii, 396.
Fröhlich, *A.*, and *A.* **Solé**, influence of acids and alkalis on the action of some convulsive poisons, i, 334.
Frölich, *P. K.*, carbon error in the quantitative deposition of nickel and iron from complex oxalate electrolytes, ii, 604.
Fröschl, *I.*, constitution of phosphoric acid, ii, 19.
Frohnmayer, *W.* See *R.* **Glocker**.
Fromageot, *C.*, adsorption and cataphoresis, ii, 128.

Fromageot, *C.*, and *R.* **Wurmser**, comparative adsorption of some organic acids and their sodium salts, ii, 384.
Fromageot, *C.* See also *V.* **Henri**.
Fromm, *E.* [with *H.* **Barrenscheen**, *J.* **Frieder**, *L.* **Pirk**, and *R.* **Kapeller**], derivatives of cyanamide, i, 594.
Fromm, *E.*, and *L.* **Engler**, trithioacetaldehydes and the mechanism of their transformations, i, 1231.
Fromm, *E.*, and *H.* **Jörg**, derivatives of monothioethylene glycol, i, 352.
Fromm, *E.*, and *P.* **Szendrö**, derivatives of di-*o*-tolylhydrazodithiodicarbonamide, i, 985.
Fromm, *E.*, and *A.* **Truka**, action of benzoyl chloride on 4- and 1-phenylthiosemicarbazide, i, 703.
Frossard, *R.* See *R.* **Fabre**.
Frumkin, *A.*, phase boundary forces at gas–liquid interfaces. II. Adsorption and orientation of molecules of aliphatic compounds, ii, 109.
potential differences between liquids and air, ii, 544.
theory of adsorption and partition, ii, 856.
simple method of testing Gibbs' theorem, ii, 856.
capillary curves of higher fatty acids and the equation of state of the surface film, ii, 856.
phase boundary forces at gas–liquid interfaces. III. Electrical properties of unimolecular films of insoluble substances, ii, 873.
Fryling, *C. F.* See *F. O.* **Rice**.
Fuchs, *E.* See *B* **Neumann**.
Fuchs, *R.* See *G.* **Heller**.
Fuchs, *W.*, and *E.* **Honsig**, simple laboratory apparatus for electrodialysis, ii, 897.
Füchtbauer, *C.*, and *E.* **Holm**, influence of temperature on the ultra-violet absorption bands of oxygen; short-wave iodine spectrum, ii, 626.
Füchtbauer, *C.*, *F.* **Waibel**, and *E.* **Holm**, absorption line of the iodine atom, ii, 338.
Fürth, *O.*, may insulin affect the assimilatory or dissimilatory functions of oxygenated yeast? i, 107.
Fürth, *O.*, and *A.* **Fischer**, determination of the tyrosine content of proteins. III., ii, 448.
Fürth, *R.*, dielectric constants of good conductors, ii, 631.
physical chemistry of colouring matters. I. Measurement of the electric charge of solutions of colouring matters, ii, 1057.
Fürth, *R.*, and *R.* **Pechhold**, physical properties of serum on addition of "water-binding" substances, ii, 1056.
Fürth, *W. E.*, oxidation of uric acid with iodine, i, 1462.
Fues, *E.*, spectroscopic shift law. I., ii, 340.
Fujimaki, *Y.*, action of potassium cyanide and copper on the isolated frog's heart, i, 333.
Fujimoto, *G.* See *A. L.* **Dean**.
Fujio, *C.* See *S.* **Komatsu**.
Fujioka, *Y.* See *S.* **Nakamura**.
Fujita, *A.*, electrical properties and ionic permeability of membranes. III. Potential differences at parchment membranes, ii, 1151.
Fujita, *A.* See also *L.* **Michaelis**.
Fujumura, *Y.* See *B.* **Kubota**.
Fukuda, *M.*, spectrum of mercury under heavy current excitation, ii, 613.
change of wave-lengths for certain lines of zinc, cadmium, and mercury in a condensed discharge, ii, 1101.
Fukuda, *M.* See also *T.* **Takamine**.
Fuller, *A. T.*, and *J.* **Kenyon**, resolution of α-terpineol, i, 48.
Fulmer, *E. I.*, effect of ammonium salts on the swelling of colloids and the growth of yeast at various temperatures, i, 1508.
Fulmer, *E. I.* See also *L. M.* **Christensen**.
Fulton, *H. R.* See *W. W.* **Coblentz**.
Fulton, *J. D.* See *T. S.* **Patterson**.
Funck, *M.* See *K.* **Schaum**.
Funk, *C.*, and *S.* **Kon**, simplified method of micro-combustion; the micro-Dennstedt method, ii, 998.
Funk, *C.* See also *H. E.* **Dubin**, and *S.* **Kon**.
Funk, *H.*, formation of aluminium borides, ii, 705.
Funk, *H.*, and *H.* **Winter**, determination of boric acid in presence of aluminium, iron, or chromium salts, ii, 714.
Funke, *A.* See *H.* **Gault**.
Funke, *K.* See *E.* **Philippi**, and *A.* **Zinke**.
Funnell, *W. S.* See *J. B.* **Ferguson**.
Furman, *N. H.*, diphenylamine as indicator in the reduction of vanadic acid, ii, 442.
Furusawa, *K.*, muscular exercise, lactic acid, and the supply and utilisation of oxygen. IX. Muscular activity and carbohydrate metabolism in the normal individual, i, 849.
muscular exercise, lactic acid, and the supply and utilisation of oxygen. X. Oxygen intake during exercise while breathing mixtures rich in oxygen, i, 993.

Furusawa, *K.*, *A. V.* **Hill**, *C. N. H.* **Long**, and *H.* **Lupton**, muscular exercise, lactic acid, and the supply and utilisation of oxygen. VII.—VIII., i, 92.
Fuse, *N.*, cetacea. IX. Serological investigation of the biological relationship of various types of whale, i, 1348.
cetacea. X. Synovial fluid of whales, i, 1348.
cetacea. XVII. Peritoneal fluid, i, 1349.
comparative biochemistry of urine, i, 1350.
Fuson, *R. C.*, naphthalene and the centroid structure, i, 253.
bromo-α-naphthols and orientation of certain classes of disubstituted naphthalene derivatives, i, 540.
quinoline and the centroid structure, i, 1098.
Fussgänger, *R.* See *J. von* **Braun**.

G.

Gaarder, *T.*, and *O.* **Hagem**, nitrification in acid solutions, i, 480.
Gabel, *G. O.*, Δ$^{\alpha}$-hypogæic anhydride, i, 504.
interaction of ethylene oxide and aniline, i, 535.
Gadamer, *J.*, *M.* **Oberlin**, and *A.* **Schoeler**, synthesis of aporphine, i, 576.
Gadamer, *J.*, *M.* **Thiessen**, and *K.* **Winterfeld**, chelidonium alkaloids. III., i, 287.
Gadamer, *J.*, *K.* **Winterfeld**, and *A.* **Stichel**, chelidonium alkaloids. III., i, 284.
Gädke, *W.* See *O.* **Diels**.
Gainsborough, *H.* See *J. A.* **Gardner**.
Galanos, *S.* See *R.* **Dietzel**.
Galbrun, *G.* See *Max* **Polonovski**.
Gale, *E. C.*, "temper" colours [of steel], ii, 109.
Galecki, *A.*, physico-chemical studies on gold hydrosols, ii, 516.
Galizzi, *A.* See *R.* **Ciusa**.
Gall, *H.*, and *W.* **Manchot**, catalytic hydrogenation of inorganic substances, ii, 412.
Gall, *H.* See also *W.* **Manchot**.
Gallerani, *G.*, pyrrole and melanins; spectrophotometric studies, ii, 266.
Galley, *R.* See *G.* **Wiegner**.
Gallissi, *M.* See *G.* **Charrier**.
Galt, *R. L.* See *S. A.* **Koser**.
Galwiale, *M. J.*, photosynthesis of carbohydrates, i, 870.
Gambarjan, *S.*, benzoyl peroxide and secondary amines, i, 1260.
Gamble, *J. L.*, and *S. G.* **Ross**, dehydration following pyloric obstruction, i, 1352.
Gammal, *C. A.* See *M. C.* **Taylor**.
Ganassini, *D.*, and *U.* **Santi**, does a bismuth cacodyl exist? i, 893.
Gandelman, *A.* See *P.* **Petrenko-Kritschenko**.
Ganesan, *A. S.*, polarisation of light scattered by organic vapours, ii, 643.
Ganguly, *K. L.*, halogenation of 2:4:6-trinitrotoluene, i, 647.
Ganguly, *K. L.* See also *G.* **Schultz**.
Gans, *R.*, reversible permeability, ii, 173.
Gante, *J.* See *A.* **Schaarschmidt**.
Garard, *I. D.*, and *G. E.* **Duckers**, preparation and properties of some protected silver sols, ii, 391.
Garbutt, *C. D.* See *G. W.* **Gray**.
Garcia, *F.* See *A. H.* **Wells**.
Gardner, *J. A.*, and *F. W.* **Fox**, determination of cholesterol and its esters in tissues. II., i, 182.
Gardner, *J. A.*, and *H.* **Gainsborough**, cholesterol secretion in the urine. I., i, 1204.
Gardner, *J. A.* See also *F. W.* **Fox**.
Garelli, *F.*, cryoscopy of solutions of gases in various solvents, ii, 1151.
Garey, *R. M.* See *A.* **Henwood**.
Garland, *C. E.*, and *E. E.* **Reid**, derivatives of *cyclo*hexanone, i, 1280.
Garland, *C. E.* See also *J. W.* **Farren**.
Garlock, *B.* See *V. G.* **Heller**.
Garner, *W. E.*, biochemistry of muscle contraction, i, 607.
heterogeneous catalysis, ii, 140.
critical increment of chemical reactions, ii, 552, 1167.
Garner, *W. E.*, and *E. A.* **Ryder**, alternation in molecular volume of the normal monobasic fatty acids, ii, 355.
Garner, *W. E.*, and *S. W.* **Saunders**, explosion of acetylene and nitrogen. IV. Spectra of explosions of gases containing hydrogen, carbon, nitrogen, and oxygen, ii, 627.
Garner, *W. E.* See also (*Miss*) *M. J.* **Field**.
Garrard, *J. D.*, preparation of dust-free liquids by distillation, ii, 704.
Garratt, *D. C.* See *C. T.* **Bennett**.
Garreau, (*Mlle.*) *Y.* See *W.* **Mestrezat**.
Garrison, *A.*, behaviour of silver iodide in the photo-voltaic cell. II. New type of silver iodide photo-voltaic cell, ii, 212.
photomagnetic properties of the silver halides, ii, 371.

Garry, *R. C.*, determination of uric acid by the Hopkins–Folin method, i, 605.
Gaschler, *A.*, transmutation of uranium into uranium-*X*, ii, 925.
Gassner, *G.*, "forcing" (plants) by means of hydrogen cyanide, i, 1029.
Gastaldi, *C.* [with *E.* **Repossi**], α-ketoformhydroxamic acids and their derivatives. X., i, 987.
Gates, *S. F.* See *B.* **Lambert**.
Gatewood, *E. S.*, substituted biurets, i, 805.
action of alkali on substituted uric acids. II. 9-Phenyl-1:3:7-trimethyluric acid, i, 1188.
action of alkali on substituted uric acids. III. 1:3:7:9-Tetramethyluric acid and 1:3:9-trimethyluric acid, i, 1189.
Gatti, *U.* See *C.* **Porlezza**.
Gaubert, *P.*, modification of crystal faces owing to their syncrystallisation with foreign matter dissolved in the mother-liquor, ii, 271.
Gauger, *A. W.*, resistance of platinum films in presence of hydrogen, ii, 1040.
thin films of platinum and nickel and catalytic activity, ii, 1072.
Gaul, *R.* See *H.* **Finger**.
Gault, *H.*, and *V.* **Altchidjian**, pyrogenic decomposition of hexadecene, i, 110.
Gault, *H.*, and *A.* **Funke**, alkylidenebenzoylpyruvic esters, i, 37.
Gault, *H.*, and *F. A.* **Hessel**, pyrogenic dissociation of hexadecane, i, 109.
Gault, *H.*, and *T.* **Salomon**, α-alkyllævulic acids, i, 115.
Gaumer, *M.* See *K.* **Elbs**.
Gauzit, *J.* See *J.* **Cabannes**.
Gavedovskaja, *M.* See *N. D.* **Zelinski**.
Gavrilov, *N. I.*, 3-cyanoindole, i, 578.
Gavrilov, *N. N.*, preparation of colloidal ferric hydroxide solutions by oxidation of ferrous hydrogen carbonate, ii, 860.
Gavrilov, *N. N.* See also *G.* **Stadnikov**.
Gay, *L.*, thermodynamics of surface actions, ii, 539.
Gay, *L.*, and *N.* **Perrakis**, properties of physical systems in the neighbourhood of the critical state, ii, 669.
Gaylor, *M. L. V.* See *D.* **Hanson**.
Gazzoni, *F.*, determination of thorium-*X*, ii, 441.
Geake, *A.* See *D. A.* **Clibbens**.
Gebhardt, *H.* See *W.* **Marckwald**.
Gedroiz, *K. K.*, chemical analysis of soil, i, 489.
Geel, *W. C. van*, intensities of Zeeman components of multiplets, ii, 1016.
Geel, *W. C. van*. See also *L. S.* **Ornstein**.
Gehrcke, *E.*, recent results in the investigation of fine structure, ii, 1098.
Gehrcke, *E.*, and *E.* **Lau**, spectrum of hydrogen, ii, 609.
Gehring, *A.*, and *O.* **Wehrmann**, action of calcium carbonate on the soil, i, 1031.
Gehrke, *M.* See *F.* **Knoop**.
Geiger, *E.* See *G.* **Mansfeld**, and *H.* **Staudinger**.
Geiger, *H.* See *W.* **Bothe**.
Geiling, *E. M. K.* See *J. J.* **Abel**.
Geilinger, *H.* See *T. von* **Fellenberg**.
Geilmann, *W.*, microchemical determination of sulphur. I. Determination of sulphur in easily soluble sulphides, ii, 1000.
Geiss, *W.*, flow of single crystals, ii, 96.
density determinations of rock-salt crystals, ii, 278.
Geiss, *W.*, and *J. A. M. van* **Liempt**, significance of cold working in the light of electrical measurements. II., ii, 372.
electrical measurements on metals of great purity (tungsten, molybdenum, and nickel), ii, 638.
density-changes of tungsten with working, ii, 762.
Geissler, *F.* See *M.* **Trautz**.
Geissler, *H.* See *E.* **Koenigs**.
Gelbach, *R. W.* See *J. N.* **Pearce**.
Gelissen, *H.*, and *P. H.* **Hermans**, syntheses by means of organic peroxides. I. Action of benzoyl peroxide and some of its derivatives on boiling benzene, i, 379.
syntheses by means of organic peroxides. II. Action of benzoyl peroxide on toluene, i, 545.
syntheses by means of organic peroxides. III. Action of benzoyl peroxide on benzene in the presence of aluminium and iron chlorides, i, 545.
syntheses by means of organic peroxides. IV. Action of benzoyl peroxide on diphenyl, i, 663.
syntheses by means of organic peroxides. V. Action of benzoyl peroxide on alcohols, i, 663.
syntheses by means of organic peroxides. VI. Action of benzoyl peroxide on acetic acid, i, 664.
analogies between certain reactions of organic peroxides and diazo compounds, i, 813.
Gelissen, *H.* See also *J.* **Boëseken**.
Gellhorn, *E.* See *E.* **Abderhalden**.

Geloso, *M.*, formation of colloidal manganese dioxide in the reduction of permanganate by arsenious acid; influence of its adsorptive power on the extent of the reaction, ii, 661.
Genders, *R.*, and *G. L.* **Bailey**, alpha phase boundary in the copper–zinc system, ii, 297.
Genevet, *R.* See *E.* **Canals**.
Genin, *A.* See *H.* **Pringsheim**.
Gentner, *R.* See *D.* **Holde**.
Geoffroy, *R.* See *C.* **Courtot**.
George, *E.*, active principles of the African squill, *Urginea burkei* (slangkop), i, 823.
George, *H.* See *E.* **Bayle**.
Georgescu, *V.* See *D.* **Radulescu**.
Georgian, *N.* See (*Mrs.*) *C.* **Kollo**.
Gerasimov, *A. F.*, determination of the mobility of colloid particles by the method of cataphoresis, ii, 204.
Gerding, *H.*, and *A.* **Karssen**, theories of passivity, ii, 406.
Gerding, *H.* See also *A.* **Smits**.
Gerke, *R. H.*, electrode potentials, ii, 403.
Gerlach, *H.* See *F.* **Krauss**.
Gerlach, *W.*, magnetic atom moments and directional quantisation, ii, 258.
quantitative spectral analysis, ii, 711.
Gerlach, *W.*, and *W.* **Schütz**, life periods of excited atoms, ii, 171.
Germann, *A. F. O.*, action of chlorine on mercury, ii, 59.
densities of solutions of aluminium chloride in phosgene [carbonyl chloride], ii, 288.
carbon monoxide, a product of electrolysis, ii, 568.
conductivity of solutions of aluminium chloride in carbonyl chloride at 25°, 0°, and −45°, ii, 1066.
general theory of solvent systems, ii, 1143.
Germann, *A. F. O.*, and *G. H.* **McIntyre**, properties of phosgene [carbonyl chloride] solutions: vapour tension curves of aluminium chloride solution at 0° and 25°, ii, 196.
Germann, *A. F. O.*, and *C. R.* **Timpany**, preparation of "phosgeno salts," ii, 1085.
Germann, *A. F. O.* See also *H.* **Schlundt**.
Germann, *F. E. E.* See *R. N.* **Traxler**.
Germer, *L. H.*, distribution of initial velocities among thermionic electrons, ii, 730.
Germer, *L. H.* See also *C.* **Davisson**.
Gerngross, *O.*, preparation of *N*-aralkylated iminazolylalkylamines [aminoalkylglyoxalines], i, 440.
Gerstdorff, *C. E. F.* See *D. B.* **Jones**.
Gerwig, *W.* See *M.* **Trautz**.
Gessner, *H.* See *G.* **Wiegner**.
Getman, *F. H.*, molecular association of furfuraldehyde, ii, 511.
absorption of ultra-violet light by inorganic halides, ii, 837.
Getz, *D.* See *W. M.* **Thornton**, *jun.*
Gex, (*Mlle.*) *M.* See *F.* **Vlès**.
Gfeller, *H.* See *A.* **Tschirch**.
Ghigi, *E.* See *G.* **Plancher**.
Ghigliotto, *C.*, detection of small quantities of formaldehyde in cases of poisoning, ii, 445.
Ghose, *T. P.* See *J. N.* **Sen**.
Ghosh, *B. N.* See *J. N.* **Mukherjee**.
Ghosh, *J.* See *S.* **Mali**.
Ghosh, *J. C.*, and *K.* **Basu**, bromination of lactic acid and calcium lactate in the presence of light, i, 1234.
Ghosh, *J. C.*, and *J. N.* **Chakravarty**, dehydrogenation of methyl alcohol and formaldehyde with copper as catalyst; conditions of equilibrium in the system $CH_2O \rightleftharpoons CO + H_2$, ii, 1161.
Ghosh, *J. C.*, and *J.* **Mukherjee**, photochemical reaction between bromine and tartaric acid in aqueous solution. I., ii, 1179.
Ghosh, *J. C.* See also *K. M.* **Chakravarty**.
Ghosh, *R. N.*, specific heat of liquids, ii, 275.
electrical conductivity of heated gas, ii, 461.
duration of fluorescence of mercury vapour, ii, 1026.
Ghosh, *R. N.* See also *N. K.* **Sur**.
Ghosh, *S.*, and *N. R.* **Dhar**, adsorption. IX. Influence of various substances and importance of the adsorption of anions in the coagulation of arsenious and antimonious sulphide sols, ii, 386.
adsorption. X. Coagulation of diluted sols by electrolytes, acclimatisation, and behaviour towards mixed electrolytes, ii, 511.
coagulation of Prussian blue and ferric hydroxide sols, ii, 778.
Giacomini, *F. A.*, molecular heats of gases at low temperatures, ii, 757.
Gianfranceschi, *G.*, theory of the Zeeman effect, ii, 830.
Gibbs, *H. D.* See *W. M.* **Clark**, and *B.* **Cohen**.
Gibbs, *R. E.*, *X*-ray investigation of the lower members of the fatty acid series, ii, 269.
variation with temperature of the intensity of reflexion of *X*-rays from quartz and its bearing on the crystal structure, ii, 367.

Gibbs, *W. M.*, *H. W.* **Batchelor**, and *H. P.* **Magnuson**, effects of alkali salts on bacteriological activities in soil. I. Ammonification. II. Nitrification. III. Ammonification, nitrification, and crop yield, i, 1030.

Gibson, *C. S.*, and *J. L.* **Simonsen**, formation of *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid from *d*-camphorquinone, i, 919.

Gibson, *C. S.* See also *H. C.* **Bell**, *H.* **Burton**, and *W. M.* **Colles**.

Gibson, *D. T.*, *C. J.* **Miller**, and *S.* **Smiles**, syntheses of disulphoxides, i, 1137.

Gibson, *G. P.*, nitro derivatives of *o*-cresol, i, 388.

Gibson, *K. S.*, tests on the accuracy of measurement with the rotatory dispersion colorimetric photometer, ii, 934.

Gibson, *R. A.*, mechanism of Kolbe's electrosynthesis, ii, 312.

Gibson, *R. E.*, *R. W. G.* **Wyckoff**, and *H. E.* **Merwin**, valerite and μ-calcium carbonate, ii, 1183.

Gicklhorn, *J.*, and *R.* **Keller**, selective vital staining, i, 468.

Giddings, *G. W.* See *G. F.* **Rouse**.

Gidon, *M.* See *E.* **Canals**.

Giemsa, *G.*, and *K.* **Bonath**, cinchona alkaloids. VI. Action of sulphuric acid on hydrocinchonine, hydroquinine, hydroquinidine, and quinine; *apo*quinine, i, 291.

Gierisch, *W.*, determination of pentosans in wood, i, 1122.

Giesel, *W.* See *R.* **Stollé**.

Gieseler, *H.*, and *W.* **Grotrian**, completion of the series in the arc spectrum of lead, ii, 1103.

Gigon, *A.*, effect of continued administration of sugar on the formation of glycogen, i, 192.

synthesis and degradation of carbohydrates in the organism, i, 463.

variations in the hydrogen-ion concentration of the blood under different conditions. I. Effect of single administrations of nutrient substances. II. Effect of insulin and other organ extracts, i, 1219.

Gigon, *A.*, and *W.* **Brauch**, synthesis and degradation of carbohydrates in the organism. II., i, 611.

Gilard, *P.* See *A.* **Lacrenier**.

Gilbert, *C. S.* See *F. B.* **Kenrick**.

Gilbert, *E. C.*, electrometric titration of hydrazine and its salts, ii, 239.

Gilbert, *H. W.*, and *P. E.* **Shaw**, electrical charges arising at a liquid–gas interface, ii, 795.

Gilbert, *L. F.*, system, chromium trioxide–boric acid–water, ii, 869.

Gilbert, *M.*, and *J. C.* **Bock**, determination of sugar in small amounts of blood, i, 179.

Gill, *A. F.* See *W. F.* **Seyer**.

Gillespie, *L. J.*, equation for the Haber equilibrium, ii, 294, 532.

equilibrium pressures of individual gases in mixtures and the mass-action law for gases, ii, 532.

Gillot, *P.*, extraction of maltose from tubers of *Mercurialis perennis*, L., i, 487.

characteristics of oils of the *Euphorbiaceæ*, i, 760.

seeds of *Mercurialis*, i, 1224.

Gilman, *H.*, and *N. J.* **Beaber**, preparation of hydrocarbons by the reaction between alkyl sulphonates and organo-magnesium halides, i, 802.

alkylation of mercaptans by means of sulphonic esters, i, 811.

Gilman, *H.*, *N. J.* **Beaber**, and *C. H.* **Myers**, reaction between aryl sulphonates and organo-magnesium halides, i, 1057.

Gilman, *H.*, and *W. B.* **King**, reactions of substituted mercapto-magnesium halides, i, 810.

Gilman, *H.*, and *H. H.* **Parker**, optimum conditions for the preparation of *n*-valeric acid from magnesium butyl bromide and carbon dioxide, i, 228.

reaction between magnesium organohalides and cupric chloride, i, 237.

Gilman, *H.*, and *R. M.* **Pickens**, correlation of some aromatic types with physiological action; local anæsthetics containing the furan, thiophen, and pyrrole nuclei, i, 333.

mechanism of reduction of azobenzene by magnesium organo-halides, i, 1336.

Gilman, *H.*, and *F.* **Schulze**, quantitative colour test for the Grignard reagent, ii, 1011.

Gilman, *H.*, and *J. B.* **Shumaker**, reaction between disubstituted acetylenic hydrocarbons and the Grignard reagent, i, 493.

Gilman, *H.*, *L. E.* **Smith**, and *H. H.* **Parker**, constitution of disulphoxides, i, 656.

Gilman, *H.*, and *C. C.* **Vernon**, 2-chloromethylfuran from 2-furylcarbinol, i, 53.

Gilmour, *G. van B.*, invert-sugar as a reagent for boric acid determinations, ii, 68.

Gilta, *G.*, crystalline form of organic derivatives of arsenic. II., ii, 93.
Ginsburg, *J. M.*, respiration apparatus for plant and soil studies, i, 1120.
composition and appearance of soya-bean plants grown in culture solutions each lacking a different essential element, i, 1121.
Giordani, *F.*, behaviour of diaphragm electrolysers with circulation of the alkali chlorides. IV., ii, 550.
behaviour of diaphragm electrolysers with circulation of the alkali chlorides. V., ii, 551.
chemico-physical investigations on the catholyte of diaphragm electrolysers with circulation of the sodium chloride, ii, 551.
Giordani, *F.* See also *M.* **Bakunin.**
Giorgi, *G.*, reduction of picric acid in the liver, kidney, and spleen, i, 733.
Girard, *A.*, and *E.* **Fourneau**, separation and determination of bismuth, ii, 1207.
Girard, *A.* See also *C.* **Levaditi.**
Girard, *R.*, action of dilute acid solutions on ferrous metals, ii, 879.
action of sodium chloride on ferrous metals, ii, 1192.
Girardet, *F.* See *P.* **Lasseur.**
Giribaldo, *D.*, rational notation for the expression of the reaction of solutions, ii, 325.
Girndt, *O.*, choline as the hormone of peristalsis. VIII. Does intestinal choline originate from the suprarenal bodies? IX. Inability of isolated intestinal wall to produce choline, i, 1363.
Gisiger, *F.* See *H.* **Rupe.**
Gittleman, *I.* See *B.* **Kramer.**
Giua, *M.* [with *G.* **Guastalla**], polymerisation of cinnamylideneacetophenone derivatives, i, 1283.
Giua, *M.*, and *E.* **Monath**, chloro-acetato compounds of quadrivalent titanium, i, 531.
Giua, *M.*, and *R.* **Petronio**, constitution of benzene and substitution processes in the benzene nucleus, i, 1396.
Gjaldbaek, *J. K.*, solubility of magnesium hydroxide. I. Existence of different modifications of magnesium hydroxide, ii, 652.
solubility of magnesium hydroxide. II. Solubility products and dissociation constants of the magnesium hydroxides, ii, 653.
potential difference between 0·1*N* and 3·5*N* calomel electrodes, ii, 1066.
Gladstone, *R. J.* See *J. W.* **Pickering.**
Glaser, *A.*, new phenomenon in the diamagnetism of gases, ii, 82.
new property of diamagnetic gases at low pressures, ii, 642.
Glaser, *E.*, and *L.* **Wittner**, blood-sugar depressant action of plant extracts and oxydases; detection of enzymes in insulin, i, 209.
Glaser, *F.*, psychological effects on the calcium content of blood-serum; [psychophysical reactions], i, 860.
Glaser, *R. W.*, hydrogen-ion concentrations in the blood of insects, i, 853.
Glasser, *O.* See *H.* **Fricke.**
Glassett, *J. W.* See *S. O.* **Rawling.**
Glasstone, *S.*, electrolytic polarisation. I. Cathodic overvoltage of lead, ii, 43.
electrolytic polarisation. II. Cathodic overvoltage of mercury, ii, 133.
overvoltage and surface forces at the lead cathode, ii, 301.
influence of hydrogen-ion concentration on the colorimetric determination of pyrogallol and pyrocatechol derivatives, ii, 331.
effect of small alternating currents on some polarised electrodes, ii, 548.
modified electrometric method for the determination of hydrogen-ion concentration, ii, 822.
electrolytic polarisation. III. The diffusion layer, ii, 979.
Glattfield, *J. W. E.*, and *L. P.* **Sherman**, "C_4-saccharinic acids." III. Preparation of *dl*-α,β-dihydroxy*iso*-butyric acid and some of its derivatives, i, 881.
Gleason, *J. M.* See *F. G.* **Wick.**
Gleditsch, (*Mlle.*) *E.*, atomic weight of chlorine, ii, 174.
Gleditsch, (*Mlle.*) *E.*, and *E.* **Botolfsen**, *X*-ray spectra of praseodymium, neodymium, and samarium, ii, 612.
Gleditsch, (*Mlle.*) *E.*, (*Mme.*) **Dorenfeldt**, and *O. W.* **Berg**, determination of the atomic weight of a mixture of lead isotopes present in clevite from Aust-Agdar, Norway, ii, 732.
Gley, *E.*, and *J.* **Cheymol**, presence of iodine in the venous blood of the thyroid, i, 456.
Gley, *E.* See also *R.* **Arnold.**
Glocker, *G.*, critical potential of methane and its absorption in the ultra-violet, ii, 262.
Glocker, *R.*, deformation- and recrystallisation-structure of metals, ii, 272.
Glocker, *R.*, and *W.* **Frohnmayer**, Röntgen-spectroscopic determination of the proportion by weight of an element in mixtures and compounds, ii, 270.

Glockler, *G.*, double impacts by electrons in helium, ii, 617.
predicted ionisation-potentials of niton and hydrofluoric acid, ii, 1105.
Gluschke, *A.* See *G.* **Schroeter.**
Gnädinger, *F.* See *H.* **Lecher.**
Goard, *A. K.*, and *E. K.* **Rideal**, surface tension of aqueous phenol solutions, ii, 510.
surface tension of aqueous phenol solutions. II. Activity and surface tension, ii, 961.
Godchot, *M.*, octahydrophenazine, i, 436.
Godchot, *M.*, and *P.* **Bedos**, chlorination of 1-methyl*cyclo*hexan-4-one, i, 258.
the two 1:3-dimethyl*cyclo*hexan-4-ones and the corresponding dimethyl-*cyclo*hexanols, i, 537.
Godden, *W.* See *M. B.* **Richards.**
Godinho, *A. P.*, appearance of red colouring matter (in the urine) after administration of pure chlorophyll. II., i, 460.
Goebel, *F.* See *P.* **Pfeiffer.**
Goebel, *W. F.*, derivatives of citraconic acid. I. Synthesis of methyltartaric acid and decomposition of dihydroxymaleic acid, i, 1038.
Gönningen, *H.* See *H.* **Remy.**
Goens, *E.* See *E.* **Grüneisen.**
Göring, *E.* See *G.* **Heller.**
Goetz, *A.*, thermoelectric behaviour of pure iron at its transition points, ii, 187.
glow electronic emission at transition and melting points, ii, 459.
connexion between thermo-electric power and space lattice for pure iron, ii, 485.
Götz, *F.* See *F.* **Henrich.**
Götzky, *S.* See *G.* **Schroeter.**
Goez, *W.* See *W.* **Fraenkel.**
Goiffon, *E.*, determination of the total organic acids of urine; their relationship to nitrogen nutrition and to ketonuria, i, 459.
Gokhale, *A. G.*, mahua flowers as raw material for the acetone fermentation process, i, 1216.
Goldberg, *W.* See *A.* **Henwood.**
Goldberger, *A. von.* See *G.* **Bredig.**
Goldberger, *J.*, and *W. F.* **Tanner**, pellagra-preventive action of dried beans, caseinogen, dried milk, and brewer's yeast, i, 1517.
Goldblatt, *M. W.*, determination of acetoacetic acid and β-hydroxybutyric acid in urine, i, 1204.
Goldschmidt, *H.*, and *H.* **Aarflot**, conductivity of acids of medium strength in methyl alcohol, and their catalytic action, ii, 976.
Goldschmidt, *H.*, and *P.* **Dahll**, conductivity and catalytic action of the three strong halogen acids in methyl and ethyl alcohol, ii, 128.
Goldschmidt, *H.*, *S.* **Johnsen**, and *E.* **Overwien**, diazoamino conversion, ii, 138.
Goldschmidt, *S.*, and *F.* **Christmann**, constitution of nitroso compounds, i, 649.
Goldschmidt, *S.*, *R.* **Endres**, and *R.* **Dirsch**, reactions of ethyl hypochlorite with organic substances, i, 502.
Goldschmidt, *S.*, and *H.* **Schüssler**, action of chlorine monoxide on organic compounds, i, 497.
Goldschmidt, *S.*, and *C.* **Steigerwald**, degradation of proteins by hypobromite, i, 1109.
Goldschmidt, *S.*, *A.* **Vogt**, and *M. A.* **Bredig**, univalent oxygen. IV., i, 1434.
Goldsworthy, *L. J.*, resolution of *trans-cyclo*butane-1:2-dicarboxylic acid, i, 33.
Gollwitzer-Meier, *K.*, dependence of the excitability of the respiratory centre on a definite ionic equilibrium in the blood, i, 177.
chemical regulation of respiration in blood of alkaline reaction, i, 177.
connexion between the reaction and the total ionic equilibrium of the blood, i, 1482.
Gollwitzer-Meier, *K.*, and *C.* **Kroetz**, chemistry of the blood during sleep, i, 322.
Golse, *J.*, micro-determination of urea and ammonium salts, i, 609.
Gomberg, *M.*, and *L. C.* **Anderson**, 3:3′:3″-trimethylaurin (*o*-cresaurin) and 3:3′:3″-trimethyl-*N*:*N*′:*N*″-triphenylpararosaniline (triphenylros-*o*-toluidine), i, 1064.
Gomberg, *M.*, and *G. C.* **Forrester**, triphenylmethyl. XXXIV. 2:5-, 2:4-, and 3:4-Dimethoxytriphenylmethyls, i, 1266.
Gomberg, *M.*, and *W. J.* **McGill**, tautomerism of *o*-hydroxytriarylcarbinols which contain naphthyl groups, i, 1269.
Gomberg, *M.*, and *H. R.* **Snow**, condensation of carbon tetrachloride and phenol: aurin, i, 660.
Gombos, *H.*, lack of correspondence between spectroscopic and spectrophotometric absorption maxima, ii, 178.
possibility of determining spectrophotometrically substances oxidisable by permanganate, ii, 237.
Gonell, *H. W.* See *R. O.* **Herzog.**

González, *A.*, isomerism of the crotonic acids, i, 629.
González, *F.* See *O.* Hönigschmid.
Goode, *K. G.*, continuous reading hydrogen-ion meter, ii, 1196.
Goodson, *J. A.*, and *T. A.* Henry, echitamine, i, 1166.
Goodwin, *G. M.*, and *H. J.* Shelley, sugar content of the cerebro-spinal fluid and its relation to the blood-sugar, i, 853.
Goodwin, *R. C.*, and *J. R.* Bailey, 2-phenylsemicarbazide, i, 318.
reduction of phenylhydrazones, i, 843.
Gorbatschev, *A.*, derivation of adsorption isotherms, ii, 959.
Gordon, *A. R.*, polarisation and concentration changes at the cathode during electrolysis of copper salts, ii, 549.
Gordon, *H. B.*, monochromatic illuminator for gas flames, ii, 588.
Gordon, *J.* See *J. W.* McLeod, and *H. R.* Whitehead.
Gordon, *N. E.* See *R. E.* Marker.
Gordonov, *T.*, pharmacology of proteinogenous cholines, i, 1502.
Gore, *H. C.*, effect of hydrogen-ion concentration on the determination of diastatic power by the polarimetric method, i, 335.
Gore, *S. N.*, detection and determination of indican in urine by the cotton-wool plug test, i, 186.
Gorgas, *A.* See *D.* Holde.
Gori, *G.*, determination of camphor in plants and industrial and pharmaceutical products, ii, 1009.
Goris, *A.*, and *M.* Métin, presence of two alkaloids in *Aconitum anthora*, L., i, 761.
chemical composition of the hybrid of *Aconitum anthora*, L., and *A. napellus*, i, 762.
Gorodissky, *H.*, micro-methods for the quantitative determination of brain lipins, i, 1487.
Gorr, *G.* See *C.* Neuberg.
Gorter, *K.*, chemical composition of the latex of *Hevea*, i, 622.
Gortner, *R. A.*, mechanism of the tyrosine–tyrosinase reaction, i, 474.
Gortner, *R. A.*, and *W. F.* Hoffman, determination of chlorides and sulphates in expressed plant-tissue fluids, i, 485.
evidence of a new amino-acid in proteins, i, 602.
Gortner, *R. A.*, and *W. M.* Sandstrom, proline and tryptophan as factors influencing the accuracy of Van Slyke's method for the determination of nitrogen distribution in proteins, ii, 908.
Gortner, *R. A.* See also *W. F.* Hoffman.
Gosman, *B. A.*, dropping mercury cathode. XI. Influence of anions, ii, 678.
Goss, *F. R.*, *C. K.* Ingold, and *J. F.* Thorpe, glutaconic acids. XVIII. Three-carbon tautomerism in the *cyclo*-propane series. IV., i, 549.
Gossner, *B.*, chemical constitution of the gehlenite–melilite group, ii, 821.
Goswami, *M. N.*, direct hydrogenation and dehydrogenation of acenaphthene, i, 127.
Goth, *E.* See *W.* Hückel.
Gottfried, *C.* See *Ernst* Müller.
Gottlieb, *E.*, propepsin in blood and urine, i, 742.
Gottschalk, *A.*, acetaldehyde in intermediary cell metabolism, i, 191.
hormonal regulation of intermediate carbohydrate metabolism. I. Importance of adrenaline and insulin in the utilisation of dextrose by warm-blooded animals, i, 481.
hormonal regulation of intermediate carbohydrate metabolism. II. Insulin–adrenaline antagonism in the frog, i, 1513.
Gottschalk, *A.*, and *C.* Neuberg, esterification of phosphoric acid by yeast, i, 337.
Gottschalk, *A.* See also *C.* Neuberg.
Goudsmit, *S.*, ground term of the neon spectrum, ii, 450.
determination of the terms in the lanthanum spectrum, ii, 454.
allocation of terms to some multiplets in the iron spectrum, ii, 611.
complex structure of spectra, ii, 725.
Goudsmit, *S.*, and *R. de L.* Kronig, intensities of the Zeeman components, ii, 917.
Goudsmit, *S.*, *J. van der* Mark, and *P.* Zeeman, magnetic resolution of the scandium spectrum. I., ii, 912.
Graaff, *W. C. de*, and *A. J.* Le Fèvre, bacterial fermentation, particularly in the *coli–typhosus* group, i, 478.
Grabbe, *H.* See *K.* Ziegler.
Graber, *M. E.*, optical constants of magnesium and zinc crystals, ii, 1041.
Grabfield, *G. P.*, and *A. M.* Prentiss, effect of iodides on the human nitrogen metabolism, i, 1002.
Grabowska, *M.*, and *S.* Weil, condensation of formaldehyde with *p*-aminoacetophenone, i, 260.
Gracanin, *M.* See *A.* Nemec.
Gränacher, *C.*, anhydrides of amino-acid derivatives, i, 594.
Gränacher, *C.* See also *P.* Karrer.

Graevenitz, *F. von*, fatty degeneration caused by some essential oils, i, 195.
pharmacological investigation of methylated guanidines, i, 734.
Graevenitz, *F. von*. See also *M.* **Schenck**.
Graf, *F.* See *H.* **Lecher**.
Grafe, *V.*, plant phosphatides, i, 1522.
Grafe, *V.*, and *V.* **Horvat**, water-soluble phosphatides from the root of the sugar beet. I., i, 1522.
Grafflin, *M. W.* See *M. S.* **Kharasch**.
Grafton, *E. H.* See *W. D.* **Harkins**.
Graham, *S.* See *G. H.* **Anderson**.
Graham, *V. A.* See *J. B.* **Sumner**.
Graire, *A.*, reduction of oxides of nitrogen in presence of sulphuric and sulphurous acids, ii, 227.
Grandadam, *R.*, purification and m. p. of potassium and sodium cyanides, ii, 704.
Grandadam, *R.* See also *L.* **Hackspill**.
Grandsire, *A.* See *H.* **Colin**.
Grant, *J.*, concentration cells in methyl alcohol. II. Solutions containing tetraethylammonium iodide, ii, 301.
Grant, *R.* See *A. R.* **Penfold**.
Grassner, *F.* See *W.* **Küster**.
Grau, *E.* See *R.* **Lorenz**.
Grau, *R.* See *K.* **Hess**, and *H.* **Ley**.
Gray, *G. W.*, and *G. D.* **Garbutt**, determination of phosphorus in the presence of vanadium, ii, 600.
Gray, *J. A.*, effective wave-lengths of γ-rays, ii, 84.
scattering and absorption of γ-rays, ii, 84.
Gray, *L. T. M.*, effect of colloids in the displacement of lead and copper from their salts by zinc, ii, 578.
Gray, *W. H.*, aromatic esters of acylecgonines, i, 829.
Gray, *W. H.* See also **Wellcome Foundation, Ltd.**
Graymore, *J.*, solvent action of trialkyltrimethylenetriamines on uric acid, i, 76.
Graz, *C.* See *L.* **Duparc**.
Greasley, *T.* See *F. S.* **Kipping**.
Greaves, *J. E.*, and *D. H.* **Nelson**, iron, sulphur, and chlorine contents of grains and the influence of irrigation water on them, i, 757.
Greaves, *R. H.*, and *J. A.* **Jones**, temper-brittleness of steels; susceptibility to temper-brittleness in relation of chemical composition, ii, 487.
Grebe, *L.*, variation of the energy absorbed by ionisation in air when excited by *X*-rays of varying wave-length, ii, 615.
Grebe, *L.*, and *L.* **Kriegesmann**, energy consumption in ionisation by *X*-rays of different wave-lengths, ii, 79.
Grebenshchikov, *J. V.* See *N. A.* **Pushin**.
Green, *G.*, law of force within the atom, ii, 466.
Green, *G.* See also *E. B. R.* **Prideaux**.
Green, *J. B.*, structure of the red lithium line 6708 Å., ii, 1013.
Green, *J. B.*, and *M.* **Petersen**, double excitation spectra of magnesium and related elements, ii, 451.
Greenberg, *D. M.*, and *C. L. A.* **Schmidt**, formation and ionisation of compounds of casein with alkali. I. Transport numbers of alkali caseinate solutions. II. Conductivities of alkali caseinate solutions. III. Electrochemical behaviour of racemic casein, ii, 129.
Greenewalt, *C. H.*, partial pressure of water out of aqueous solutions of sulphuric acid, ii, 493.
Greenwald, *I.*, new type of phosphoric acid compound from blood; effect of substitution on the rotation of *l*-glyceric acid, i, 712.
Jaffe's reaction for creatinine. II. Effect of substitution in the creatinine molecule and a possible formula for the red tautomeride, i, 839.
Jaffe's reaction for creatinine. III. 2:6-dinitrophenol, ii, 1212.
Greenwald, *I.*, *J.* **Gross**, and *J.* **Samet**, nature of sugar in normal urine. I. Comparison of dextrose equivalent of various sugars in different methods for determination of dextrose, i, 185.
nature of sugar in normal urine. II. Sugar excretion on various diets; influence of diet on dextrose tolerance; nature of action of insulin, i, 185.
Greenwood, *C. V.* See *H. B.* **Stocks**.
Greenwood, *G.*, crystal structure of cuprite and rutile, ii, 93.
crystallographic data for some organic compounds, ii, 1037.
Greer, *W. N.* See *C. A.* **Kraus**.
Greider, *C. E.* See *J. C. W.* **Frazer**, and *W. A.* **Patrick**.
Greig, *J. W.*, formation of mullite from cyanite, andalusite, and sillimanite, ii, 987.
Greig, *J. W.* See also *N. L.* **Bowen**.
Grenacher, *M.*, variation of dielectric constants of organic liquids with pressure, ii, 741.
Grenet, *L.*, iron–nickel and iron–cobalt equilibrium diagrams, ii, 973.

Grevemeyer, *C. F.* See *G.* **Tammann.**
Griebel, *C.*, occurrence of acetaldehyde in fruits and other parts of plants, i, 763.
Grieveson, *C. J. W.*, absorption of ultra-violet light in dilute solutions, ii, 472.
Griffith, *E.* See *F. N.* **Peters**, *jun.*
Griffith, *H. D.*, construction of Nernst filaments, ii, 896.
Griffith, *R. H.*, substituted carbonates derived from *p*-cresol, i, 135.
Griffith, *R. H.*, and *E.* **Hope**, synthesis of 5:5′-dibromo-6:6′-dimethoxy-2:2′-bisoxythionaphthen, i, 827.
Griffith, *R. O.*, and *A.* **McKeown**, photochemical and thermal decomposition of ozone, ii, 1080, 1168.
Griffith, *W. H.*, influence of diet on synthesis of hippuric acid, i, 1002.
Griffiths, *J. P.*, and *C. K.* **Ingold**, tautomerism of dyads. IV. Evidence of the tautomeric mobility of oximes, i, 1190.
Griffiths, *W. T.* See *J. L.* **Haughton.**
Grigaut, *A.*, determination of lecithin in blood, i, 453.
Grignard, *V.*, and *M.* **Dubien**, action of organo-magnesium compounds on Δγ-hepten-β-one and on its olefinic alcohol, i, 111.
Grignard, *V.*, and *R.* **Escourrou**, synthetic rhodinol, i, 772.
selective hydrogenation of geraniol, i, 772.
catalytic hydrogenation of nitriles under reduced pressure; synthesis of aldimines, i, 931.
Grignard, *V.*, and *A.* **Vesterman**, γ-hydroxy-β-ethylhexaldehyde and β-ethyl-Δβ-hexenaldehyde, i, 513.
Grilli, *V.* See *G.* **Sani.**
Grimm, *H. G.*, structure and molecular dimensions of non-metallic hydrides, ii, 1123.
Grimm, *H. G.* See also *W.* **Biltz.**
Grindley, *G. C.*, and *A. M.* **Tyndall**, mobility in air of ions produced in another gas, ii, 80.
Grischkevitsch-Trochimovski, *E.*, action of nitrous acid on the nitrile of aminomalonic acid, i, 1104.
Grischkevitsch-Trochimovski, *E.*, and *L.* **Kotko**, structure of dicyanotriazole, i, 1104.
Grischkevitsch-Trochimovski, *E.*, and *A.* **Semencov**, condensation of aldehydes with aminomalononitrile, i, 1069.
Groe, (*Mlle.*) *M.* See **Javillier.**
Groebbels, *F.*, and *F.* **Sperfeld**, vitamins. IV. Influence of avitaminosis on gastric digestion of white mice, i, 1514.
Groebe, *W.* See *K.* **Brand.**
Gróh, *J.*, cause of the colour change in cobalt chloride solutions, ii, 963.
Gróh, *J.*, and *I.* **Kelp**, diffusion of iodine in pure and mixed solvents, ii, 1049.
Grollman, *A.*, combination of phenol-red and proteins, i, 1000.
Grollman, *A.*, and *J. C. W.* **Frazer**, vapour-pressure lowering of aqueous sulphuric acid solutions at 25°, ii, 398.
Grollman, *A.* See also *D. I.* **Macht.**
Gromelski, *A.*, influence of the method of obtaining serum on its protein concentration, i, 95.
Groot, *W. de*, measurements on small tungsten arcs, ii, 1137.
Gross, *E.*, and *A.* **Terenin**, fine structure of optically excited spectrum lines, ii, 915.
Gross, *F.*, selective photo-electric effect on metallic films prepared in various ways, ii, 344.
constitution of magnetic iron, ii, 1134.
Gross, *J.* See *I.* **Greenwald.**
Gross, *L.* See *P.* **Eggleton.**
Gross, *P.*, and *O.* **Halpern**, dilution laws and distribution coefficients of strong electrolytes from the Debye theory, ii, 117.
mixed electrodes of the second type, ii, 405.
parameters depending on temperature in statistics: the Debye theory of electrolytes, ii, 866.
electrolytes in solutions of low dielectric constant, ii, 1152.
Grosse, *A. von*, relationships between hydrogen and alkyl compounds of non-metals, ii, 843.
Grosse, *A. von.* See also *E.* **Krause.**
Grotrian, *W.* See *H.* **Gieseler.**
Grube, *G.*, hydrogen overvoltage at arsenic cathodes, ii, 43.
Grube, *G.*, and *L.* **Baumeister**, influence of light and *X*-rays on anodically polarised platinum electrodes, ii, 46.
Grube, *G.*, and *M.* **Staesche**, determination of equilibria between stages of oxidation by potential measurements. II. Manganese in phosphoric acid solution, ii, 893.
Gruber-Rehenburg, *R.* See *R.* **Kremann.**
Grün, *A.*, and *F.* **Wittka**, oxidation of unsaturated fatty acids, i, 1377.
Grün, *S.* See *M.* **Kohn.**
Grünbaum, *A.* See *J.* **Snapper.**
Grüneisen, *E.*, and *E.* **Goens**, metal crystals. I. and II., ii, 22.
metal crystals. III. Thermal expansion of zinc and cadmium, ii, 488.

Grüss, *J.*, mechanism of action of hydrogenase in the cell, i, 738.
Grützmacher, *M.*, dielectric constants of liquid mixtures, ii, 263.
Grützner, *M.* See *A.* **Lottermoser.**
Gruhn, *E.*, excretion of the stereo-isomeric cocaines in the urine and their relation to toxicity, i, 736.
Grumbach, *A.*, surface phenomena in photo-electric elements with a fluorescent liquid, ii, 549.
Grundherr, *G. E. von.* See *R.* **Kuhn.**
Grundmann, *W.*, preparation of well-defined silica acid sols, ii, 775.
Grunert, *H.*, internal friction of aqueous sulphate solutions, ii, 859.
Grunmach, *L.*, and *G.* **Schweikert,** surface tension of "tetralin," "decalin," and lubricating oil, ii, 31.
Gruskin, *B.*, determination of urea and sugar in blood, i, 1113.
Guastalla, *G.* See *M.* **Giua.**
Guckel, *M.* See *H.* **Kohn.**
Gucker, *F. T.* See *T. W.* **Richards.**
Gudden, *B.*, and *R.* **Pohl,** photo-electric primary current in sodium chloride crystals, ii, 343.
mechanism of the photo-electric primary current in crystals, ii, 344.
electron conduction in crystals, ii, 943.
Günther, *F.* See *R.* **Meyer-Bisch.**
Günther, *P.*, viscosities of gases [hydrogen and helium] at low temperatures, ii, 100.
Günther, *P.*, and *G.* **Wilcke,** Röntgen spectroscopic method of quantitative analysis, ii, 237.
Günther-Schulze, *A.*, cathode fall, current density, and dark space in mixtures of gases which do not react chemically, ii, 341.
processes in the vacuum mercury arc, ii, 341.
pseudo-high vacuum, ii, 342.
work of escape of positive ions, ii, 342.
relation between energy of escape of electrons and electrochemical normal potential, ii, 477, 546.
electrolysis with gas cathodes, ii, 549.
chemical reactions in the glow discharge, ii, 553.
Günzel, *E.*, and *E.* **Marcus,** lead bromate and diacetato-diplumbobromate, ii, 1086.
Guernsey, *E. W.*, and *M. S.* **Sherman,** mechanism of the fixation of nitrogen as sodium cyanide, ii, 889.
Guertler, *W.*, and *T.* **Liepus,** chemical resistance of metals and alloys, especially those containing molybdenum, ii, 1146.
Guéry, *F.*, magnetic field of a moving electron, ii, 252.
Guest, *H. H.*, preparation of primary acetylenic alcohols, i, 627.
Guggenbühl, *G. A.* See *H.* **Rupe.**
Guha, *P. C.*, and *S. C.* **De,** hetero-ring formations with thiocarbohydrazide, i, 599.
Guha, *P. C.*, and *H. P.* **Rây,** constitution of the so-called dithiourazole of Martin Freund. III. Synthesis of some monosubstituted thiodiazoles, i, 702.
Guha, *P. C.*, and *S. K.* **Ray,** *o*-aminophenylhydrazine and some interesting heterocyclic compounds derived from it, i, 1461.
Guichard, *F.* See *E.* **André.**
Guichard, *M.*, dynamic study of dehydration by means of a hydrostatically-compensated balance, ii, 427.
rate of dehydration in the system, water-alumina, ii, 558.
rapidity of dehydration at increasing temperature, ii, 559.
Guillaumin, *A. J. A.* See *L. J.* **Simon.**
Guinot, *H.*, method and laboratory apparatus for dehydrating alcohol, i, 1229.
Guittonneau, *G.*, ammonification of amino-nitrogen by the *Microsiphoneæ* of the soil, i, 106.
utilisation of mineral nitrogen by the *Microsiphoneæ* of the soil, i, 341.
formation of thiosulphates at the expense of sulphur by micro-organisms of the soil, i, 766.
conversion of sulphur into sulphate by micro-organisms of the soil, i, 1218.
Gulevitsch, *W.* [mechanism of the catalytic reduction of oximes], i, 653.
Gulland, *J. M.*, and *R.* **Robinson,** synthetical experiments in the naphthyridine groups, i, 1186.
Gunnaiya, *D.* See *A. L.* **Narayan.**
Gunnelius, *A.* See *E.* **Oman.**
Guntz, *A.*, and *F.* **Benoit,** analysis of lithium minerals, ii, 1202.
Gupta, *B. K. S.* See *A. C.* **Sircar.**
Gupta, *I. S.* See *G. C.* **Chakravarti.**
Gupta, *P. N. D.* See *P. R.* **Rây.**
Gupta, *R. S.* See *M.* **Prasad,** and *D. L.* **Shrivastava.**
Gupta, *S. R. D.* See *E.* **Stiasny.**
Gurchot, *C.* See *W. D.* **Bancroft.**
Gurevitsch, *W. G.* See *W. F.* **Timoféev.**

Gurney, *R. W.*, ionisation by α-particles in monatomic and diatomic gases, ii, 256.
stopping-power of gases for α-particles of different velocities, ii, 256.
Gurvitsch, *L.*, colloidal properties of soap solutions, ii, 517.
Guss, *A. B.* See *L. A.* **Congdon**.
Gustafson, *F. G.*, hydrogen-ion concentration of plant juices. I. Changes in the hydrogen-ion concentration of plants during their development, i, 1023.
diurnal changes in acidity of *Bryophyllum calycinum*, i, 1221.
Gustavson, *K. H.*, effect of sodium chloride on hydrogen-ion concentration and stability towards alkali of chromic chlorides, ii, 1086.
Gutbier, *A.*, dialysis of easily decomposable colloidal systems, ii, 965.
Gutbier, *A.*, and *H.* **Brintzinger** [with *W.* **Bubam**], composition of the ash evolved from the volcano Acatenango in Guatemala on June 12th, 1925, ii, 1195.
Gutbier, *A.*, and *T.* **Kautter**, colloidal bismuth, ii, 860.
Gutbier, *A.*, and *H. O.* **Meyer**, colloidal lead dioxide from lead tetra-acetate, ii, 290.
Gutbier, *A.*, and *W.* **Niemann**, isomeric potassium pentachlororuthenites, ii, 231.
Guth, *B.*, higher fungi. XVIII. The muscarine question, i, 1247.
Gutmann, *A.*, action of normal sodium arsenite on azido compounds, i, 84.
sodium arsenite as a reagent for loosely-combined halogen, ii, 238.
sodium arsenite as a reagent for loosely-combined reactive oxygen, sulphur, and nitrogen, i, 1059.
Guttmann, *L. W.* See *M.* **Kohn**.
Guy, *W. G.* See *W. D.* **Harkins**.
Guye, *C. E.*, *P.* **Mercier**, and *J. J.* **Weiglé**, explosion potential in carbon dioxide at high pressures, ii, 490.
Guyot, *J.*, Volta effect between metals and electrolytes, ii, 402.
Gyemant, *A.*, measurement of fluorescence of solids, ii, 13.
mechanism of breakdown of damp liquid insulators, ii, 1028.
György, *P.*, problem of permeability, i, 322.
calcium ionisation in the blood, i, 324.
effect of neutral salts on the excretion of acids in the urine, i, 459.
György, *P.* See also *T.* **Brehme**, and *R.* **Essinger**.
Gyulai, *Z.*, quantum equivalent for photo-electric conductivity in sodium chloride crystals, ii, 476.
absorption process in photo-electrically-conducting sodium chloride crystals, ii, 837.

H.

Haag, *W.* See *Erich* **Schmidt**.
Haar, *A. W. van der*, saponins and related substances. XI., XII., and XIII., i, 50.
saponins and related substances. XIV. Structure of hederagenin: an example of steric hindrance, i, 946.
Haas, *G.*, and *E. F.* **Schlesinger**, determination of free phenol and cresol in small amounts of blood and its prognostic significance in cases of poisoning, i, 334.
Haas, *P.*, and *T. G.* **Hill**, *Mercurialis*. I. Development of a blue pigment on drying, i, 759.
Mercurialis. II. Occurrence of a chromogen showing a remarkable avidity for free oxygen, i, 759.
Haas, *R.* See *W.* **Küster**.
Haase, *W.* See *E. H.* **Riesenfeld**.
Haber, *F.*, practical results of the theoretical development of chemistry, ii, 395.
Haber, *F.*, and *J.* **Jaenicke**, Rhine water, ii, 997.
Hackl, *O.*, certain and exact establishment of the end-point in the titration of manganese, ii, 440.
direct determination of tervalent iron in silicates insoluble in acids; use of the method in determining the ratio of ferric to ferrous iron after decomposition of the mineral with sulphuric and hydrofluoric acids, ii, 1004.
Hackmann, *C.* See *F.* **Kieferle**.
Hackspill, *L.*, and *R.* **Grandadam**, displacement of alkali metals by iron, ii, 233.
reduction of metallic oxides by alkali cyanides, ii, 419.
Haden, *R. L.*, modification of the Kramer–Tisdall method for the determination of sodium in blood, i, 1112.
preparation of colloidal gold solution by the Mellanby–Anwyl–Davies technique, ii, 895.
Haden, *R. L.*, and *T. G.* **Orr**, chemical constituents of the blood of the dog, i, 1484.
Hadley, *A. C.* See *M.* **Nierenstein**.
Haebler, *W. T.* See *P.* **Karrer**.

Häffner, *H.* See *B.* **Emmert.**
Hägglund, *E.*, unsaturated aldehydes and their relation to α-lignin, i, 643.
homogeneity of α-lignin, i, 1026.
Hägglund, *E.*, and *A. M.* **Augustson**, relation between alcoholic fermentation and hydrogen-ion concentration. I., i, 476.
Haehn, *H.*, and *A.* **Pülz**, new oxido-reduction system and its biochemical significance, i, 858.
Haemmerli, *A.* See *E.* **Herzfeld.**
Händel, *M.*, detoxicating function of the liver. I. Coupling of sulphuric acid and of glycuronic acid in liver diseases, i, 610.
Händel, *M.* See also *A.* **Benatt**, and *J. A.* **Collazo.**
Haenny, *E.* See *F.* **Kehrmann.**
Haerdi, *W.*, and *J. F.* **Thorpe**, conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. VII. Influence of the phenyl group on the formation of the *cyclo*propene ring, i, 923.
Haeseler, *P. E.*, preparation of diacetonamine, i, 644.
Häusler, *H.*, and *O.* **Loewi**, insulin and the distribution of sugar between fluid and non-fluid systems, i, 753.
Haffner, *F.*, and *T.* **Komiyama**, pharmacological assay of preparations of thyroid gland, i, 1119.
Hafner, *E. A.*, and *L.* **Kürthy**, salting-out, ii, 283.
Hagedorn, *H. C.*, apparatus for the graphic recording of oxygen consumption and carbon dioxide output, especially adapted for clinical work, i, 177.
Hagem, *O.* See *T.* **Gaarder.**
Hagene, *P.* See *R.* **Fosse.**
Hager, *E.* See *E.* **Philippi.**
Hager, *G.*, determination of the acidity of mineral soils, i, 489.
Haggard, *H. W.*, toxicology of hydrogen sulphide, i, 1357.
Hahn, *A.*, and *H.* **Fasold**, salt-formation between creatine and sodium hydroxide, ii, 653.
reciprocal conversion of creatine and creatinine, i, 1496.
Hahn, *D. A.*, and *A. G.* **Renfrew**, synthesis of the polypeptide-hydantoin: 1-methyl-4-*p*-hydroxybenzylhydantoin-3-acetic acid, i, 581.
Hahn, *F. L.*, conversion of cupric into cuprous sulphide by heating in a current of hydrogen, ii, 160.
determination of magnesium in presence of aluminium, ii, 601.
Hahn, *F. L.*, detection of minute quantities of material at very great dilution, i, 1095.
Hahn, *F. L.*, and *G.* **Jaeger**, sensitive reaction for nitrate, ii, 1199.
contradictions and errors in analytical chemistry. VI. Ferrous sulphate test for nitrate and nitrite and the diphenylamine reaction, ii, 1199.
Hahn, *F. L.*, and *S.* **Scheiderer**, contradictions and errors in analytical chemistry. V. Precipitation of magnesium ammonium phosphate from solutions containing aluminium, ii, 69.
Hahn, *F. L.*, and *H.* **Wolf**, stable triammine salts, i, 813.
separation of arsenic and antimony by distillation, ii, 68.
complexes with two unsymmetrical co-ordination valencies, ii, 578.
Hahn, *F. V. von*, electrosynthesis of sulphide hydrosols, ii, 522.
colloid chemistry of the vitamin problem, ii, 664.
Hahn, *O.*, capacity for emanating of finely-divided precipitates as a means of determining surface variation, ii, 177.
isotopes of uranium, ii, 921.
Hahn, *O.*, and *L.* **Meitner**, β-ray spectrum of radium, ii, 9.
Haines, *L. B.*, and *H.* **Adkins**, reaction of certain organic compounds with nitrogen pentoxide, i, 801.
Haines, *T. M.* See (*Sir*) *W. J.* **Pope.**
Haines, *W. B.*, physical properties of soils. I. Mechanical properties concerned in cultivation, i, 876.
Haken, *W.* See *F.* **Paneth.**
Halban, *H. von*, nature of the undissociated acids, ii, 511.
absorption of light by solutions of electrolytes, ii, 1083.
Haldane, *J.* See *J. B.* **Shoesmith.**
Haldane, *J. B. S.*, production of acidosis by ingestion of magnesium chloride and strontium chloride, i, 723.
Haldane, *J. B. S.* See also *G. E.* **Briggs.**
Hale, *C.* See *D. T.* **Englis.**
Hall, *A. L.* See *G. A.* **Molengraaff.**
Hall, *E. H.*, number of free electrons with a metal, ii, 252.
the four transverse effects and their relations in certain metals, ii, 846.
Hall, *J. A.*, glucosides of the navel orange, i, 760.
Hall, *J. A.*, and *C. P.* **Wilson**, volatile constituents of Valencia orange juice, i, 1521.

Hall, *R. E.* See *W. H.* **Rinkenbach.**
Hall, *R. I. E.*, action of sodium on the acetates of *o*- and *p*-cresol, i, 23.
Hall, *W. J.* See *S. A.* **Shorter.**
Haller, *A.*, *C.* **Bauer**, and *P.* **Ramart**, syntheses with sodamide. XIII. Mono-, di-, and tri-allylacetophenones, alkylallylacetophenones, and allyl*iso*-butyrones, i, 1260.
Haller, *A.*, and *R.* **Cornubert**, constitution of the dimethyl*cyclo*pentanone and dimethyl*cyclo*hexanone obtained by methylation in presence of sodamide, i, 1070, 1071.
Haller, *A.*, and *F. S.* **Legagneur**, diketones and mixed ketones derived from the α-mononitrile of camphoric acid and from methyl cyanocampholate, i, 683.
action of magnesium methyl iodide on esters of camphoric acid α-mononitrile, i, 924.
Haller, *A.*, and *R.* **Lucas**, rotatory power of certain camphor derivatives, ii, 742.
Haller, *H. L.* See *J. A.* **Ambler**, and *P. A.* **Levene.**
Haller, *R.*, adsorption compounds. V., ii, 287.
Hallett, *L. T.* See *E. H.* **Archibald.**
Hallimond, *A. F.*, chemical classification of the mica group. I. Acid micas, ii, 819.
Halpern, *O.* See *P.* **Gross.**
Ham, *L. B.*, relation of spectral lines to mass variations within the atom, ii, 734.
theory of the fine structure of H and He+ lines, ii, 1098.
Hamann, *F.* See *O.* **Reisser.**
Hamburger, *R. J.*, and *A. von* **Szent-Györgyi**, influence of oxygen tension on biological oxidation, i, 709.
Hamer, (*Miss*) *F. M.*, reduction of the carbocyanines, i, 305.
Hamer, *R.*, photoelectric thresholds of elements, ii, 7.
Hamilton, *B.*, concentrations of inorganic substances in blood-serum and spinal fluid, i, 1352.
Hamilton, *C. S.*, and *R. T.* **Major**, symmetrical bisarsinoarylbenzamidocarbamides, i, 990.
Hamilton, *C. S.*, and *C.* **Sly**, action of alkyl chloroformates on aminoarylarsinic acids, i, 600.
Hamlin, *M. L.*, laboratory vacuum gauge, ii, 431.
Hammarsten, *E.*, osmotic pressure of electrolytes of high molecular weight, ii, 195.
Hammer, *W.*, and *H.* **Pychlan**, behaviour of the α-particles from radium-*F* in a longitudinal electric field, ii, 621.
Hammett, *F. S.*, bone growth. I. Changes in ash, organic matter, and water during growth in the albino rat, i, 1001.
bone growth. II. Changes in calcium, magnesium, and phosphorus of bone during growth. III. Changes in composition of ash, i, 1208.
refractometric studies of neutralisation, ii, 289.
Hammett, *L. P.*, and *C. T.* **Sottery**, reagent for aluminium, ii, 601.
Hammett, *L. P.* See also *H. T.* **Beans.**
Hammick, *D. L.*, and *J. A.* **Currie**, system, sodium sulphite–sodium hydroxide–water, ii, 869.
Hammond, *J.* See *H. E.* **Woodman.**
Hamsik, *A.*, oxyhæmin and its salts, i, 845.
hydroxyhæmin, i, 1476.
Hance, *F. E.*, inhibition of bumping in the determination of nitrogen in soil, i, 1032.
Hance, *F. E.* See also *L. M.* **Dennis.**
Hancock, *J. S.* See *A. F.* **Joseph.**
Handovsky, *H.*, colloidal composition of blood-serum; significance of cholesterol, i, 322.
structure of blood-serum, i, 715.
water metabolism and pharmacological action, ii, 36.
Handy, *J. A.*, and *L. F.* **Hoyt**, [determination of] ethyl phthalate. III., ii, 1210.
Hanemann, *H.*, recrystallisation phenomena as functions of the crystal growth after hot deformation, ii, 1134.
Hanke, *G.* See *G.-M.* **Schwab.**
Hanle, *W.*, influence of magnetic fields on the polarisation of resonance fluorescence, ii, 629.
Hann, *R. M.*, condensation of rhodanic acids with isatin; 3-arylrhodanylidene-$\Delta^{5,3'}$-oxindoles, i, 987.
condensation of isomeric tolyl-2-thio-4-ketothiazolidines (rhodanic acids) with substituted vanillins, i, 1105.
Hann, *R. M.*, and *J. F. T.* **Berliner**, toluidine derivatives. I. Quantitative preparation of 5-iodo-*o*-toluidine and some of its derivatives, i, 908.
Hann, *R. M.*, and *G. C.* **Spencer**, additive compounds of 3:5-dibromo-*o*-toluidine with metallic salts, i, 653.

Hann, *R. M.* See also *G. L.* **Keenan**, and *K. S.* **Markley.**
Hanot, (*Mlle.*) *M.*, width of rays in the Balmer series in the oscillating discharge, ii, 170.
Hans, *F.*, oxidation of tervalent chromium by silver oxide in alkaline solution, ii, 316.
Hanselmayer, *F.* See *A.* **Zinke.**
Hansen, *G.*, fine structure of hydrogen lines, ii, 1097.
Hansen, *K.*, alcohol tolerance in man, i, 1503.
Hansen, *T. S.*, diastase in the urine in pancreatic diseases, i, 856.
Hansen-Schmidt, *E.* See *H. P.* **Kaufmann.**
Hanson, *D.*, and (*Miss*) *G. W.* **Ford**, effects of impurities on copper. II. Effect of iron on copper, ii, 317.
Hanson, *D.*, and *M. L. V.* **Gaylor**, constitution of alloys of aluminium, copper, and zinc, ii, 974.
Hanson, *D.* See also *F. S.* **Tritton.**
Hantzsch, *A.*, isatoid and the so-called "isatole," i, 700.
supposed "3-hydroxyindazole" and the so-called "structural association" of G. Heller, i, 702.
nature of hydrogen halides, ii, 359.
nature of undissociated acids, ii, 512.
Hantzsch, *A.* [with *L.* **Wolf**], constitution of nitric acid and the nitronium salts formed from it by perchloric and sulphuric acids, ii, 634.
Hantzsch, *A.*, and *H.* **Carlsohn**, halides of the fourth group as homopolar compounds on the basis of an additive relationship in m. p., ii, 1043.
Hanzlik, *P. J.*, and *N. E.* **Presho**, salicylates. XV. Liberation of salicyl from and excretion of salicyl salicylate. XVI. Liberation of salicyl from and excretion of methyl salicylate, with a note on the irregular toxicity of the ester in man, i, 1501.
Happold, *F. C.*, and *H. S.* **Raper**, tyrosinase-tyrosine reaction. III. Supposed deaminising action of tyrosinase on amino-acids, i, 474.
Hara, *R.*, and *H.* **Miura**, synthesis of sodium cyanide from sodium sulphate or sodium chloride, i, 645.
Hara, *R.*, and *H.* **Sinozaki**, saturated vapour pressure of hydrocyanic acid, ii, 279.
catalytic oxidation of hydrogen cyanide, ii, 983.
Hara, *T.*, catalytic action. VIII. Catalytic reduction of β-naphthylamine, i, 536.
Hara, *T.*, and *S.* **Komatsu**, catalytic action. XVI. Synthesis of nitriles, i, 893.
Harada, *T.* See *C. A.* **Kraus.**
Harasty, *D.* See *E.* **Abel.**
Harden, *A.*, fermentation by dried yeast preparations, i, 1010.
Harder, *H.* See *H.* **Staudinger.**
Harder, *M.* See *K.* **Freudenberg.**
Harding, *L.*, artificial "saccharin" substances; synthesis of diphenyl-4:4′-dicarboxy-3:3′-sulphimide (diphenyl-4:3:4′:3′-dicarboxylicsulphinide), i, 670.
Harding, *V. J.*, *K. D.* **Allin**, *B. A.* **Eagles**, and *H. B. van* **Wyck**, effect of high fat diets on content of uric acid in blood, i, 604.
Harding, *V. J.*, *K. D.* **Allin**, and *H. B. van* **Wyck**, influence of sodium chloride on uric acid of blood, i, 94.
Harger, *R. N.*, additive compounds of quinol with aliphatic amines, i, 28.
oxidation of quinol in presence of aliphatic amines; formation of bisalkylaminobenzoquinones, i, 24.
Hargreaves, *R.*, proposed model for the α-particle, and some nuclear series, ii, 835.
Hári, *P.*, testing insulin preparations, i, 617.
Hariharan, *K. V.*, and *J. J.* **Sudborough**, bromo derivatives of *p*-methoxycinnamic acid, i, 1149.
Harington, *C. R.*, synthesis of 4-(3′:4′:5′-tri-iodophenyl)-2-pyrrolidone-5-carboxylic acid, i, 1094.
Harkins, *W. D.*, the separation of chlorine into isotopes (isotopic elements) and the whole number rule, ii, 1108.
orientation of molecules in the surfaces of liquids, ii, 1148.
Harkins, *W. D.*, and *H. S.* **Adams**, overvoltage as a function of current density and the effects of time, temperature, stirring, pressure, nature of surface, and of a superimposed alternating current, ii, 301.
Harkins, *W. D.*, and *N.* **Beeman**, oriented wedge theory of emulsions, ii, 1154.
Harkins, *W. D.*, and *G. L.* **Clark**, effect of sodium hydroxide on the surface tension of a solution of sodium nonoate, ii, 857.
Harkins, *W. D.*, and *E. H.* **Grafton**, unimolecular films on water; oriented adsorption of derivatives of benzene, ii, 658.
Harkins, *W. D.*, and *W. G.* **Guy**, radioactivity of potassium, rubidium, and other elements, ii, 1109.

Harkins, *W. D.*, and *H. M.* **McLaughlin**, unimolecular films between liquids: butyric acid between water and hexane, and acetic acid between water and benzene, ii, 771.
structure of films of water on salt solutions. I. Surface tension and adsorption for aqueous sodium chloride solutions, ii, 959.
Harkins, *W. D.*, and *J. W.* **Morgan**, multimolecular and unimolecular films, ii, 1148.
Harkins, *W. D.*, and *S. B.* **Stone**, isotopic composition and atomic weight of chlorine in meteorites, ii, 921.
isotopic composition of the element chlorine: the atomic weight of meteoric and terrestrial chlorine, ii, 1108.
Harkins, *W. D.* See also *L. J.* **Bircher**.
Harle, *J. A.* See *W. M.* **Thornton**.
Harman, *R. W.*, aqueous solutions of sodium silicates. I. Preparation and electrical conductivity, ii, 1065.
Harman, *R. W.*, and *F. P.* **Worley**, hydrolysis of alkali cyanides in aqueous solution, ii, 783.
Harned, *H. S.*, activity coefficient of sodium hydroxide in aqueous solution, ii, 397.
activity coefficient of sodium hydroxide in sodium chloride solutions, ii, 398.
activity coefficient of potassium hydroxide in potassium chloride solutions, ii, 398.
activity coefficient and ionic concentration product of water in sodium and potassium chloride solutions, ii, 538.
thermodynamics of solutions of simple electrolytes, ii, 977.
Harned, *H. S.*, and *M. H.* **Fleysher**, activity coefficients of hydrochloric acid in solutions of ethyl alcohol, ii, 538.
transference numbers of hydrochloric acid in solutions of ethyl alcohol, ii, 542.
Harned, *H. S.*, and *R. D.* **Sturgis**, free energy of sulphuric acid in aqueous sulphate solutions, ii, 538.
Harper, *H. J.*, determination of ammonia in soils, i, 224.
Harpuder, *K.*, pharmacological effects on the purine metabolism of men. I. Effect of sympathico- and vago-tropic drugs, i, 613.
Harris, *C. R.* See *S. A.* **Mahood**, and *A. S.* **Wheeler**.
Harris, *D. T.*, biological action of light, i, 1021.
Harris, *H.*, measurement of the dielectric constants of liquids, ii, 631.
Harris, *J.* See *O. L.* **Brady**.
Harris, *J. A.*, *W. F.* **Hoffmann**, and *A. H.* **Johnson**, reaction of the cotton plant, i, 758.
Harris, *J. A.*, *J. V.* **Lawrence**, and *Z. W.* **Lawrence**, chloride content of the leaf-tissue fluids of Egyptian and upland cotton, i, 216.
Harris, *L. J.*, combination of proteins, amino-acids, etc., with acids and alkalis and their combining weights as determined by physico-chemical measurements, i, 450.
acid–base titrations and equilibria of weak bases and acids, ii, 155.
Harrison, *D. C.*, catalytic action of traces of iron on the oxidation of cysteine and glutathione, i, 13.
Harrison, *G. A.*, solubilities of calcium soaps, ii, 190.
Harrison, *G. R.*, series limit absorption in sodium vapour, ii, 5.
relative transition probabilities in the sodium atom, ii, 734.
photographic sensitometry with fluorescent oils, ii, 930.
Harrison, *G. R.*, and *J. C.* **Slater**, line breadths and absorption probabilities in sodium vapour, ii, 911.
Harrison, *G. R.* See also *C. S.* **Forbes**.
Harrison, *J. B.*, occurrence of palladium and of rhodium in British Guiana, ii, 592.
Harrison, *J. B.*, and *C. L. C.* **Bourne**, occurrence of palladium amalgam (palladium mercuride) in British Guiana, ii, 593.
Harrison, *W. F.* See *G. T.* **Morgan**.
Hart, *E. B.*, *H.* **Steenbock**, and *C. A.* **Elvehjem**, calcium assimilation. V. Effect of light on calcium and phosphorus equilibrium in mature lactating animals, i, 108.
Hart, *E. B.*, *H.* **Steenbock**, *C. A.* **Elvehjem**, and *J.* **Waddell**, iron in nutrition. I. Nutritional anæmia on whole milk diets; utilisation of inorganic iron in formation of hæmoglobin, i, 1354.
Harteck, *P.* See *M.* **Bodenstein**.
Harteneck, *A.* See *E.* **Waldschmidt-Leitz**.
Hartig, *H. E.*, apparent transmission of low-velocity electrons through aluminium foil, ii, 921.
Hartl, *K.* See *W.* **Starlinger**.
Hartley, *H. B.*, and *H. R.* **Raikes**, preparation of pure methyl alcohol, i, 498.

Hartley, *H. B.* See also *J. E.* **Frazer**, and *G.* **Nonhebel**.
Hartman, *A. M.* See *W. A.* **Turner**.
Hartman, *F. W.* See *A.* **Bolliger**.
Hartman, *H.* See *P. E.* **Verkade**.
Hartmann, *F.* See *K. A.* **Hofmann**.
Hartmann, *M.*, and *H.* **Kägi**, *N*-carboxylic esters of asymmetrically substituted ethylenediamines, i, 1045.
Hartmann, *W.*, determination of vanadium, ii, 604.
determination of molybdenum as trioxide after precipitation as trisulphide, ii, 1206.
Hartong, *B. D.* See *I. M.* **Kolthoff**.
Hartree, *D. R.*, relations between the optical spectra of different atoms of the same electron structure. I. Lithium-like and sodium-like atoms, ii, 2.
spectra of some lithium-like and sodium-like atoms, ii, 2.
methods of estimating the successive ionisation potentials of any element, ii, 5.
quantum defect and atomic number, ii, 467.
atomic structure factor in the intensity of reflection of *X*-rays by crystals, ii, 735.
ionisation potential of ionised manganese, ii, 918.
Hartridge, *H.*, and *F. J. W.* **Roughton**, improvements in the apparatus for measuring the velocity of very rapid chemical reactions, ii, 47.
kinetics of hæmoglobin. III. Velocity with which oxygen combines with reduced hæmoglobin, ii, 557.
Hartung, *E. J.*, photochemical decomposition of silver bromide, ii, 57.
Hartung, *K.* See *P. W.* **Neber**.
Hartwell, *G. A.*, brown and white bread in the diet of the rat, i, 211.
possible correlation between dietary protein and loss of fur in young growing rats, i, 464.
comparison of dried and evaporated milks by a dietetic method, i, 751.
improved technique for use with synthetic diets, i, 1514.
Harvey, *C. O.*, reduction of chloric acid and chlorates by ferrous sulphate, ii, 1197.
Harvey, *E. H.*, electro-dialysis of agar, ii, 293.
physico-chemical study of U.S.P. agar, ii, 965.
Harvey, *E. M.*, rôle of carbohydrates and nitrogen in the growth of summer shoots of the apple, i, 1367.
Harvey, *E. N.*, inhibition of *Cypridina* luminescence by light, i, 1212.
Harvey, *H. W.*, oxidation in sea water, ii, 1171.
Harvey, *R. B.*, enzymes of thermal algæ, i, 746.
Harvey, *W. G.*, production of metallic magnesium from fused salts, ii, 570.
Harwood, *H. F.* See *A.* **Brammall**, and *A.* **Russell**.
Hasche, *R. L.*, new oxide of nitrogen, nitroso-nitrogen trioxide, and its bearing on the oxidation of nitric oxide, ii, 988.
Hasche, *R. L.*, and *W. A.* **Patrick**, rate of oxidation of nitric oxide. II. Velocity of the reaction between nitric oxide and oxygen at 0° and 30°, ii, 681.
Hasenfratz, *V.* See *L. J.* **Simon**.
Hashimoto, *H.*, blood chemistry in acute histamine intoxication, i, 1005.
Hashimoto, *T.*, chaulmoogra oil. I., i, 1234.
Haslam, *J.* See *F.* **Challenger**.
Haslam, *R. T.*, *R. L.* **Hershey**, and *R. H.* **Keen**, effect of gas velocity and temperature on rate of absorption, ii, 106.
Haslam, *R. T.*, *W. G.* **Lovell**, and *R. D.* **Kunneman**, radiation from non-luminous flames, ii, 475.
Hassel, *O.*, crystal structure of potassium dihydrogen phosphate and its isomorphs, ii, 1130.
Hastings, *A. B.*, *J.* **Sendroy**, *jun.*, and *W.* **Robson**, acidosis. XXI. Colorimetric determination of p_H of urine, i, 1490.
Hastings, *A. B.* See also *C. D.* **Murray**, and *J. M.* **Neill**.
Hatano, *J.*, taka-rennin, i, 102.
hydrolysis of silk fibroin peptone by taka-diastase, i, 201.
hydrolysis of amygdalin by taka-diastase, i, 201.
hydrolysis of various β-glucosides by taka-diastase, i, 201.
Hatcher, *P. R.* See *M.* **Nierenstein**.
Hatcher, *W. H.*, and *G. W.* **Holden**, hydrogen peroxide as an oxidising agent in acid solution. II. (i) Oxalic acid. (ii) Formic acid, ii, 684.
Hatley, *C. C.*, index of refraction of calcite for *X*-rays, ii, 21.
Hatschek, *E.*, effect of drying on permanently deformed gels, ii, 667.
elasticity of ammonium oleate solutions and the variable viscosity of two-phase systems, ii, 862.
Hatschek, *E.*, and *R. H.* **Humphry**, physical differences between sols and gels of agar, ii, 34.

Hatschek, *E.*, and *P. C. L.* Thorne, metal sols in non-dissociating liquids. II. Composition of the disperse phase of nickel sols in benzene and toluene, ii, 197.

Hattori, *S.*, acaciin, a new flavone glucoside from the leaves of *Robinia pseudacacia*, L., i, 1443.

Haubold, *E.* See *W.* **Eller.**

Hauer, *F. von*, entropy and probable state of ideal gases, ii, 495.

Hauestadt, *L.* See *R.* **Fricke.**

Hauge, *S. M.*, and *C. W.* **Carrick,** antiscorbutic properties of eggs, i, 1021.

Hauge, *S. M.* See also *C. W.* **Carrick.**

Haughton, *J. L.*, and *W. T.* **Griffiths,** β-transformations in copper–zinc alloys, ii, 973.

Haunschild, *H.* See *W.* **Manchot.**

Haupt, *B.* See *A.* **Pieroni.**

Haurowitz, *F.*, and *W.* **Petrou,** pancreatic enzymes. XIII. Optimum p_H for gastric lipase in different animals, i, 742.

Haurowitz, *F.* See also *P.* **Rona,** and *R.* **Willstätter.**

Hause, *W.* See *F.* **Henning.**

Hauser, *F.* See *R.* **Eder.**

Haussmann, *H.* See *H.* **Wieland.**

Havestadt, *L.*, and *R.* **Fricke,** synthesis of certain dipeptides of complex natural amino-acids, i, 162.

Havighurst, *R. J.*, crystal structure of mercurous halides, ii, 748.

Havighurst, *R. J.*, *E.* Mack, *jun.*, and *F. C.* **Blake,** precision crystal measurements on alkali and ammonium halides, ii, 17.

solid solutions of the alkali and ammonium halides, ii, 502.

Havighurst, *R. J.* See also (*Miss*) *A. H.* **Armstrong.**

Haworth, *R. D.*, and *W. H.* **Perkin, *jun.*,** synthetical experiments in the *iso*quinoline group. I., III., and IV., i, 968, 969, 970.

Haworth, *R. D.*, *W. H.* Perkin, *jun.*, and *H. S.* **Pink,** synthetical experiments in the *iso*quinoline group. V. Synthesis of substances allied to oxyberberine, i, 1168.

Haworth, *R. D.*, *W. H.* Perkin, *jun.*, and *J.* **Rankin,** synthetical experiments in the *iso*quinoline group. II., i, 969.

synthesis of *dl*-dicentrine, i, 1314.

Haworth, *R. D.*, and *H. S.* **Pink,** action of phosphorus pentachloride on 2-oximino-1-hydrindones, i, 929.

Haworth, *W. N.*, revision of the structural formula of dextrose, i, 1133.

Haworth, *W. N.*, *D. A.* Ruell, and *G. C.* **Westgarth,** amylene- and butylene-oxidic forms of tetramethylgalactose, i, 117.

Haworth, *W. N.* See also *S.* **Baker.**

Hay, *R.* See *J. H.* **Andrew.**

Hayashi, *K.*, influence of alcohol on the viscosity of blood-serum, ii, 663.

Hayner, *L. J.*, persistence of the radiation excited in mercury vapour, ii, 1017.

behaviour of mercury arc lines after removal of the exciting potential, ii, 1102.

Haynes, *D.*, physiology of apples. I. Change in the acid content of stored apples and its physiological significance, i, 345.

Headden, *W. P.*, luminescence in the Ingleside calcites affected by acids, ii, 89.

Heap, *H.*, and *B. H. E.* **Cadness,** influence of carbohydrates on hydrogen sulphide production by *Bacillus ærtrycke* (mutton), i, 480.

Heaps, *C. W.*, thermo-electric power and the Hall coefficient, ii, 1135.

Heathcote, *R. St. A.*, pharmacological action of cryptopine, i, 734.

Hebeisen, *J.*, compressibilities of some organic liquids, ii, 763.

Heckel, *H.*, and *R.* **Adams,** platinum oxide as a catalyst in the reduction of organic compounds. X. Reduction of aminophenols to cyclic amino-alcohols, i, 909.

Heckscher, *H.*, fat + cholesterol content of the blood of cretins, i, 999.

fat + cholesterol content of the blood of thyroidectomised horses, i, 999.

Heckscher, *H.* See also *H. J.* **Bing.**

Heckscher, *R.* See *R.* **Kuhn.**

Heczko, *T.*, determination of large quantities of manganese by titration with permonophosphoric acid, ii, 440.

Hedestrand, *G.*, influence of thin surface films on the evaporation of water, ii, 102.

Hedges, *E. S.*, and *J. E.* **Myers,** some metallic couples decomposing water at the ordinary temperature, ii, 306.

periodic dissolution of metals, ii, 309.

periodic electrochemical phenomena, ii, 680.

periodic crystallisation of pure substances, ii, 1168.

Hedin, *S. G.*, application of the law of mass action to the course of enzyme action, i, 1212.

Hedvall, *J. A.*, reactivity of solid phases, ii, 125.

complex uranyl carbonates, ii, 990.

Hedvall, *J. A.*, and *J.* **Heuberger**, reactions between solid phases. IV., ii, 306.
Hee, *A.* See *E. F.* **Terroine**.
Heermann, *P.*, action of ultra-violet light on "dye and textile fibre" systems, ii, 144.
Heess, *W.* See *W.* **Küster**.
Hefner, *H.* See *W.* **Autenrieth**.
Hefter, *J.*, organic bases in urine, i, 1350.
decomposition of carnosine by intestinal bacteria, and its relation to autointoxication, i, 1362.
Hefti, *F.*, and *W.* **Schilt**, preparation of [citric] esters, i, 394.
Heiduschka, *A.*, and *E.* **Komm**, relation between constitution and taste of α-amino-acids, i, 522.
relation between constitution and taste of α-amino-acids. II. Relation between "degree of sweetness" and concentration of aqueous solutions of amino-acids, i, 1389.
Heiduschka, *A.*, and *C.* **Pryiki**, isolation of lignoceric acid from arachis oil, i, 229.
Heilbron, *I. M.*, *T. A.* **Forster**, and *A. B.* **Whitworth**, interaction of ethyl acetoacetate and *o*-hydroxydistyryl ketones. II., i, 1284.
Heilbron, *I. M.*, *F. N.* **Kitchen**, *E. B.* **Parkes**, and *G. D.* **Sutton**, chemical reactivity and conjugation. II. Reactivity of the 2-methyl group in the 4-quinazolone series, i, 1320.
Heilbron, *I. M.*, *G. H.* **Walker**, and *J. S.* **Buck**, styrylbenzopyrylium salts. V. Distyryl derivatives of 7-hydroxy-2:4-dimethylbenzopyrylium chloride, i, 694.
Heilbron, *I. M.* See also *W. H.* **Cooke**, and *G. H.* **Walker**.
Heilbrunn, *V.*, electrical charges of living cells, i, 1492.
Heilingötter, *R.*, separation of small quantities of calcium from large amounts of magnesium, ii, 437.
Heilmann, *R.* See *R.* **Locquin**.
Hein, *F.* [with *E.* **Petzchner**, *K.* **Wagler**, and *F. A.* **Segitz**], behaviour as salts of alkali alkyls dissolved in metal alkyls, ii, 217.
Hein, *F.*, and *K.* **Wagler** [with *W.* **Retter**], preparation of symmetrical organic compounds of mercury, i, 1341.
Hein, *F.*, and *H.* **Meininger**, metallo-organic bases, ii, 842.
Heinelt, *H.*, phosphorus and calcium metabolism in an adult male, i, 1497.
Heinlein, *H.*, melanotic pigments, i, 449.
Heinlein, *H.* See also *H.* **Reinwein**.
Heisenberg, *W.*, anomalous Zeeman effects, ii, 3.
influence of the deformation of ions on optical and chemical constants, ii, 16.
quantum theory of multiplet structure and the anomalous Zeeman effect, ii, 729.
Hektoen, *L.*, and *K.* **Schulof**, precipitin reaction of thyroglobulin, i, 1345.
Hektoen, *L.*, and *W. H.* **Welker**, precipitin reactions of serum proteins, i, 323.
precipitin reaction of Bence-Jones' protein, i, 328.
precipitin reactions of fibrinogen, i, 1487.
Helberg, *H.*, freezing-point curve of aqueous sodium nitrite solutions, ii, 971.
Helbig, *M.* See *E.* **Knickmann**.
Heldermann, *W. D.* See *E.* **Cohen**.
Hele, *T. S.* See *H. I.* **Coombs**.
Helfer, *L.* See *A.* **Pictet**.
Helferich, *B.*, and *J.* **Becker**, synthesis of a disaccharide-glucoside, i, 9.
Helferich, *B.*, and *H.* **Dehe**, triphenylcarbinol hydrochloride, i, 1269.
Helferich, *B.*, and *F. A.* **Fries**, hydroxyaldehydes. VIII., i, 1039.
Helferich, *B.*, *L.* **Moog**, and *A.* **Jünger**, replacement of reactive hydrogen atoms in sugars, hydroxy- and amino-acids by the triphenylmethyl residue, i, 790.
Helferich, *B.*, and *W.* **Schäfer**, hydroxyaldehydes. VII., i, 7.
Helferich, *B.*, *G.* **Sprock**, and *E.* **Besler**, *d*-glucose ε-dichlorohydrin, i, 792.
Helleberg, *K.* See *E.* **Melin**.
Hellenbrand, *W.*, and *G.* **Joachimoglu**, antiseptic action of mercuric chloride in solvents of different dielectric constants, i, 466.
Heller, *G.*, organic thiosulphates, i, 313.
Heller, *G.* [with *A.* **Buchwaldt**, *R.* **Fuchs**, *W.* **Kleinicke**, and *J.* **Kloss**], tautomerisation phenomena in heterocyclic compounds, i, 1323.
Heller, *G.* [with *E.* **Göring**, *J.* **Kloss**, and *W.* **Köhler**], quinazolones from acylated *o*-aminobenzhydrazides, i, 1322.
Heller, *G.*, and *K.* **Müller-Bardorff**, *o*-4-bromo-*m*-toluoylbenzoic acid, i, 546.
Heller, *G.*, and *G.* **Spielmeyer**, isomerism of anilino-*m*-nitrophenylacetonitrile, i, 814.
indazoles from *o*-nitromandelonitrile, i, 838.

Heller, *G.*, and *R.* **Fuchs**, new isomerism in the isatin series, i, 1166.
Heller, *J.* See *J. K.* **Parnas**.
Heller, *V. G.*, *C. H.* **McElroy**, and *B.* **Garlock**, effect of bacterial flora on biological test for vitamin-*B*, i, 1365.
Hellmann, *H.*, and *H.* **Zahn**, new method for determining the dielectric constants of electrolytes which conduct well, ii, 1117.
Hellweg, *H.* See *H.* **Braune**.
Helman, *F. D.* See *A. F.* **Hess**.
Helmholz, *K.* See *G. y* **Roig**.
Helmick, *P. S.*, quantity of ultra-violet light energy required to render developable a grain of photographic silver bromide, ii, 143.
Helmrich, *G.* See *W.* **Eller**.
Helwig, *H.* See *K.* **Lindner**.
Henderson, *G. G.* See *J. M.* **Robertson**.
Henderson, *G. H.*, capture and loss of electrons by α-particles, ii, 922.
Henderson, *J. M.*, effect of irradiation and diet on calcium and phosphorus metabolism, i, 485.
Henderson, *J. M.* See also *J. B.* **Orr**.
Henderson, *L. J.*, and *C. D.* **Murray**, blood as a physicochemical system. III. Deductions concerning the capillary exchange, i, 1483.
Hendricks, *S. B.* See *L.* **Pauling**.
Hendrix, *B. M.*, and *D. B.* **Calvin**, loss of basis in diuresis and its effect on the alkali reserve of the blood, i, 1350.
Hendrixson, *W. S.*, action of some oxidising agents on sulphite and its [volumetric] determination with iodate, ii, 712.
action of some oxidising agents on sulphite. II., ii, 1001.
Hendry, *J. L.* See *E. J.* **Cohn**.
Henglein, *F. A.*, thermal expansion of alkali-metal halides at low temperatures. I. and II., ii, 375, 950.
molecular volumes of crystals, ii, 477.
thermal expansion of crystals and chemical constitution, ii, 935.
Henley, *R. R.*, mechanism of the reaction between formaldehyde and serum proteins, i, 716.
Henning, *F.*, and *W.* **Hause**, micropyrometer of the spectrometer type, ii, 427.
Henri, *V.*, and *C.* **Fromageot**, absorption spectra of pyruvic acid; existence of tautomeric forms, ii, [illegible]
Henri, *V.*, and *M. C.* **Teves**, absorption spectrum and constitution of sulphur vapour, ii, 19, 87.
Henri, *V.* See also *J.* **Errera**.
Henrich, *F.*, and *F.* **Götz**, dyes and other derivatives of cresorcinol, i, 913.
Henrijean, *E.*, and *W.* **Kopaczewski**, colloids and mineral waters, ii, 291.
Henry, *D. C.*, and *V. A.* **Morris**, influence of anions on the coagulation of a negative colloidal sol, ii, 34.
Henry, *T. A.*, and *H.* **Paget**, chenopodium oil. II. The hydrocarbon fraction, i, 1162.
Henry, *T. A.*, *T. M.* **Sharp**, and *H. C.* **Brown**, bactericidal action of some organic compounds of mercury, i, 1006.
Henry, *T. A.* See also *J. A.* **Goodson**, and **Wellcome Foundation, Ltd.**
Hensel, *A.* See *H.* **Stobbe**.
Hensle, *A.* See *G.* **Scheuing**.
Henstock, *H.*, action of natural waters on copper, ii, 696.
Hentschel, *H.*, lactic acid "fatigue maximum" of different muscles of the frog, i, 728.
Hentschel, *H.* See also *G.* **Embden**.
Henwood, *A.*, *R. M.* **Garey**, *W.* **Goldberg**, and *E.* **Field**, generation of hydrogen sulphide, ii, 705.
Henze, *H. R.* See *A. J.* **Hill**.
Hepburn, *J. R. I.*, mechanism of the formation of malachite from basic cupric carbonate, ii, 696.
Hepburn, *J. S.*, and *R. H.* **Stroh**, chemistry of alkatan, i, 108.
Heppenstall, *J. A.*, and *W. J.* **Shutt**, conditions of the appearance of anode effect in the electrolysis of fused chlorides, ii, 45.
Herasymenko, *P.*, solutions of mannitoaluminates, i, 774.
dropping mercury cathode. IV. Changes in overvoltage with the concentration of hydrogen ions, ii, 675.
reduction of uranyl salts by means of a dropping mercury cathode, ii, 695.
Herboth, *L.*, glucoside content of woodruff (*Asperula odorata*), i, 760.
use of aminosulphonic acid as a standard in volumetric analysis, ii, 155.
Herbst, *H.*, influence of salt content on the adsorptive power of an active charcoal and a review of the chief properties of the more important technical active charcoals, ii, 956.
Heresco. See **Banu**.

Hérissey, *H.*, presence of a glucoside hydrolysed by emulsin in *Baillonia spicata*, H. Bn., and its products of hydrolysis, i, 147.
chemical composition of *Asperula odorata* (woodruff); extraction and properties of a new glucoside, asperuloside, i, 1165.
asperuloside, a glucoside obtained from odoriferous *Asperula*, i, 1369.
Hérissey, *H.*, and *J.* **Cheymol**, extraction and properties of gein, the glucoside containing eugenol, of *Geum urbanum*, L., i, 487.
sugars obtained from gein, i, 1383.
Hermann, *L.* See *A.* **Schaarschmidt**.
Hermans, *P. H.*, constitution of the boric acids and some of their derivatives, i, 500.
solubility curves in the systems, mannitol-boric acid-water and *cis*-tetrahydronaphthalene-1:2-diol-boric acid-water at 25°, i, 501.
adsorption of the two stereoisomeric hydrobenzoins on charcoal, ii, 31.
reaction of some glycols with acetone, ii, 50.
Hermans, *P. H.* See also *J.* **Berk**, and *H.* **Gelissen**.
Hermersdörfer, *C.* See *A.* **Scheunert**.
Hermsen, *W.* See *H.* **Wieland**.
Herr, *W. N.* See *F. O.* **Anderegg**.
Herrmann, *F.*, and *M.* **Rohner**, colloidal theory of hæmolysis, i, 1202.
Herrmann, *K.*, influence of the gas content on the photo-electric behaviour and electrical conductivity of platinum, ii, 947.
Herschkovitsch, *M.*, volumetric determination of copper with potassium iodide, ii, 904.
Herschmann, *O.* See *S.* **Fränkel**.
Hershey, *R. L.* See *R. T.* **Haslam**.
Hertz, *G.*, resonance lines of neon, ii, 723.
Hertz, *G.*, and *R. K.* **Kloppers**, excitation and ionisation potentials of the noble gases, ii, 342, 730.
Hertz, *G.*, and *J. C. S. de* **Visser**, excitation of spectral lines by electron impact. II., ii, 338.
Hertzmann, *A. B.*, and *H. C.* **Bradley**, autolysis. XIII. Kinetics of autolytic mechanism, i, 102.
Herz, *W.*, temperatures of corresponding densities, ii, 494.
validity of gas equations. I., ii, 496.
saturation pressure of liquids at corresponding densities, ii, 850.
equal viscosities, ii, 1049.
density and temperature. V., ii, 1141.
Herz, *W.*, and *W.* **Bloch**, physico-chemical investigations on compounds of the *cyclo*hexane series, ii, 98.
Herz, *W.*, and *E.* **Martin**, solubility of lead chloride in acetic acid, ii, 283.
Herz, *W.*, and *A.* **Wegner**, relative internal friction, ii, 482.
Herz, *W.* See also *R.* **Lorenz**.
Herzberg, *G.* See *H.* **Kautsky**.
Herzer, *F.* See *L.* **Vanino**.
Herzfeld, *E.*, and *W.* **Engel**, lipases from the thyroid stable to quinine and atoxyl, i, 201.
Herzfeld, *E.*, and *A.* **Haemmerli**, bile in metabolism; determination of bile acids, i, 722.
Herzfeld, *K. F.*, vapour pressures and miscibilities of binary liquid mixtures, ii, 1143.
Herzfeld, *K. F.*, and *K. L.* **Wolf**, classical dispersion formula in the case of monatomic gases and vapours, ii, 182, 478.
dispersion of potassium chloride and sodium chloride, ii, 1119.
Herzog, *R. O.*, ethers of polysaccharides and hydroxy-acids, i, 371.
constitution of proteins, i, 450.
constitution of cellulose, i, 639.
cellulose fibre, i, 1045.
Herzog, *R. O.*, and *H. W.* **Gonell**, Röntgen spectrographic comparison of tunicin and lichenin with cellulose, i, 371.
nature and production of inorganic structures in the organism, i, 718.
collagen, i, 1488.
Herzog, *R. O.*, and *K.* **Weissenberg**, the molecule in crystals, ii, 942.
Herzog, *W.*, relation between resin-forming capacity and chemical constitution, i, 386.
Heslinga, *J.*, determination of carbon, hydrogen, and nitrogen in organic compounds, ii, 65.
Hess, *A. F.*, and *F. D.* **Helman**, phosphatide and total phosphorus content of human and cow's milk, i, 1204.
Hess, *A. F.*, and *M.* **Weinstock**, antirachitic properties imparted to inert fluids and to green vegetables by ultra-violet irradiation, i, 212.
antirachitic properties imparted to inert substances by ultra-violet irradiation, i, 750.
antirachitic value of irradiated cholesterol and phytosterol. II. Change in biological activity. III. Chemical change shown by absorption spectra, i, 1020.

Hess, *A. F.*, *M.* **Weinstock**, and *F. D.* **Helman**, antirachitic value of irradiated phytosterol and cholesterol. I., i, 750.
Hess, *K.* [action of alkali on ethyl alcohol and the "nitric oxide reaction" of W. Traube], i, 58.
cellulose, i, 118.
hydro- and oxy-cellulose, i, 519.
mercerisation of cellulose, ii, 782.
Hess, *K.* [with *W.* **Weltzien** and *H.* **Nakamura**], determination of the reducing power of cellulose products, ii, 245.
Hess, *K.*, and *R.* **Bappert**, syntheses in the undecane series, i, 349.
hygrine alkaloids. V. Degradation of cuskhygrine to undecane and undecan-6-ol, i, 424.
Hess, *K.*, and *R.* **Grau**, asymmetric tervalent nitrogen atom. V. Conhydrine and methyl*iso*pelletierine, i, 425.
Hess, *K.*, and *E.* **Messmer**, composition of solutions of cellulose in ammoniacal copper oxide, ii, 662.
Hess, *K.*, *E.* **Messmer**, and *N.* **Ljubitsch**, cellulose. XVII. Characterisation of cellulose preparations, i, 1246.
Hess, *K.*, and *G.* **Salzmann**, octaethylcellobiose and its acetolysis, compared with cellobiose and octa-acetylcellobiose, i, 1383.
Hess, *K.*, *G.* **Schultze**, and *E.* **Messmer**, cellulose. XVI. Crystalline cellulose acetates. II., i, 1245.
Hess, *K.*, and *W.* **Weltzien**, cellulose. XI. Trimethylcellulose-*A* and its scission, i, 517.
Hess, *K.*, *W.* **Weltzien**, and *R.* **Singer**, cellulose. XIII. Acetolysis of cellulose. I., 641.
Hesse, *A. R. F.* See *R.* **Willstätter**.
Hessel, *F. A.* See *H.* **Gault**.
Hetényi, *G.* See *A. von* **Fejér**.
Hetterschij, *C. W. G.* See *E.* **Cohen**.
Heuberger, *J.* See *J. A.* **Hedvall**.
Heubner, *W.*, calcium content of organs of cats treated with calcium [salts]. V., i, 613.
Heuck, *C.* See *H.* **Lecher**.
Heumann, *J.* See *P. A.* **Thiessen**.
Heuser, *E.*, alkali-cellulose, i, 119.
depolymerisation of cellulose, i, 1387.
Heuser, *E.*, and *R.* **Bartunek**, alkali-cellulose. II., i, 520.
Heuser, *E.*, and *A.* **Brotz**, chemical nature of deciduous woods, i, 889.
Heuser, *E.*, and *W.* **Niethammer**, alkali-cellulose. I., i, 520.
Heuser, *E.*, and *W.* **Schott**, degradation of cellulose by formic acid, i, 370.
Hevesy, *G. von*, atomic weights of zirconium and hafnium, ii, 255.
discovery and properties of hafnium, ii, 708.
regularity in the rare earth and titanium groups, ii, 938.
Hevesy, *G. von*, and *V.* **Berglund**, density of zirconium and hafnium oxides, ii, 25.
Hevesy, *G. von*, *J. A.* **Christiansen**, and *V.* **Berglund**, solubility of the double fluorides of zirconium and hafnium, ii, 505.
Hevesy, *G. von*, and *V. T.* **Jantzen**, hafnium content of zirconium ores. II., ii, 430.
Hevesy, *G. von*, and *K.* **Kimura**, phosphates of zirconium and hafnium, ii, 1085.
solubilities of the phosphates of zirconium and hafnium, ii, 1147.
Hevesy, *G. von*, and *E.* **Madsen**, separation of hafnium from zirconium, ii, 425.
Hevesy, *G. von*, and *A.* **Obrutsheva**, self-diffusion in solid metals, ii, 500.
Hewetson, *S. W.* See *O. L.* **Brady**.
Hewitt, *L. F.*, diazo reaction in uræmic sera, i, 726.
Hewitt, *L. F.*, and *J.* **Kenyon**, dependence of rotatory power on chemical constitution. XXV. Three optically active alcohols containing a phenyl group and some esters derived therefrom, i, 914.
Heydweiller, *F.* See *H.* **Lecher**.
Heyn, *W.* See *F.* **Straus**.
Heyrovský, *J.*, electrolysis at the mercury dropping cathode, ii, 43, 133.
significance of the electrode potential, ii, 211.
electrode, contact, and electro-kinetic potentials of galvanic cells, ii, 404.
solvation of ions and the electrode potential, ii, 544, 672.
dropping mercury cathode. I., ii, 673.
dropping mercury cathode. III. Theory of over-potential, ii, 675.
analytical chemistry of indium, ii, 717.
physical significance of electrolytic solution tension, ii, 793.
Heyrovský, *J.*, and *M.* **Shikata**, dropping mercury cathode. II. The polarograph, ii, 674.
Heyse, *M.* See *Hans* **Fischer**.
Hibbard, *P. L.*, determination of nitrates, ii, 240.
Hibbert, *E.* See *E.* **Knecht**.

Hibbert, *H.*, and *C. P.* **Burt**, benzoyl-hydroperoxide [perbenzoic acid]; preparation and application to organic synthesis, i, 1147.
Hibino, *S.*, conditions influencing production of colouring matter of *Monascus purpureus*, Went, i, 1118.
Hickethier, *C. F.*, and *A.* **Jacobucci**, presence of iodate in surface waters, ii, 1197.
Hickinbottom, *W. J.* See *G. T.* **Morgan**.
Hicks, *C. S.*, relationship of thyroxin to tryptophan, ii, 473.
Hicks, *W. M.*, Sommerfeld's and Lundé's rules for classification of terms and Zeeman patterns in spectra, ii, 3.
generally accepted explanation of the Zeeman triplet on a quantum basis, ii, 729.
Hidnert, *P.*, thermal expansion of aluminium and various important aluminium alloys, ii, 375.
Hieber, *W.* [with *R.* **Becker**, and *R.* **Wagner**], ring formation in additive compounds. II. Constitution of compounds of stannic chloride with polycarboxylic esters; compounds of stannic halides with isomeric diamines, i, 1325.
Hiebert, *P. G.* See *O.* **Maass**.
Hiemesch, *H.* See *D.* **Vorländer**.
Hieulle, *A.* See *R.* **Fosse**.
Higginbotham, *L.*, *A.* **Lapworth**, and *C.* **Simpson**, interaction between ethyl ethylidenemalonate and anilinophenylacetonitrile, i, 35.
Higginbotham, *L.* See also *R. G.* **Fargher**.
Hilberg, *H.* See *E.* **Becker**.
Hilditch, *T. P.* See *E. F.* **Armstrong**.
Hildt, *E.*, analysis of mixtures of sugars, ii, 244.
Hilger, *J.* See *Hans* **Fischer**.
Hill, *A. E.*, and *J.* **Mosbacher**, binary system consisting of *o*-cresol and *p*-cresol, ii, 1161.
Hill, *A. J.*, and *H. R.* **Henze**, condensation reactions of cyclic ketones. I. Action of isatin and isatin α-chloride on certain hydantoins, i, 805.
Hill, *A. J.* See also *A. W.* **Francis**.
Hill, *A. V.* See *K.* **Furusawa**.
Hill, *E. E.* See *A. G.* **Tool**.
Hill, *L.* See *T. A.* **Webster**.
Hill, *R.*, hæmoglobin in relation to other metallo-hæmatoporphyrins, i, 994.
Hill, *R. A.*, photochemical decomposition of gaseous sulphur dioxide, ii, 56.
Hill, *T. G.* See *P.* **Haas**.
Hiller, *A.*, *G. C.* **Linder**, and *D. D. Van* **Slyke**, reducing substances of the blood, i, 1200.
Hilmer, *H.* See *Hans* **Fischer**.
Hingst, *G.* See *O.* **Mumm**.
Hinsberg, *O.*, derivatives of *iso*-β-naphthyl-3:4-dihydroxy-α-naphthylsulphone, i, 1062.
Hinshelwood, *C. N.*, critical increment of chemical reactions, ii, 874.
Hinshelwood, *C. N.*, and *R. E.* **Burk**, thermal decomposition of ammonia upon various surfaces, ii, 691.
Hinshelwood, *C. N.*, and *C. R.* **Prichard**, comparison between the homogeneous thermal decomposition of nitrous oxide and its heterogeneous catalytic decomposition on the surface of platinum, ii, 310.
catalytic decomposition of nitrous oxide on the surface of gold: a comparison with the homogeneous reaction, ii, 567.
relation of homogeneous to catalysed reactions; catalytic decomposition of hydrogen iodide on the surface of gold, ii, 981.
interaction of carbon dioxide and hydrogen on the surface of tungsten, ii, 983.
Hinshelwood, *C. N.*, and *C. W.* **Thornton**, energy distribution law appropriate to the theory of chemical reaction velocity, ii, 1167.
Hinshelwood, *C. N.* See also *C. R.* **Prichard**.
Hiraidzumi, *T.* See *S.* **Komatsu**.
Hiratsuka, *E.*, occurrence of tryptophan in silk fibroin, i, 836.
Hirsch, *B.* See *O.* **Ruff**.
Hirsch, *E. F.*, adsorption of cresol-red by serum in spectrophotometric determination of p_H, i, 606.
Hirsch, *J.*, biochemistry of *Vibrio cholerœ*, i, 479.
Hirschberg, *E.* See *H.* **Winterstein**.
Hirschfelder, *A. D.* See *H. H.* **Jensen**, and *T. P.* **Quigley**.
Hirsch-Kauffmann, *H.*, determination of lactic acid in animal organs, i, 96.
Hirschkind, *W.*, analysis of xanthate, ii, 1212.
Hirsch-Mamroth, *P.*, and *H.* **Rindfleisch**, pepsin determinations on gastric juice by the method of Boas, i, 1213.
Hirst, *E. L.*, *A. K.* **Macbeth**, and *D.* **Traill**, action of hydrazine on halogen derivatives of malonamides and acetoacetic esters, i, 1251.
Hirst, *E. L.*, and *G. J.* **Robertson**, constitution of the normal monosaccharides. II. Arabinose, i, 364.
Hirst, *E. L.* See also *J.* **Pryde**.
Hirst, *H. S.*, thermal decomposition of nitrogen pentoxide, ii, 554.

Hirzel, *H.*, preparation of benzylresorcinol, i, 393.
Hissink, *D. J.*, base exchange in soils, i, 222.
saturation capacity of mineral soils, i, 490.
Hissink, *D. J.*, and *J. van der* **Spek**, acidity of soils, i, 1525.
Hissink, *D. J.* See also *R. M.* **Barnette**.
Hitchcock, *D. L.*, protein films on collodion membranes, ii, 1054.
Hjalmar, *E.*, and *M.* **Siegbahn**, anomalous dispersion in the field of *X*-rays, ii, 92.
Hjort, *A. M.*, *S. C.* **Robison**, and *F. H.* **Tendick**, active extract from external parathyroid glands of the ox, i, 1364.
Hoagland, *D. R.*, effect of the plant on the reaction of the culture solution, i, 1368.
Hoagland, *D. R.* See also *W. C.* **Dayhuff**.
Hocart, *R.* See *H.* **Copaux**.
Hochstetter, *H. von.* See *K.* **Freudenberg**.
Hock, *A.* See *H.* **Niklas**.
Hock, *L.*, Joule effect in rubber, ii, 969.
Hodel, *E.*, biochemistry of the alkaline earths, i, 1496.
Hodel, *E.* See also *H.* **Rupe**.
Hodel, *P.*, and *N.* **Neuenschwander**, fermentation and iron salts, i, 615.
Hodson, *H. H.*, action of lead monoxide on *oo'*-dithioaniline; an example of simple thiazine formation, i, 596.
behaviour of the sulphides of sodium in aqueous and alcoholic media; a contribution towards elucidating the structure of sulphide dyes, i, 1104.
nitro compounds with special reference to the nitration of *m*-chloronitrobenzene and *p*-chlorotoluene, i, 1397.
Hodgson, *H. H.*, and *H. G.* **Beard**, 2-nitro-*m*-cresol and 2-amino-*m*-cresol, i, 540.
bromo derivatives of *m*-hydroxybenzaldehyde, i, 674.
Hodgson, *H. H.*, and *F. H.* **Moore**, nitration of *m*-chlorophenol, i, 1144.
nitrosation of phenols. II. Nitrosation of 3-bromo-, 2-bromo-, 3-iodo-, and 2-iodo-phenol; evidence for the nitroso formula of 4-nitrosophenol, i, 1408.
Hodgson, *H. H.*, and *J. H.* **Wilson**, reactions of sodium mono-, di-, and tri-sulphides with 1-chloro-2-nitro-, 1-chloro-4-nitro-, and 1:4-dichloro-2-nitro-benzene, i, 532.
Hodler, *A.* See *A.* **Magnus**.
Höber, *R.*, theory of the bioelectric cell, ii, 131.
Hoefer, *T.* See *R.* **Schwarz**.
Hoeffel, *G. N.*, and *M. E.* **Moriarty**, amino-acid content of blood of infants and children, i, 1484.
Högler, *F.*, and *K.* **Ueberrack**, sugar content of blood-corpuscles, i, 453.
Hoehn, *E.*, 4:5-diamino-*o*-benzoquinone and derivatives, i, 938.
Hoehn, *E.* See also *F.* **Kehrmann**.
Hoek, *H.* See *H.* **Wieland**.
Höllen, *J.*, colostrum, i, 1490.
Hölzl, *F.* See *Robert* **Müller**.
Hönig, *R.* See *Robert* **Müller**.
Hönigschmid, *O.*, and *M.* **Steinheil**, atomic weight of silicon; analysis of silicon chloride, ii, 174.
Hönigschmid, *O.*, and *E.* **Zintl**, atomic weight of hafnium, ii, 255.
atomic weight of hafnium; analysis of hafnium bromide, ii, 347.
atomic weight of the gold obtained from mercury by Miethe and Stammreich, ii, 924.
Hönigschmid, *O.*, *E.* **Zintl**, and *F.* **González**, atomic weight of zirconium, ii, 174.
Hönl, *H.*, and *F.* **London**, intensities of band lines, ii, 1024.
Hönl, *H.* See also *A.* **Sommerfeld**.
Hoenshel, *H. D.* See *W. M.* **Latimer**.
Hoeven, *B. J. C. van der.* See *P. A.* **Levene**.
Hoeven, *C. van der*, volumetric determination of sugar by Schoorl's process, ii, 331.
Hoff, *W.* See *J. A.* **Wilkinson**.
Hoffarth, *H.* See *K.* **Schaum**.
Hoffert, (*Miss*) *D.* See (*Mrs.*) *I. S.* **Maclean**.
Hoffman, *A. L.* See *L.* **Neuffer**.
Hoffman, *W. F.*, sulphur in proteins. II. Effect of mild alkaline hydrolysis on hair, i, 1480.
Hoffman, *W. F.*, and *R. A.* **Gortner**, proteins. I. Prolamines: their chemical composition in relation to acid and alkali binding, i, 1479.
proteins. II. Alkali binding; comparison of the electrometric titration of proteins and of phosphoric acid with sodium and calcium hydroxides, ii, 1011.
electrodialysis of agar; preparation of the free agar acid, ii, 1158.
Hoffman, *W. F.* See also *R. A.* **Gortner**, and *J. A.* **Harris**.
Hoffman, *W. S.*, isolation of adenine nucleotide from blood, i, 711.
Hoffmann, *F. K.* See *E.* **Koenigs**.

Hoffmann, *G.*, penetrating radiations observed at sea-level, ii, 1110.
Hoffmann, *H.* See *D.* **Vorländer.**
Hoffmann, *J.* See *G.* **Schroeter.**
Hoffmann, *W.* See *A.* **Kötz.**
Hoffmann-La Roche & Co., *F.*, preparation of *O-O*-diacyl derivatives of diphenolisatin and its products of substitution in the phenol and isatin groups, i, 66.
preparation of readily soluble compounds of *C*-substituted dialkyl- and arylalkyl-barbituric acids, i, 300.
Hofmann, *F.*, melting point of platinum, ii, 99.
Hofmann, *F. B.*, and *A.* **Kohlrausch**, determination of smell thresholds, i, 732.
Hofmann, *H.* See *K.* **Elbs.**
Hofmann, *K.*, heterogeneous dissociation equilibria of water vapour and of carbon dioxide over iron and its oxides, ii, 537.
mechanism of reduction of iron oxides in a current of gas, ii, 991.
Hofmann, *K. A.*, and *A.* **Dolde**, acceleration of the catalysis of mixtures of hydrogen and oxygen by oxygen carriers and by the alternating current, ii, 139.
Hofmann, *K. A.*, *F.* **Hartmann**, and *K.* **Nagel**, action of ammonium chloride vapour on metals and the conformity of ammonium salts with hydroxonium salts as acids, ii, 685.
Hofmeier, *H.* See *A.* **Schaarschmidt.**
Hofstetter, *M.*, detection of chlorophyll degradation products in urine, i, 460.
Hogben, *L. T.* See *C. F. A.* **Pantin.**
Hogness, *T. R.*, and *E. G.* **Lunn**, ionisation of hydrogen by electron impact as interpreted by positive ray analysis, ii, 839.
Hohlfeld, *E.* See *O.* **Ruff.**
Holben, *F. J.* See *J. W.* **White.**
Holbøll, *S. A.* See *E.* **Fock**, and *C.* **Lundsgaard.**
Holborn, *L.*, and *J.* **Otto**, isotherms of several gases between +400° and −183°, ii, 851.
Holde, *D.*, and *R.* **Gentner**, linoleic acid and its anhydride, i, 882.
anhydrides of saturated fatty acids containing an even number of carbon atoms (C_8—C_{18}), i, 1005.
stability of the anhydrides of saturated fatty acids towards atmospheric moisture and sodium carbonate solution, i, 1035.
Holde, *D.*, and *A.* **Gorgas**, additive products of iodine monobromide and hypoiodous acid with unsaturated compounds. I., i, 882.
Holde, *D.*, and *M.* **Selim**, thallium salts of the higher fatty acids, i, 504.
Holde, *D.*, and *K.* **Takehara**, thallous salts of lauric and myristic acid, i, 1233.
Holden, *G. W.* See *W. H.* **Hatcher.**
Holden, *H. F.*, presence of glutathione in the corpuscles of mammalian blood, i, 1484.
Holgersson, *S.*, and *E.* **Sedström**, experimental investigation of the lattice structure of some alloys, ii, 20.
Holland, *F.*, measurement of "negative" oxygen-bands in the visible spectrum region, ii, 1113.
Holleman, *A. F.* See *V. S. F.* **Berckmans.**
Holler, *H. D.*, method of studying electrode potentials and polarisation, ii, 793.
Holló, *J.*, and *S.* **Weiss**, clinical method for determining the bicarbonate content of blood plasma, i, 95.
acid–base equilibrium. II. Determination of the hydrogen-ion concentration of the blood. III. Determination of alveolar carbon dioxide tension. IV. Titrimetric determination of hydrogen carbonate in the blood, i, 709.
Holluta, *J.*, mechanism of the reduction of permanganate and its physico-chemical basis. IX. Reduction of permanganate passing from neutral to alkaline solution, ii, 49.
mechanism of the reduction of permanganate and its physico-chemical basis. X., ii, 407.
decomposition of permanganate, ii, 422.
Holluta, *J.*, and *A.* **Martini**, autocatalytic reaction: ferric chloride–sodium thiosulphate, ii, 215.
kinetics and mechanism of reaction of the reduction of ferric salts by thiosulphate in weakly acid solution, ii, 305.
influence of hydrogen ions on the mechanism of the reduction of ferric salts by sodium thiosulphate, ii, 702.
Holluta, *J.*, and *J.* **Obrist**, oxidimetric determination of manganese in hydrofluoric acid solution. II., ii, 160.
Holm, *E.* See *C.* **Füchtbauer.**
Holm, *S.*, and *H.* **Tómasson**, protein determination in 0·1 c.c. serum, i, 1485.

Holmberg, *B.*, stereochemical studies. IX. Dithiocarbomalic acids, i, 1238.

Holmberg, *B.*, and *Emil* **Müller**, stereochemical studies. VIII. Optically active *aa'*-dibromoadipic acids, i, 1236.

Holmberg, *B.*, and *W.* **Rosén**, stereochemical studies. X. *l-O*-Menthylthiourethanes, i, 1291.

Holmes, *B. E.*, and *E. G.* **Holmes**, brain metabolism. I. Carbohydrate metabolism, i, 1001.

Holmes, *B. E.* See also *E. G.* **Holmes**.

Holmes, *E.* See *G. T.* **Morgan**.

Holmes, *E. G.*, and *B. E.* **Holmes**, brain metabolism. II. Carbohydrate metabolism, i, 1495.

Holmes, *E. G.* See also *B. E.* **Holmes**.

Holmes, *E. L.*, and *C. K.* **Ingold**, alternating effect in carbon chains. III. Directive efficiencies of oxygen and nitrogen atoms in aromatic substitution, i, 1142.

Holmes, *H. N.*, and *J. A.* **Anderson**, new type of silica gel, ii, 518.

Holmes, *H. N.*, and *H. A.* **Williams**, iodine as an emulsifying agent, ii, 531.

polar emulsifying agents, ii, 1156.

Holmes, *L. H. A.*, and *E. E.* **Turner**, potassium antimonoxalate, ii, 1130.

Holmes, *R. M.*, effect of light on the thermoelectric power of selenium, ii, 811.

Holmes, *R. S.* See *W. O.* **Robinson**.

Holmes, *W. C.*, influence of constitutional variation on the absorption and stability to hydrogen ions of certain halogenated derivatives of fluorescein, i, 255.

spectrophotometric identification of dyes. III. Basic violets of the triphenylmethane group, ii, 1212.

Holmes, *W. C.*, and *E. F.* **Snyder**, spectrophotometric determination of hydrogen-ion concentrations and of the apparent dissociation constants of indicators. II. Thymol-blue. III. Bromocresol-green, ii, 325.

spectrophotometric determination of hydrogen-ion concentrations and of the apparent dissociation constants of indicators. IV. Sodium *a*-naphthol-2-sulphonate indophenol, ii, 999.

Holmsen, *J.* See *E.* **Langfeldt**.

Holschneider, *F.* See *H.* **Lecher**.

Holt, *L. E.*, *jun.*, calcification. III. Equilibria concerned with calcification of bone, i, 1209.

Holt, *L. E.*, *jun.*, *V. K.* **LaMer**, and *H. B.* **Chown**, calcification. I. Solubility product of secondary and tertiary calcium phosphate. II. Delayed equilibrium between the calcium phosphates and its biological significance i, 1209.

Holtsmark, *J.*, and *B.* **Trumpy**, broadening of spectral lines. III., ii, 338.

Holtz, *F.* [ultra-balance], ii, 1091.

Holtz, *F.*, and *W. H. F.* **Kuhlmann**, ultra-balance, ii, 319.

Holtz, *F.*, and *Helmut* **Müller**, basic constituents of the rye plant: the ergot question, i, 488.

Holtz, *F.*, and *F.* **Thielmann**, extractives of *Arbutia pustulosia*, i, 720.

Holtz, *F.* See also *D.* **Ackermann**.

Holtzelaw, *J. B.* See *C.* **Barkenbus**.

Holverscheit, *W.* See *W.* **Biltz**.

Holweck, *F.*, exact measurements of spectral frequencies in the region between light and *X*-rays (*L*$_{III}$-discontinuities of Cl, S, P, Si, Al), ii, 336.

exact determination of characteristic atomic frequencies in the spectral region between visible light and *X*-rays, ii, 728.

Holzlöhner, *E.*, action of Na- and Ca-ions on frog's heart, i, 1500.

Honda, *K.*, definitions of steel and cast iron, ii, 378.

formation of martensite in carbon steels, ii, 972.

Honda, *K.*, and *T.* **Ishigaki**, law of depression of freezing points in metallic alloys, ii, 1050.

Honda, *K.*, and *Y.* **Okubo**, coefficients of thermal expansion for aluminium alloys and alloys of nickel–iron and cobalt–iron, ii, 104.

Honeyman, *A. J. K.* See *J. H.* **Andrew**.

Honeywell, *E. M.*, and *H.* **Steenbock**, synthesis of vitamin-*C* by germination, i, 751.

Honnelaitre, *A.*, molybdic complexes, i, 509.

Honnelaitre, *A.* See also *E.* **Darmois**.

Honsig, *E.* See *W.* **Fuchs**.

Hooft, *F. V.* See *C. B. van* **Niel**.

Hooft, *Van 't*, production and occurrence of acetylmethylcarbinol in vinegar, i, 772.

Hooker, *H. D.*, changes produced in apple trees by various types of pruning, i, 1367.

Hoop, *L. de*, and *J. A. van* **Laer**, diastatic breakdown of starch, i, 470.

Hooper, *D.*, cinchonine as a tannin precipitant, with special reference to the analysis of cutch and gambier, ii, 443.
Hope, *E.* See *R. H.* **Griffith.**
Hope, *W. B.* See *J. B.* **Ferguson.**
Hopfield, *J. J.*, chlorine spectrum in the extreme ultra-violet, ii, 1100.
Hopfield, *J. J.* See also *R. T.* **Birge.**
Hopkins, *B. S.* See *M. C.* **Crew**, and *F. H.* **Driggs.**
Hopkins, *E. F.*, relation of low temperatures to respiration and carbohydrate changes in potato tubers, i, 344.
Hopkins, *E. S.*, permanent standards as a possible source of error in iron determinations, ii, 1096.
Hopkins, *F. G.*, glutathione; its influence in oxidation of fats and proteins, i, 1499.
Hopkins, *F. G.*, and *M.* **Dixon**, separation of the Schardinger enzyme from milk, i, 1506.
Hopper, *I. V.*, semicarbazones of benzoin. I., i, 895.
Hopwood, *F. L.*, and *W. V.* **Mayneord**, *X*-ray stimulation of phosphorescence of fused silica, ii, 839.
Horii, *M.*, and *K.* **Komori**, photographic developers. III. Preparation of *p*-aminophenol sulphate from β-phenylhydroxylamine, i, 1410.
Horn, *T.*, carbohydrates in foliage leaves in relation to water content, i, 1121.
Hornbeck, *J. W.*, photo-electric response of potassium at low temperatures, ii, 81.
Horne, *E. V.*, gelatin. VIII. Osmotic pressure of gelatin in solutions of sodium salicylate, i, 91.
Hornemann, *C.*, influence of phosphate manuring on the production of vitamin-*B* in plants, i, 623.
Horner, *J.* See *G. R.* **Stewart.**
Horovitz, *K.*, formation of mixed electrodes at phase boundaries, ii, 673.
Horst, *F. W.*, highly sensitive Congo paper, ii, 1196.
Horsters, *H.* See *T.* **Brugsch.**
Horton, *H. V.* See *O. L.* **Brady.**
Horvat, *V.* See *V.* **Grafe.**
Horvath, *A. A.*, apparatus for the determination of urea by the urease method, ii, 237.
Hoshino, *T.* See *R.* **Majima.**
Hoskins, *W. M.* See *H. A.* **Doerner.**
Hosmer, *H. R.* See *M.* **Dresbach.**
Hosokawa, *T.*, auxoureases, i, 104.
Hossfeld, *R.* See *A.* **Windaus.**
Hotchkiss, *H. T.* See *I.* **Bencowitz.**
Hotes, *E.* See *A.* **Sonn.**
Hotta, *S.* See *H.* **Nomura.**
Hou, *C. L.*, hydrogen-ion equilibrium in the blood. I. Influence of temperature on the p_H of blood. II. Influence of dilution on the p_H of the blood and serum, i, 1483.
Houghton, *S.* See *J. F.* **Durand.**
Houldsworth, *H. S.*, and *J. W.* **Cobb**, behaviour of clays, bauxites, etc. on heating. III., ii, 671.
Hout, *M. A. H. van den*, *P. A.* **Neeteson**, and *A. L. van* **Scherpenberg**, determination of invert-sugar by the reduction titration method in liquids containing sucrose, ii, 74.
volumetric determination of invert-sugar by reduction in presence of sucrose, ii, 445.
Hovorka, *F.*, and *W. H.* **Rodebush**, freezing points of very dilute solutions of electrolytes, ii, 772.
Hovorka, *F.* See also *E. K.* **Carver.**
Howard, *A.* See *L. A. P.* **Anderson.**
Howard, *J. W.*, addition of chloroform to aldehydes, i, 557.
Howard, *R. L.*, and *T.* **Sollman**, interfacial tension of some aqueous solutions against oils, as corrected for specific gravity, ii, 109.
Howarth, *J. T.*, and *P. F.* **Burt**, apparatus to measure the coefficient of deviation from Boyle's law; determination for acetylene, ii, 818.
Howe, *A. B.* See *J. R.* **Partington.**
Howe, *P. E.*, and *E. S.* **Sanderson**, globulin and albumin fractions of blood plasma of cows and calves in relation to infection with *Bacillus abortus*, i, 477.
Howell, *W. H.*, purification of heparin and its presence in blood, i, 1346.
Howlett, *F. S.*, nitrogen and carbohydrate composition of the developing flowers and young fruits of the apple, i, 1121.
Hoyt, *F. C.*, harmonic analysis of electron orbits, ii, 252.
Hoyt, *L. F.* See *J. A.* **Handy.**
Hrywakowski, *C.*, determination of the molecular weights of non-volatile substances by the isothermal distillation of their solutions, ii, 187.
Hsü, *K.*, metabolism of cold-blooded animals. I., i, 1208.
Hubbard, *R. S.*, and *D. O.* **Meeker**, effect of high concentrations of alkali on the colour of phenolsulphonephthalein, i, 1115.
Hubbard, *R. S.*, and *C. V.* **Noback**, concentration of acetone substances in normal blood and urine, i, 712.

Huber, *O.* See *K.* **Freudenberg.**
Hudleston, *L. J.* See *J. D. C.* **Anthony.**
Hudson, *C. S.*, relations between rotatory power and structure in the sugar group. VI. Rotatory powers of α- and β-forms of methyl-*d*-xyloside and of methyl-*l*-arabinoside, i, 232.
relations between rotatory power and structure in the sugar group. VII. Methylglycosidic derivatives of the sugars, i, 233.
relations between rotatory power and structure in the sugar group. VIII. Some terpene alcohol glycosides of glucose, glycuronic acid, maltose, and lactose, i, 514.
relations between rotatory power and structure in the sugar group. IX. Rotation of the α-form of methyl-gentobioside, i, 636.
Hudson, *C. S.*, and *A.* **Kunz**, relations between rotatory power and structure in the sugar group. X. Chloro-, bromo-, and iodo-acetyl derivatives of lactose, i, 1043.
Hudson, *C. S.*, and *E. P.* **Phelps**, relations between rotatory power and structure in the sugar group. V. Chloro- and bromo-acetyl derivatives of arabinose; nomenclature of α- and β-forms in the sugar group; some derivatives of 1:6-bromoacetylglucose, -gentiobiose, and -maltose, i, 8.
Hudson, *J. C.*, precision *X*-ray spectrometers, ii, 17.
the solubility of sulphur dioxide in water and in aqueous solutions of potassium chloride and sodium sulphate, ii, 765.
Hübbenet, *E.* See *V.* **Palladin.**
Hübner, *H. M.* See *A.* **Lottermoser.**
Hueck, *H.*, proteins of the blood. I., i, 1484.
Hückel, *E.*, theory of concentrated aqueous solutions of strong electrolytes, ii, 513.
theory of membrane equilibria, ii, 528, 668.
Hückel, *E.* See also *R.* **Zsigmondy.**
Hückel, *W.*, stereoisomeric forms of decahydronaphthalene, i, 1254.
Hückel, *W.* [with *E.* **Brinkmann**, and *E.* **Goth**], stereochemistry of dicyclic ring-systems. I. Decahydronaphthalene and its derivatives, i, 258.
Hückel, *W.*, and *E.* **Goth**, transformation of stereoisomeric acids and their esters, i, 402.
Hümmelchen, *W.*, and *H.* **Kappen**, decomposition of neutral salts by colloids, i, 218.
Hüttig, *G. F.*, geometry of the co-ordination number. II., ii, 362.
water-combination in colloids, ii, 516.
migratory constituents in the crystal lattice, ii, 640.
Hüttig, *G. F.*, and *F.* **Brodkorb**, system, chromium–hydrogen, ii, 702.
Hüttig, *G. F.*, and *M.* **Keller**, contraction, refractivity, and absorption of light in solutions of lithium salts, ii, 963.
Hüttig, *G. F.*, and *A.* **Krajewski**, lithium. III. Lithium hydride, ii, 296.
Hüttig, *G. F.*, and *H.* **Kükenthal**, quartz apparatus with filtering bottoms, ii, 998.
Hüttig, *G. F.*, and *M.* **Nette**, use of glass filters in qualitative analysis, ii, 431.
Hüttig, *G. F.*, and *O.* **Schliessmann**, lithium. V. The alkali polybromides and polychlorides, ii, 1181.
Hugget, *J. L.* See *W. F.* **Seyer.**
Hughes, *A. L.*, and *F. E.* **Poindexter**, substitute for a liquid air trap for mercury vapour in vacuum systems, ii, 818.
potassium as a mercury-vapour trap, ii, 895.
Hughes, *T. P.* See *W. F.* **Petersen.**
Hugounenq, *E.*, and *J.* **Loiseleur**, constitution and mode of action of proteolytic enzymes, i, 1507.
Hugounenq, *L.*, *G.* **Florence**, and *E.* **Couture**, preparation and some properties of picrolonic acid, i, 435.
Hugounenq, *L.*, and *J.* **Loiseleur**, superposition of the phenomena of dissociation and selective adsorption in the case of proteolytic diastases, i, 1198.
Hulbert, *E. O.*, and *G.* **Breit**, momentum imparted to electrons by radiation, ii, 252.
Hull, *A. W.*, and *N. H.* **Williams**, determination of elementary charge *E* from measurements of shot-effect, ii, 253.
Hulle, *E. van.* See *G.* **Schroeter.**
Hulthén, *E.*, origin of the mercury band spectrum; a new band of mercury, ii, 11.
band spectrum of mercury, ii, 470.
relations between the band spectra of zinc, cadmium, and mercury and their atomic spectra, ii, 1113.
Hulthén, *E.*, and *G.* **Johansson**, second positive nitrogen bands, ii, 11.
Humble, *H.* See *J. E.* **Humphries.**

Hume, *E. M.*, and *H. H.* **Smith**, effect of irradiation of the environment with ultra-violet light on the growth and calcification of rats fed on a diet deficient in fat-soluble vitamins; part played by irradiated sawdust, i, 211.
Hume, *J.*, hydrates of calcium carbonate, ii, 697.
Humphries, *J. E.*, and *R.* **Evans**, bromination of acyl derivatives of phenylhydrazine; preparation of 2:4-dibromophenylhydrazine, i, 1339.
Humphries, *J. E.*, *H.* **Humble**, and *R.* **Evans**, action of halogens on phenylhydrazones. II. Action of chlorine, i, 989.
Humphreys, *F. B.*, formation of acraldehyde from glycerol by *Bacillus welchii*, i, 340.
Humphreys, *R. W.* See *J.* **Pryde**.
Humphry, *R. H.* See *E.* **Hatschek**.
Hund, *F.*, configuration of polyatomic polar molecules. II. Molecules consisting of a negative ion and hydrogen nuclei, ii, 479.
interpretation of complicated spectra particularly of the elements from scandium to nickel, ii, 912.
significance of the magnetism of the rare earths, ii, 1038.
explanation of complex spectra. II., ii, 1104.
isotropic ions, building of molecules and the crystal lattice, ii, 1132.
Hunn, *J. V.* See *G. G.* **Brown**.
Hunneman, *R. D.* See *R. T.* **Haslam**.
Hunnius. See *A.* **Densch**.
Hunt, *A. F.*, and *E. E.* **Turner**, aromatic chlorovinylarsines, i, 843.
Hunt, *F. L.* See *V. P.* **Barton**, and *R. W. G.* **Wyckoff**.
Hunt, *J. K.*, and *F.* **Daniels**, rate of decomposition of nitrogen pentoxide at low concentrations, ii, 801.
Hunt, *R.*, and *R. R.* **Renshaw**, effects of arsonium, phosphonium, and sulphonium compounds on the autonomic nervous system, i, 861.
Hunter, *A.*, and *J. A.* **Dauphinee**, approximative colorimetric method for the determination of urea, with an application to the detection and determination of arginase, i, 104.
distribution of arginase in fishes and other animals, i, 104.
indicator method for the determination of urea and arginase, ii, 247.
Hunter, *A.*, and *R. G.* **Smith**, liberation of ammonia in tryptic digestion, i, 473.
Hunter, *A. S.*, and *W. A.* **Patrick**, salvarsan. I. Determination of an isoelectric point, i, 1106.
Hunter, *G.*, diazo reaction in urine, i, 459.
carnosine of muscle and iminazole excretion in the urine, i, 459.
colour standards for use in the determination of glyoxalines, ii, 332.
Hunter, *G.* See also *F. M. R.* **Bulmer**.
Hunter, *R. F.*, physiological action of certain benzthiazoles and mercaptan derivatives, i, 702.
phenyldiethylthiocarbamide and the condensation of phenylthiocarbimide with diethylamine, i, 805.
bromination of 4′-amino-1-phenyl-5-methylbenzthiazole [dehydrothiotoluidine] and of 1:1-bisbenzthiazole, i, 987.
chlorobenzthiazole dibromide, i, 987.
aminobenzthiazoles. I. 1-Anilinobenzthiazole and its tolyl homologues, i, 1335.
Huppert, *P.* See *R.* **Suhrmann**.
Hurd, *C. D.*, and *H. J.* **Brownstein**, rearrangement of diphenyl-*p*-tolylacethydroxamic acid, i, 661.
preparation of hydroxylamine, ii, 587.
Hurd, *C. D.*, and *W. H.* **Tallyn**, optimum conditions for the preparation of keten from acetone, i, 785.
ketenic decomposition of ketones; acetylacetone, diacetyl, and pinacolin, i, 885.
Husband, *A. D.* See *F. C.* **Kelly**.
Hussey, *R. E.* See *J. B.* **Conant**.
Huston, *R. C.*, action of aromatic alcohols on aromatic compounds in the presence of aluminium chloride. III. Condensation of benzyl alcohol and phenol, i, 249.
Huthsteiner, *H.* See *O. S.* **Duffendack**.
Huttenlocher, *R.* See *W.* **Küster**.
Hyden, *W. L.* See *W. A.* **Patrick**.
Hyndman, *O. R.* See *D. I.* **Macht**.

I.

Ibbs, *T. L.*, thermal diffusion measurements, ii, 376.
Ichihara, *K.* See *Y.* **Kotake**.
Ichikawa, *J.*, condensation of vanillin with methyl ethyl ketone, i, 1156.
Iitsuka, *D.*, equilibrium diagram of the copper–zinc system, ii, 651.
Ikeuti, *H.*, β-rays produced in air by short-wave *X*-rays, ii, 460.
Ilahi, *B.* See *N. A.* **Yajnik**.
Iliesco, (*Miss*) *M.* See *S.* **Minovici**.
Iljin, *B.*, adsorption activity and surface energy of solids, ii, 856.
adsorption and surface energy at the boundary of different phases, ii, 958.

Iljin, *B.*, electrical theory of adsorption, ii, 958.
adsorption forces and their electrical nature. II. The electrical moment of the adsorbed molecule and the superficial energy of the adsorbent, ii, 1149.
Illeg, *E.* See *H.* **Reihlen.**
Illing, *H.* See *P.* **Karrer.**
Illjuvijev, *V.* See *V.* **Palladin.**
Imas, *E.* See *P.* **Thomas.**
Imker, *A.* See *R.* **Schenck.**
Ingall, *D. H.*, relationship between tensile strength, temperature, and cold-work in some pure metals and single solid solutions, ii, 190.
Ingersoll, *A. W.*, complete mutual resolution of inactive acids and bases, i, 814.
Ingersoll, *A. W.* See also *L. J.* **Bircher.**
Ingersoll, *L. R.*, and *S. S. de* **Vinney**, non-magnetic films of nickel, ii, 846.
Ingold, *C. K.*, formation of unsaturated and cyclic compounds from halogen open-chain derivatives. VI. Products derived from halogenated α-methylglutaric acids, i, 357.
alternating effect in carbon chains. I. Directive influence of the nitroso group in aromatic substitution, i, 646.
additive formation of four-membered rings. VII. Synthesis and division of some dimethylene-1:3-oxaimines, i, 840.
Ingold, *C. K.*, and (*Mrs.*) *E. H.* **Ingold**, alternating effect in carbon chains. II. Directing influence of the α-methoxyvinyl group in aromatic substitution, i, 657.
Ingold, *C. K.*, and *S. D.* **Weaver**, additive formation of four-membered rings. VI. Addition of azo compounds to ethylenes and some transformations of the dimethylene-1:2-diimine ring, i, 580.
Ingold, *C. K.* See also *J. P. C.* **Chandrasena**, *M. D.* **Farrow**, *F. R.* **Goss**, *J. P.* **Griffiths**, and *E. L.* **Holmes.**
Ingold, (*Mrs.*) *E. H.*, correlation of additive reactions with tautomeric change. IV. Effect of polar conditions on reversibility, i, 357.
tautomerism of dyads. III. Effect of the triple linking on the reactivity of neighbouring atoms, i, 779.
Ingold, (*Mrs.*) *E. H.* See also *C. K.* **Ingold.**
Invidiato, *R.*, Sicilian eucalyptus oil, i, 688.
Ionescu, *A.*, and (*Mlle.*) *E.* **Spirescu**, comparison of certain chemical methods for the determination of dextrose, ii, 331.
Ionescu, *T. V.*, velocity of sound in liquids and its relation to the heat of vaporisation, ii, 644.
Ipatiev, *V.*, and *A.* **Andrjuschtschenko**, absorption of carbon dioxide by salt solutions under pressure, ii, 956.
Ipatiev, *V.*, and *N.* **Kijukvin**, polymerisation phenomena under the simultaneous action of aluminium oxide and metallic iron at high temperatures and pressures, i, 226.
pyrogenic decomposition of naphthalene under the simultaneous action of oxides of aluminium and nickel, i, 241.
Ipatiev, *V.*, and *V.* **Verchovski**, solution of zinc in hydrochloric acid at high pressures, ii, 1069.
Iredale, *T.*, adsorption from the gas phase at a liquid–gas interface, ii, 508.
Ireland, *S. J.* See *F. D.* **Chattaway.**
Ireton, *H. J. C.*, extreme ultra-violet spectrum of germanium and scandium, ii, 453.
Irvine, *E.* See *V. H.* **Stott.**
Irving, *L.*, carbonic acid–carbonate equilibrium and other weak acids in sea-water, i, 1022.
Irwin, *M.*, accumulation of dye in *Nitella*, i, 1368.
Isaac, *S.*, and *E.* **Adler**, dihydroxyacetone in metabolism; theory of the action of insulin, i, 343.
Isbekov, *W.*, thermal analy-is of the binary systems, aluminium bromide and various halides, ii, 417.
decomposition potentials of solutions of metallic bromides in molten aluminium bromide, ii, 796.
Isely, *F. C.*, relation between the mechanical and piezo-electrical properties of a Rochelle salt crystal, ii, 23.
Isgarischev, *N.*, and *S.* **Berkmann**, effect of alternating current on polarisation during metal deposition, ii, 548.
Isgarischev, *N.*, and *A.* **Pomeranzeva**, velocity of the hydrogen ion in gels under the action of the electric current, ii, 300.
Ishibashi, *M.*, electrolytic reduction of oximes. II. γ-Oximinovaleric acid and α-oximinopropionic acid, i, 1382.
electrolytic reduction of oximes. III. Benzildioxime, i, 1431.

Ishida, *S.* See *Y.* **Tanaka.**
Ishigaki, *T.* See *K.* **Honda.**
Ishikawa, *S.*, condensation of nitriles with thioamides. IV. Thioamides with phenylimidoacyl chlorides, i, 917.
condensation of nitriles with thioamides. V. Action of sulphur monochloride on thioamides, i, 1149.
Ishimasa, *M.* See *S.* **Komatsu.**
Ishiwara, *F.*, bactericidal properties and chemical structure, i, 750.
Isihara, *T.*, equilibrium diagram of the copper–tin system, ii, 122.
equilibrium diagram of the aluminium–zinc system, ii, 298, 786.
Iskyul, *V.*, constitution of the silicates; chlorites, ii, 152.
Itallie, *L. van*, and *A. J.* **Steenhauer**, products of putrefaction in toxicological analysis, i, 719.
microchemical reactions for tyramine and histamine, ii, 608.
Ito, *T.* See *R. W.* **Seuffert.**
Ivanov, *A.* See *J.* **Bredt.**
Ivanov, *D.*, condensation of furfuraldehyde with aliphatic aldehydes, i, 421.
preparation of organic acids by the Grignard reaction, i, 503.
Ivanov, *N. N.*, cause of the varying urea content of fungi, i, 344.
urea in the lower plants an analogue of asparagine, i, 344.
excretion of urea by fungi, i, 746.
decomposition products of the proteins, i, 1480.
Ives, *H. E.*, photo-electric properties of thin films of alkali metals, ii, 344.
Ives, *H. E.*, and *A. L.* **Johnsrud**, normal and selective photo-electric effects in the alkali metals and their alloys, ii, 341.
Ivy, *H. C.* See *E. I.* **McEnery.**
Iwase, *K.*, equilibrium states of the ternary alloys. I., ii, 535.
Iwatsuru, *R.*, influence of histamine and tyramine on the nitrogen metabolism of the rabbit, i, 1502.
fats and lipoids in blood. II. Distribution of fats and lipoids in the blood of rabbits on a vitamin-*B*-free diet, i, 1515.
Iyengar, *M. S.* See *M. G. S.* **Rao.**
Iyer, *M.*, and *F. L.* **Usher**, composition of liquid and vapour phases of glycerol–water mixtures, ii, 501.
Iyer, *S. N.*, *J. J.* **Sudborough**, and *P. R.* **Ayyar**, argemone oil, i, 1128.
Izák-Križko, *J.* See *R.* **Vondraček.**
Izumi, *S.*, metallic salts of simple nucleic acids [mononucleotides], i, 174.
the carbohydrate group of glucoproteins, i, 847.

J.

Jabłczyński, *K.*, dimensions of ions in aqueous solutions, ii, 33.
velocity of coagulation of colloids of the second order, ii, 34.
slow coagulation of colloids of the first order, ii, 35, 203.
Jabłczyński, *K.*, and *H.* **Lorentz-Zienkovska**, velocity of coagulation of colloidal mixtures, ii, 666, 1060.
Jabłczyński, *K.*, and *A.* **Przezdziecka-Jedrzejovska**, velocity of coagulation of antimony trisulphide, ii, 665, 1060.
Jabłczyński, *K.*, *W.* **Wieckowski**, and (*Frl.*) *A.* **Klein**, reaction kinetics in a system consisting of two liquid phases, ii, 410.
Jablonski, *A.* See *S.* **Pienkovski.**
Jackson, *L. C.*, paramagnetism and the electronic configuration of the atom, ii, 732.
[magneton numbers of iron in some complex salts], ii, 944.
Jackson, *R. W.* See *W. C.* **Rose.**
Jackwirth, *G.* See *F.* **Sauerwald.**
Jacob, *K.* See *B.* **Neumann.**
Jacob, *P.* See *R.* **Kuhn.**
Jacobi, *R.* See *H.* **Wieland.**
Jacobs, *M. H.*, hæmolytic action of ammonium salts, i, 1345.
Jacobs, *W. A.*, saponins. I. Sapogenin from soapnuts, i, 947.
saponins. II. Structure of hederagenin, i, 948.
saponins. III. Sapogenin occurring in *Sapindus saponaria*, L., and *S. mukorossi utilis*, i, 1028.
Jacobs, *W. A.*, and *A. M.* **Collins**, strophanthin. VI. Anhydrostrophanthidins and their behaviour on hydrogenation, i, 566.
strophanthin. VII. The double bond of strophanthidin, i, 1082.
Jacobson, *R. A.*, and *R.* **Adams**, polyhydroxymethylanthraquinones. IV. Condensation of opianic acid with substituted phenols; orientation in the preparation of anthraquinones, i, 272.
trihydroxymethylanthraquinones. V. Synthesis of morindone, i, 273.
polyhydroxy- and polyhydroxymethylanthraquinones. VI. Syntheses from opianic acid and phenols or cresols, i, 1076.

Jacobucci, *A.* See *C. F.* **Hickethier.**
Jacobus, *W.* See *A.* **Löwenbein.**
Jacoby, *Margarete.* See *Martin* **Jacoby.**
Jacoby, *Martin*, and *Margarete* **Jacoby,** action of sunlight on complement, i, 178.
Jacoby, *Martin*, and *L.* **Rosenfeld,** action of enzyme accelerators, i, 1010.
Jacoob, *N.* See *A.* **Beretta.**
Jacques, *H.* See *J. M.* **Mullaly.**
Jäger, *A.* See *J.* **D'Ans.**
Jaeger, *F. M.*, pseudo-symmetry of racemic potassium chlorosulphoacetate, ii, 948.
Jaeger, *F. M.*, and *D. W.* **Dijkstra,** mass ratio of isotopes in chemical elements, ii, 83.
Jaeger, *G.* See *F. L.* **Hahn.**
Jaeger, *W.*, and *H. von* **Steinwehr,** heats of combustion of normal substances, ii, 126.
Jäggi, *W.* See *P.* **Karrer.**
Jaenichen, *E.* See *F.* **Sauerwald.**
Jaenicke, *J.* See *F.* **Haber.**
Järvinen, *K. K.*, separation of iron, chromium, aluminium, and phosphoric acid from zinc, nickel, cobalt, and manganese, and determination of the last four elements, ii, 602.
molecular attraction and the equation of state, ii, 865.
Jaffé, *G.*, influence of ionic diffusion on almost saturated currents, ii, 253.
Jahrstorper, *M.* See *W.* **Manchot.**
Jain, *M. P.* See *N. A.* **Yajnik.**
Jajnik. See **Yajnik.**
Jakób, *W. F.*, precipitation of calcium oxalate in the presence of ammonium citrate, ii, 69.
separation from calcium of magnesium, iron, aluminium, and phosphoric acid, ii, 1095.
Jakubsohn, *S.*, and *M.* **Rabinovitsch,** electrical conductivity of solid crystal hydrates, ii, 847.
Jaloustre, *L.* See *P.* **Lemay,** and *A.* **Maubert.**
James, *C.* See *M. D.* **Williams.**
James, *F.* See *S. R.* **Carter.**
Jameson, *A. Y.* See *H. J.* **Lucas.**
Jamieson, *J. S.* See *J.* **Moir.**
Janczak, (*Mlle.*) *M.*, preparation of neutral phosphites from the hydrogen esters, i, 1051.
Jander, *G.*, and *L.* **Brandt,** amphoteric hydroxides, their alkaline solutions and alkali salts. III. Alkali antimonates from aqueous alkaline solutions, ii, 988.
Jander, *G.*, and *H.* **Schulz,** application of the diffusion coefficient to the determination of the molecular size of heavy, amphoteric hydrated oxides in alkaline solution, ii, 528.
amphoteric hydroxides. II. Tantalic acid and alkali tantalates, ii, 701.
Jander, *G.*, *E.* **Wendehorst,** and *B.* **Weber,** determination of small quantities of magnesium as magnesium ammonium phosphate in presence of much aluminium, ii, 715.
Jander, *W.*, behaviour of gold and platinum towards silicate and salt fusions, ii, 416.
Janet, (*Mlle.*) *M.* See *W.* **Mestrezat.**
Janicki, *L.*, hydrogen Balmer series, ii, 449.
Jansen, *W. H.*, calcium in man. II. Effect of different salts of calcium, i, 190.
calcium in man. III. Calcium content of human blood under pathological conditions, i, 324.
Janssen, *C., jun.* See *L.* **Elion.**
Jansson, *S.*, and *H.* **Jost,** re-synthesis of carbohydrates in the muscle of warm-blooded animals, i, 1354.
Jantzen, *V. T.* See *G. von* **Hevesy.**
Jarceva, *A. G.* See *S. S.* **Nametkin.**
Jaspers, *M.*, action of organo-magnesium compounds on nitriles, i, 936.
Jauncey, *G. E. M.*, Compton and Duane effects, ii, 368.
quantum theory of the unmodified spectrum line in the Compton effect, ii, 368, 747.
theory of the width of the modified spectrum lines in the Compton effect, ii, 483.
Jauncey, *G. E. M.*, and *O. K.* **DeFoe,** theory of the number of β-rays associated with scattered X-rays, ii, 1128.
Jausseran, *C.* See *H.* **Buisson.**
Javillier, *M.*, and *H.* **Allaire,** determination of nucleic [acid] phosphorus in animal tissues, i, 996.
Javillier, *M.*, *H.* **Allaire,** and (*Mlle.*) *M.* **Groc,** new principle for testing organotherapeutic powders, ii, 1012.
Javillier, *M.*, *P.* **Baude,** and *S.* **Levy-Lajeunesse,** attempts to identify vitamin-*A*; vitamin-*A* and phytol, i, 617.
physiological determination of vitamin-*A*, i, 1364.
Jawetz, *M.* See *M.* **Kohn.**
Jeffery, *F. H.*, electrolysis of solutions of potassium oxalate with a tin anode and an electrometric determination of the constitution of the complex anions formed, ii, 304.

Jeffreys, *H.*, rare gases of the atmosphere, ii, 83.
Jelinek, *H.* See *F.* **Jirsa**.
Jelinek, *J.* See *F.* **Jirsa**.
Jellinek, *K.*, equilibria in fused salts (reactions between alloys of alkali and alkaline-earth metals and their chlorides), ii, 1160.
Jellinek, *K.*, and *J.* **Czerwinski**, equilibria between sodium, alkaline-earth metals, and their chlorides in the fused state, ii, 123.
equilibrium between lithium, barium, and their chlorides in the molten state, ii, 124.
Jellinek, *K.*, and *J.* **Wolff**, equilibria in fused salts (reactions between molten alloys of the alkalis and alkaline-earths and their molten chlorides), ii, 974.
Jellinek, *K.*, and *J.* **Zakowski**, affinity of the metals for sulphur, ii, 401.
Jendrassik, *L.*, and *H.* **Tangl**, inhibition by atropine and the action of organic acids on the intestine, i, 1502.
Jenkins, *J. D.*, effect of various factors upon the velocity of crystallisation of substances from solution, ii, 559.
Jenkins, *R. L.* See *R.* **Adams**.
Jenkinson, *H.* See *F. A.* **Mason**.
Jensen, *A. L.* See *E.* **Biilmann**.
Jensen, *H.* See *A.* **Windaus**.
Jensen, *H. H.*, and *A. D.* **Hirschfelder**, local anæsthetic and anti-spasmodic actions of some ethers and esters of saligenin, i, 467.
Jensen, *P. B.*, kinetics of zymase fermentation, i, 337.
Jensen-Carlen, *K.* See *E. M. P.* **Widmark**.
Jernakoff, *C.* See *W.* **Biedermann**.
Jerome, *W.*, and *F.* **Pepin**, volumetric determination of small quantities of ethyl alcohol, ii, 905.
Jesse, *W. P.*, relative ionisation in different gases for slow-moving electrons, ii, 919.
Jessop, *G.* See *N. K.* **Adam**, and *F. G.* **Tryhorn**.
Jevons, *W.* See *W. E.* **Curtis**.
Jilek, *A.*, and *J.* **Lukas**, rapid separation of tin and tungsten by electroanalysis, ii, 242.
gravimetric determination of copper and its separation from cadmium and zinc, ii, 903.
Jilek, *A.* See also *J.* **Lukas**.
Jinks, *J. R. A.* See *F.* **Challenger**.
Jirsa, *F.*, theory of electrolytic oxygen evolution with anodic polarisation. II. Palladium in alkaline solution, ii, 45.
Jirsa, *F.*, higher oxides of silver. I. Ag_2O_3, ii, 314.
higher oxides of silver. II. Ag_2O_2, ii, 1162.
Jirsa, *F.* [with *J.* **Jelinek**], higher oxides of silver. I. Ag_2O_3, ii, 1182.
Jirsa, *F.*, and *H.* **Jelinek**, anodic oxidation of gold. III., ii, 54.
Jirsa, *F.*, and *K.* **Loris**, theory of electrolytic oxygen evolution with anodic polarisation. I. Magnesium, cadmium, zinc, and mercury electrodes in alkaline solutions, ii, 45.
Jirů, *P.* See *E.* **Votoček**.
Joachimoglu, *G.*, action of narcotics of the aliphatic series on the smooth musculature of the leech, i, 735.
Joachimoglu, *G.*, and *N.* **Klissiunis**, antiseptic action of mercury compounds, i, 46.
Joachimoglu, *G.* See also *W.* **Hellenbrand**, and *F.* **Paneth**.
Job, *A.*, *R.* **Reich**, and *P.* **Vergnaud**, existence of magnesium-arsines and some of their reactions, i, 173.
Job, *P.*, electrometric study of hydrolysis, ii, 117.
spectrographic study of the formation of complexes in aqueous solution, ii, 389.
spectrographic study of the iodocadmium complex, ii, 471.
spectrographic study of the formation of mercury complexes, ii, 887.
Jobst, *G.*, theory of the colour of colloidal metal suspensions, ii, 777.
Jodidi, *S. L.*, cereals. III. Polypeptides and amino-acids in the ungerminated maize kernel, i, 1027.
Jodidi, *S. L.*, and *J. G.* **Wangler**, cereals. IV. Amino-acids and polypeptides in the ungerminated rye kernel, i, 1224.
Joël, *E.* See *R.* **Zsigmondy**.
Jörg, *H.* See *E.* **Fromm**.
Joffé, *A.*, and *M.* **Lewitsky**, strength and elastic limits of rock-salt, ii, 370.
Joffe, *J. S.*, and *H. C.* **McLean**, colloidal behaviour of soils and soil fertility. I. Suction force of soils as an index of their colloidal content, i, 1372.
Joñnov, *W.*, burette for gas analysis in electrochemical processes, ii, 898.
Johansson, *C. H.*, thermal expansion of binary mixed crystal systems, ii, 487.
Johansson, *C. H.* See also *G.* **Borelius**.
Johansson, *G.* See *E.* **Hulthèn**.
Johansson, *R.* See *H. von* **Euler**.

Johlin, *J. M.*, surface concentration of gelatin at a liquid-gas interface as indicated by the change in surface tension, ii, 388.
surface concentration of casein, crystalline egg-albumin, and crystalline hæmoglobin, ii, 857.
surface concentration of sodium oleate and of colloidal sulphur, ii, 1054.
John, *H.*, administration of 1-nitroanthraquinone, i, 465.
sensitivity to light of trypaflavine, i, 465.
chemical action of light, i, 1258.
quinoline derivatives. I. Synthesis of 2-phenyl-4-aminomethylquinoline, i, 1317.
relations between constitution and tinctorial properties, i, 1336.
John, *H.*, and *V.* **Fischl**, laboratory apparatus, ii, 897.
John, *H.*, and *F.* **Noziczka**, quinoline derivatives. I. Synthesis of substituted 2-phenyl-4-methylquinolines, i, 1451.
John, *H.*, and *G.* **Weber**, quinoline derivatives. II. Substituted 2-phenyl-4-methylquinolines, i, 1452.
John, *H. J.*, glycolysis, i, 1344.
Johnsen, *S.* See *H.* **Goldschmidt**.
Johnson, *A. H.* See *J. A.* **Harris**.
Johnson, *E. B.*, and *L. M.* **Dennis**, germanium. X. Determination of germanium, ii, 442.
Johnson, *E. S.*, growth of potato plants in sand cultures treated with the "six types" of nutrient solutions, i, 1367.
Johnson, *F. M. G.* See *L. A.* **Munro**, and *E. W. R.* **Steacie**.
Johnson, *J. M.* See *C.* **Voegtlin**.
Johnson, *J. R.* See *R.* **Adams**.
Johnson, *M. C.*, experimental control of electrically broadened spectral lines, ii, 614.
Johnson, *M. C.* See also *G. L.* **Clark**.
Johnson, *N. G.* See *S. G.* **Powell**.
Johnson, *R. C.*, effect of argon on the first positive band spectrum of nitrogen, ii, 11.
further spectra associated with carbon, ii, 723.
band spectra associated with carbon, ii, 1024.
Johnson, *T. B.*, and *R. D.* **Coghill**, distribution of nitrogen in protein fraction of tubercle bacilli, i, 748.
Johnson, *T. B.*, and *P. G.* **Daschavsky**, proteins. VIII. Destructive distillation of silk fibroin, i, 176.
amines. X. Formation of tyramine by decarboxylation of tyrosine from silk, i, 540.
Johnson, *T. B.*, and *A. G.* **Renfrew**, hydantoins. XLIII. Synthesis of the polypeptide–hydantoin, "hydantoin-3-acetic acid," i, 583.
Johnson, *T. B.* See also *R. D.* **Coghill**, *D.* **Davidson**, *C.* **Roberts**, *E. M.* **Shelton**, and *M. A.* **Soderman**.
Johnson, *W. C.* See *C. A.* **Kraus**.
Johnsrud, *A. L.* See *H. E.* **Ives**.
Johnston, *J.*, solubility relations of isomeric organic compounds. I., ii, 852.
Johnston, *J.*, and *A. C.* **Walker**, preparation and analyses of constant mixtures of air and carbon dioxide, ii, 851.
Johnston, *J.* See also *D. H.* **Andrews**, and *A. W.* **Francis**.
Johnston, *J. H. S.*, and *G. H.* **Peard**, surface tension of gelatin solutions, ii, 659.
Joithe, *A.* See *K. W.* **Rosenmund**.
Jolibois, *P.*, methods of studying the chemical effects of electric sparks on gases at low pressures, ii, 1194.
Jolibois, *P.*, and *R.* **Bossuet**, spectrographic detection of traces of gold, ii, 1208.
Jolibois, *P.*, and *J.* **Maze-Sencier**, adsorption phenomena exhibited by tricalcium phosphate, ii, 770.
Jolowicz, *R. V.*, experiments on the absorption of the Balmer lines in hydrogen, ii, 1097.
Jones, *A. J.*, factors affecting the physical condition of bismuth carbonate, ii, 994.
Jones, *A. O.*, gas absorption pipette, ii, 431.
Jones, *C. M.* See *M.* **Delaville**.
Jones, *D. B.*, and *F. A.* **Csonka**, proteins of the cotton seed, i, 1225.
Jones, *D. B.*, and *C. E. F.* **Gersdorff**, proteins of wheat bran. II. Comparison of bran proteins with those of the endosperm and embryo, i, 1027.
Jones, *D. B.*, *C. E. F.* **Gersdorff**, and *O.* **Moeller**, tryptophan and cystine content of various proteins, i, 98.
proteins of bark of locust tree (*Robinia pseudacacia*). I. Enzymes associated with the proteins; composition and properties of the albumin, i, 1225.
nitrogen distribution and percentages of some amino-acids in the muscle of the shrimp, *Peneus setiferus* (L.), i, 1348.
Jones, *D. C.*, adsorption from solution by silica in varying degrees of dispersivity, ii, 382.
upper limit for the thickness of the adsorption layer on silica, ii, 509.

Jones, *D. C.* See also *W. A.* **Patrick.**
Jones, *E. G.* See *J. C.* **Russel.**
Jones, *E. R.*, and *C. R.* **Bury**, cryoscopic measurements with benzene, ii, 1040.
Jones, *H. A.* See *I.* **Langmuir.**
Jones, *I.*, condensation nuclei produced by the illumination of air–halogen mixtures, ii, 984.
Jones, *J. A.* See *R. H.* **Greaves.**
Jones, *J. E.*, determination of molecular fields. III. From crystal measurements and kinetic theory data, ii, 16.
determination of molecular fields. I. Viscosity, ii, 91.
determination of molecular fields. II. Gaseous equations of state, ii, 92.
atomic fields of helium and neon, ii, 253.
Jones, *J. H.*, and *J. C.* **Boyce**, constants of the Rydberg–Ritz equation, ii, 2.
Jones, *John Henry.* See *J. S.* **Thomas.**
Jones, *J. I. M.*, and *W.* **Kilby**, identification of vat dyes on cotton, ii, 608.
Jones, *J. O.* See *G. W.* **Robinson.**
Jones, *L. W.*, and *D. H.* **Powers**, new hydroxamic acids of hydroxy- and alkoxy-fatty acids, i, 13.
Jones, *L. W.*, and *H. F.* **Whalen**, action of acid chlorides on trimethylamine, i, 801.
Jones, *L. W.* See also *H. F.* **Whalen.**
Jones, *R. C.* See *H. G.* **Miller.**
Jones, *R. L.*, and *F. R.* **Pember**, fertiliser nutrients required by barley, wheat, and oats, as shown by both soil and water cultures, i, 1030.
Jones, *R. M.* See *W. H.* **Ross.**
Jones, *T. J.*, electrical resistance of mercury in magnetic fields, ii, 754.
Jones, *W.*, and *M. E.* **Perkins**, occurrence of plant nucleotides in animal tissues, i, 182.
nitrogenous groups of plant nucleic acid, i, 487.
Jones, *W. I.*, *H.* **McCombie**, and *H. A.* **Scarborough**, velocity of reaction in mixed solvents. VII. Influence of the base on the velocity of saponification of esters in methyl alcohol mixtures, ii, 137.
Jones, *W. J.* See *J. E.* **Myers.**
Jones, *W. N.*, polarised light and starch grains, i, 1212.
Jonesco, *S.*, action of hydrochloric acid and sodium on the flavone extracted from red leaves of *Prunus pissardi*, i, 824.
action of sodium and mineral and organic acids on certain flavones, i, 825.
Jonescu, *M.*, additive character of heterogeneous conjugated systems, i, 1153.
Jongh, *S. E. de*, and *J.* **Planelles**, determination of small amounts of glycogen in solution, i, 325.
Joos, *B.* See *P.* **Karrer.**
Joos, *G.*, regularity in the fine structure of spectral lines, ii, 612.
diamagnetism and the size of ions, ii, 736.
Jordan, *G.* See *K. W.* **Rosenmund.**
Jordan, *O.* See *K. von* **Auwers.**
Jordan, *P.*, absorption of excited neon, ii, 337.
theory of atomic structure, ii, 926.
Jørgensen, *G.*, determination of phosphoric acid as magnesium ammonium phosphate, ii, 824.
Jorissen, *W. P.*, and *J. C.* **Meuwissen**, influence of some non-inflammable vapours of organic liquids on the limits of inflammability of methane–air mixtures. II., ii, 53.
influence of some non-inflammable vapours of organic liquids on the limits of inflammability of mixtures of inflammable gases and air. III., ii, 307.
Jorissen, *W. P.*, and *B. L.* **Ongkiehong**, influence of non-inflammable vapours of organic liquids on the limits of inflammability of mixtures of inflammable gases and air. V. Influence of trichloroethylene on the limits of inflammability of hydrogen–air mixtures, ii, 875.
Jorissen, *W. P.*, and *C. van den* **Pol**, activation of oxygen in the slow oxidation of sodium sulphite, ii, 52.
induced oxidation, ii, 879.
Jorissen, *W. P.*, and *J. H. A. P. van der* **Valk**, influence of non-inflammable vapours of organic liquids on the limits of inflammability of mixtures of inflammable gases and air. IV. Influence of dichloro- and trichloroethylene on the limits of inflammability of carbon monoxide–air mixtures, ii, 874.
Jorpes, *E.*, nucleic acid of pancreas, i, 182.
Joseph, *A. F.*, clays as soil colloids, i, 1228.
action of silica on electrolytes, ii, 383.
Joseph, *A. F.*, *F. J.* **Martin**, and *J. S.* **Hancock**, electrical determination of soil alkali, i, 222.
Josephson, *K.*, enzymic hydrolysis of glucosides; β-glucosidase of emulsin, i, 1359.
enzymic synthesis of glucosides; β-glucosidase of emulsin, i, 1360.

Josephson, *K.* See also *H. von* **Euler.**
Joshi, *S. S.*, viscosity of reversible emulsions, ii, 776.
Joshi, *S. S.* See also *S. M.* **Sané.**
Jost, *H.* See *S.* **Jansson,** and *F.* **Knoop.**
Jouguet, *E.*, comparison of the theory of explosion waves with recent experiments, ii, 1169.
Jouniaux, *A.*, variation of the molecular weight of mercury with temperature, ii, 23.
variation of the molecular weights of sodium, potassium, and tellurium with temperature, ii, 187.
variation of the molecular condensation of tin with temperature, ii, 489.
extension of Trouton's law to the fusion of metals, ii, 645.
Juday, *C.* See *B. P.* **Domogalla.**
Jünger, *A.* See *B.* **Helferich.**
Jüptner, (*Baron*), kinetics of reactions, ii, 552.
Julien, *A. P.*, electrical conductance of selenium oxychloride solutions, ii, 872.
Junck, *D.* See *Erich* **Müller.**
Jung, *G.* See *A.* **Coehn.**
Jung, *H.*, *X*-ray researches on the dehydration products of gypsum, ii, 367.
Jung, *H.* See also *G.* **Linck,** and *H.* **Wieland.**
Jungck, *G.* See *B.* **Emmert.**
Jungermann, *C.* See *T.* **Sabalitschka.**
Jungfer, *O.* See *E.* **Koenigs.**
Juritz, *C. F.*, active principles of South African plants, i, 761.
Justh, *R.* See *W.* **Traube.**

K.

Kablukov, *A.*, and *V. T.* **Malischeva,** volumetric measurement of the mutual solubility of liquids; mutual solubility of the systems, ethyl ether–water and *iso*amyl alcohol–water, ii, 768.
Kadicova, (*Miss*) *H.* See *A.* **Simek.**
Käb, *G.*, influence of gas content on catalysis with platinum, ii, 564.
Kägi, *H.* See *M.* **Hartmann.**
Källner, *S.* See *F.* **Arndt.**
Kämmerer, *H.*, and *A.* **Schaulin,** clinical colorimetric determination of hæmoglobin, i, 851.
Käppler, *G.* See *F.* **Weigert.**
Kafuku, *K.*, formation of safroeugenol [3-hydroxy-4-ethoxyallylbenzene] and *iso*safroeugenol [3-hydroxy-4-ethoxypropenylbenzene] from safrole and *iso*safrole, i, 1418.
Kahil, *A. I. M.*, and *M.* **Nierenstein,** chroman series, i, 52.
Kahlenberg, *H. H.*, boron and boron suboxide, ii, 425.
Kahlenberg, *L.*, passage of boric acid through the skin by osmosis, i, 101.
Kahler, *H.*, band spectra of crystals and complex gases, ii, 626.
Kahlert, *M.* See *G.* **Embden.**
Kahn, *M.*, and *R. S.* **Postmontier,** non-protein sulphur of the blood, i, 999.
Kahn, *P.* See *A.* **Abraham.**
Kaho, *H.*, influence of alkaline-earth salts on the heat coagulation of plant plasma. VI., i, 217.
Kahre, *H.* See *H.* **Thoms.**
Kaigorodov, *A.* See *M.* **Vrevski.**
Kailan, *A.*, and *R.* **Obogi,** purification of glycerol from volatile fatty acids and their esters, i, 501.
velocity of esterification of *n*-butyric acid in glycerol, ii, 49.
Kailan, *A.*, and *H.* **Raupenstrauch,** esterification of aliphatic acids in glycerol, i, 880.
Kaiser, *W.* See *J. von* **Braun.**
Kalandyk, *S.*, conductivity of salt vapours in the chlorhydrogen flame, ii, 208.
Kalb, *L.*, and *E.* **Berrer,** indigotin group. V. 5:7:5′:7′-Tetraiodoindigotin and related substances, i, 160.
Kalb, *L.*, and *L.* **Vogel,** indigotin group. VI. 4:4′-Dichloro-5:7:5′:7′-di-iodoindigotin, 5:6:7:5′:6′:7′-hexaiodoindigotin, and related substances, i, 161.
Kalckbrenner, *E.* See *P.* **Pfeiffer.**
Kalff, *J.*, and *R.* **Robinson,** synthesis of myricetin and of a galangin monomethyl ether occurring in galanga root, i, 423.
synthesis of datiscetin, i, 1302.
Kalje. See *G.* **Povarnin.**
Kall, *G. A.* See *H.* **Reihlen.**
Kalle, *K.* See *H.* **Schmalfuss.**
Kalle & Co., preparation of a reduction product of anhydrolupinine, i, 294.
preparation of aldehydes and ketones of the pyrrole series, i, 297.
preparation of perylenetetracarboxylic acid and its derivatives, i, 406.
monoimide of perylenetetracarboxylic acid and its derivatives, i, 1277.
vat dyes, i, 1334.
Kallmann, *O.* See *B.* **Bleyer.**
Kalushski, *A. A.*, sulphofication in soils, i, 492.
sulphur as an accessory fertiliser, i, 492.
effect of sulphur on saline soils, i, 624.

Kameyama, *N.*, ionic equilibria across semi-permeable membranes, ii, 1062.
Kammer, *G. D.*, and *A.* **Silverman**, ionium. I. Recovery of ionium from carnotite. II. Adsorption of ionium–thorium by barium sulphate. III. Ionium–thorium ratio in carnotite, ii, 1186.
Kammer, *G. D.* See also *C. H.* **Viol**.
Kamura, *H.*, reduction of ferric oxide and iron ores by hydrogen, ii, 981.
Kanao, *S.* See *H.* **Leuchs**.
Kaneko, *T.*, influence of magnesium on intraocular pressure, i, 333.
Kanevskaja, *S. I.*, extraction of opium alkaloids, i, 153.
Kann, *E.* See *M.* **Bergmann**.
Kannenstine, *F. M.*, life of metastable helium, ii, 171.
Kanô, *N.*, determination of cyanides and the use of benzene as an indicator in iodometry, ii, 1010.
Kao, *C. H.* See *V.* **Lenher**.
Kapaun, *A.* See *R.* **Kremann**.
Kapeller, *R.* See *E.* **Fromm**.
Kapfhammer, *J.*, creatinine, i, 797.
Kapitza, *P.*, and *H. W. B.* **Skinner**, Zeeman effect in strong magnetic fields, ii, 918.
Kaplansky, *S.*, extractives of the lungs, i, 97.
Kapp, *J.* See *V.* **Vesely**.
Kappen, *H.*, name and significance of soil acidity, i, 221.
investigation of soil acidity by means of pot experiments, i, 874.
Kappen, *H.*, and *M.* **Lukacs**, physiological reactions of manuring salts, i. 1523.
Kappen, *H.* See also *W.* **Hümmelchen**.
Kap-Soo-Lee, power of adsorption and detoxication of various charcoals, i, 101.
Kapuscinski, *W.*, fluorescence of cadmium vapour, ii, 838.
Kar, *K. C.*, kinetic theory of compressibility of solutions and binary liquid mixtures, ii, 970.
Kar, *S. C.*, statistical basis of Volmer's equation of state for adsorbed substances, and the concentration formula, ii, 1045.
Kara-Michailova, *E.*, quantitative optical method for differentiating between α- and H-particles, ii, 621.
Karandéev, *V.*, crystalline form and optical properties of cadinylene-sulphochloride, i, 1164.
Karantassis, *T.*, preparation of mixed iodides and sulphides, ii, 993.
preparation of arsenic di-iodide, ii, 994.
Karantassis, *T.* See also *V.* **Auger**.
Karfiol, (*Mlle.*) *H.*, synthetic potassium and sodium chromosilicates, ii, 1087.
Karlsson, *K. G.*, velocity of decomposition of esters and the relation to the hydrogen-ion concentration, ii, 877.
Karlsson, *S.* See *H. von* **Euler**.
Karpfen, *O.* See *S.* **Fränkel**.
Karr, *W. G.*, determination of blood urea-nitrogen, i, 323.
Karrer, *E.* See *H. C.* **Stevens**.
Karrer, *P.*, reserve cellulose and cellulose, i, 118.
*iso*lichenin and the hydrolysis of starch, i, 1370.
Karrer, *P.*, *G. H.* **Diechmann**, and *W. T.* **Haebler**, preparation and reactions of oximinoacetanilides, i, 243.
Karrer, *P.*, and *C.* **Gränacher**, reduction of dialkyloxydihydropyrazines, i, 302.
Karrer, *P.*, and *H.* **Illing**, polysaccharides. XXX. and XXXII. Enzymic decomposition of cellulose, i, 741, 1029.
Karrer, *P.*, *W.* **Jäggi**, and *T.* **Takahashi**, configuration of naturally-occurring *l*-leucine, i, 1046.
Karrer, *P.*, and *B.* **Joos**, polysaccharides. XXX. *iso*Lichenin, i, 1028.
Karrer, *P.*, and *W.* **Klarer**, degradation of *l*-β-hydroxybutyric acid, i, 1036.
Karrer, *P.*, and *H.* **Lier**, polysaccharides. XXXIII. New sugar, lichotriose, from lichenin, i, 793.
Karrer, *P.*, *E.* **Miyamichi**, *H. C.* **Storm**, and *R.* **Widmer**, anhydrides of acyl-amino-acids, i, 594.
Karrer, *P.*, *O.* **Schnider**, and *A. P.* **Smirnov**, polysaccharides. XXIX. Chitin (II) and the configuration of glucosamine, i, 418.
Karrer, *P.*, and *M.* **Staub**, gentiobiase, i, 336.
Karrer, *P.*, and *N.* **Takashima**, constitution and molecular magnitude of the hydroxy-camphors, i, 940.
Karrer, *P.*, *F.* **Weber**, and *J. van* **Slooten**, toxins. II. Crotin, i, 1226.
Karrer, *P.*, and *R.* **Widmer**, amino-acids; action of diazomethane on hippuryl chloride, i, 593.
configuration of nicotine; optically active hygrinic acid, i, 1084.
Karrer, *P.*, *R.* **Widmer**, and *P.* **Riso**, constitution and configuration of quinic acid, i, 673.
Karrer, *S.*, phenomena in the electric arc process of nitrogen fixation, ii, 987.
Karssen, *A.* See *H.* **Gerding**, and *N. H.* **Kolkmeijer**.

Karvé, *D. D.*, thermochemical investigations on the constitution of acids in solution, ii, 633.
acid nature of some derivatives of sulphur, selenium, and tellurium, ii, 1188.
Karwacki, *L.*, action *in vitro* of certain chemical substances on the development of *Bacillus tuberculosis*, i, 1015.
Karwat, *E.* See *A.* Eucken.
Kasakevitsch, *P. P.*, vapour pressure–water content diagram and adsorptive power of aniline-black, ii, 287.
Kase, *T.*, equilibrium diagram of the iron–carbon–nickel system, ii, 973.
Kashima, *K.*, synthesis of *N*:*N*′-dimethylenesulphonates of *o*-, *m*-, and *p*-diaminoarsenobenzene, i, 1195.
Kassner, *G.*, material basis of the "nitroxan" process for the catalytic oxidation of ammonia to nitric acid, ii, 413.
Kaston, *E.* See *H.* Pringsheim.
Kato, *S.*, and *O.* Shinoda, spontaneous decomposition of lecithin, i, 773.
Katz, *J. R.*, Röntgen-spectrographic phenomena in the swelling of cellulose in various alkali hydroxide solutions, i, 639.
Röntgen-spectrographic observations, i, 640.
cause of the characteristic extensibility of caoutchouc; alteration of *X*-ray spectrum of caoutchouc on extension, ii, 667.
application of *X*-ray methods to the problem of imbibition, ii, 771.
cause of characteristic extensibility of caoutchouc. II. Joule effect and formation during stretching of a three-dimensioned structure, ii, 969.
Katz, *J. R.*, and *H.* Mark, Röntgen diagram of hydrated cellulose and its behaviour in reversion treatments, i, 640.
alteration in the fibre *X*-ray spectrogram of cellulose on swelling in concentrated aqueous solutions, ii, 660.
nature of swelling in substances giving a Debye–Scherrer diagram, ii, 666.
Kaufmann, *E.* See *L.* Beltz.
Kaufmann, *H. P.*, and *E.* Hansen-Schmidt, bromometric investigations, ii, 554.
Kaufmann, *H. P.*, and *F.* Kögler, preparation of thiocyanogen from thiocyanic acid, i, 1252.
Kaufmann, *H. P.*, and *J.* Liepe, keto-enolic tautomerism. V. Desmotropic γ-methylacetylacetones, i, 1241.
Kaufmann, *H. P.*, and *E.* Richter, keto-enolic tautomerism. IV. Ferric chloride reaction and bromine addition of enols, i, 231.
Kaufmann, *H. P.*, and *E.* Rossbach, substituted salicylic acids. V. Substituted salicylic phthalidylidene ether esters, i, 1273.
Kaufmann, *M.* See *A.* Kurtenacker.
Kaul, *L.*, decomposition of mercury atoms, ii, 177.
Kautsky, *H.*, chemiluminescence, ii, 1026.
Kautsky, *H.*, and *G.* Herzberg, permutoid structure, ii, 941.
Kautsky, *H.*, and *A.* Thiele, reaction of siloxen with halogen compounds, ii, 698.
Kautsky, *R.*, *F.* Leineweber and *L. W.* Famulener, nitrogen content in volumetrically standardised bacterial vaccines, i, 1511.
Kautter, *T.* See *A.* Gutbier.
Kawakami, *K.* See *K.* Takahashi.
Kay, *G. F.* See *J. W.* Bain.
Kay, *H. D.*, phosphorus content of the blood of ruminants, i, 994.
phosphorus compounds of milk. I. The presence in milk of organic acid-soluble phosphorus compounds, i, 998.
Kaye, *M.*, behaviour of a substance giving the nitroprusside reaction in skin and in hair, i, 180.
Kayser, *C.* See *E.* Le Breton.
Kayser, *E.*, and *H.* Delaval, radioactivity, nitrogen-fixing bacteria, and alcoholic yeasts, i, 1118.
Kaziro, *K.*, decomposition of cholic acid by *Bacillus coli*, i, 1363.
Keen, *B. A.* See *A. N.* Puri.
Keen, *R. H.* See *R. T.* Haslam.
Keenan, *G. L.*, optical properties of amino-acids, ii, 94.
Keenan, *G. L.*, and *R. M.* Hann, optical properties of coniine hydrochloride, i, 1093.
Keenen, *F. G.*, *L. W.* Prine, and *W. C.* Ebaugh, combustion of carbon. II., ii, 987.
Keeser, *R.*, action of undissociated drugs, i, 101.
cholesterol and its esters. I. and II., ii, 290, 661.
Keesom, *W. H.* See *J. de* Smedt, and *L.* Vegard.
Kehrmann, *F.*, constitution and colour. X. Constitution of coloured derivatives of triphenylmethane, i, 435.
constitution and colour. XI. Colour variations shown by acidic organic substances when forming salts with bases, i, 435.

Kehrmann, *F.*, and *C.* **Bener**, phenyl and halogen derivatives of fluoflavine, i, 443.
synthesis of oxygen analogues of fluoflavine, i, 443.
Kehrmann, *F.*, and *F.* **Cherpillod**, syntheses in the quinoneimide dye group. V. The use of hydroxy-*p*-benzoquinone, i, 302.
Kehrmann, *F.*, and *E.* **Falke**, syntheses in the quinoneimide dye group. VI. Certain *apo*safranine analogues of stilbazonium series, i, 303.
oxonium perbromides, i, 351.
Kehrmann, *F.*, and *E.* **Haenny**, syntheses in the quinoneimine dye group. XI. Derivatives of phenazine, i, 1330.
Kehrmann, *F.*, and *E.* **Hoehn**, 4-acetamido-*o*-benzoquinone and some of its derivatives, i, 560.
Kehrmann, *F.*, and *L.* **Listwa**, syntheses in the quinoneimine dye group. VIII. The eighteenth isomeride of rosinduline, i, 1332.
Kehrmann, *F.*, and *P.* **Prunier**, syntheses in the quinoneimide dye group. VII. 1-Aminophenazine, i, 304.
Kehrmann, *F.*, and *I.* **Safar**, syntheses in the quinoneimine dye group. X. Aminoazines derived from naphthalene, i, 1331.
Kehrmann, *F.*, and *M.* **Sandoz**, determination of the constitutional formulæ of colouring matters from their absorption spectra. VI., i, 983.
Kehrmann, *F.*, and *J. A.* **Schedler**, fluorindines and fluorindinium salts, i, 441.
derivatives of triphenazineoxazine and triphendioxazine, i, 444.
Kehrmann, *F.*, and *L.* **Stanoyévitch**, monophenyltetra-aminobenzene and some of its derivatives, i, 1331.
syntheses in the quinoneimine dye group. IX. Total synthesis of induline-6B, i, 1334.
Kehrmann, *F.*, and *J.* **Tschui**, carbazones [5:5-diphenyldihydroacridones]. IV. Coloured derivatives of tetraphenylmethane, i, 430.
diphenylmethylcarbazine [diphenylmethyldihydroacridine] and some nitro-derivatives. V. Coloured derivatives of tetraphenylmethane, i, 431.
Kehrmann, *F.*, and *G.* **Wild**, condensation of methylphenoxazine-*o*-quinone with *o*-aminophenol and alkylated *o*-diamines, i, 444.
Keilin, *D.*, cytochrome, a respiratory pigment common to animals, yeast, and higher plants, i, 1112.
Keller, *M.* See *G. F.* **Hüttig**.
Keller, *O.* [with **Smechel**], hellebore group. V., i, 830.
Keller, *O.*, and *X.* **Bernhard**, alkaloids of ipecacuanha (*Uragoga ipecacuanha*). IV., i, 1086.
Keller, *R.* See *J.* **Gicklhorn**.
Kellermann, *K.* See *L.* **Birckenbach**.
Kelley, *K. K.* See *G. S.* **Parkes**.
Kelly, *C. I.* See *R.* **Forsyth**.
Kelly, *F. C.*, influence of small quantities of potassium iodide on the assimilation of nitrogen, phosphorus, and calcium in the growing pig, i, 1210.
Kelly, *F. C.*, and *A. D.* **Husband**, determination of minute quantities of iodine in biological material, i, 183.
Kelly, *M. A.* See *L. A.* **Pinck**.
Kelly, *M. W.* See *A. W.* **Thomas**.
Kelp, *I.* See *J.* **Gröh**.
Kemble, *E. C.*, application of the correspondence principle to degenerate systems and the relative intensities of band lines, ii, 178.
Kémeri, *D.*, new porphyrin-like constituent of normal human fæces, i, 188.
Kemp, *M.*, oil of [Jamaica] pimenta leaves, i, 565.
Kemp, *M.* See also *H.* **Thoms**.
Kendall, *F. E.* See *C. S.* **Marvel**.
Kendall, *J.*, and *J. E.* **Booge**, stability of additive compounds between esters and acids, ii, 972.
Kendall, *J.*, and *B. L.* **Clarke**, separation of rare earths by the ionic migration method, ii, 977.
Kendall, *J.*, and *C. V.* **King**, additive compounds in the ternary system, ester–acid–water, ii, 972.
Kendall, *J.*, and *C. H.* **Sloan**, solubility of slightly soluble chlorides in concentrated chloride solutions, ii, 1052.
Kendall, *J.*, and *J. F.* **White**, separation of isotopes by the ionic migration method, ii, 83.
Kennard, *E. H.*, cause of surface tension, ii, 1046, 1148.
Kennedy, *W. P.*, influence of blood-serum and of sugars on hæmolysis, i, 717.
Kenrick, *F. B.*, *C. S.* **Gilbert**, and *K. L.* **Wismer**, superheating of liquids, ii, 99.
Kenrick, *F. B.*, *K. L.* **Wismer**, and *K. S.* **Wyatt**, supersaturation of gases in liquids, ii, 105.
Kenyon, *J.*, *H.* **Phillips**, and *H. G.* **Turley**, dependence of rotatory power on chemical constitution. XXIV. Further experiments on the Walden inversion, i, 507.

Kenyon, *J.*, and *H. E. M.* **Priston**, alcohols of the hydroaromatic and terpene series. IV. α- and β-Fenchyl alcohols and derived esters, i, 941.

Kenyon, *J.*, and *D. R.* **Snellgrove**, dependence of rotatory power on chemical constitution. XXVI. Four alcohols containing the vinyl group and some esters derived therefrom, i, 771.

Kenyon, *J.* See also *A. T.* **Fuller**, and *L. F.* **Hewitt**.

Kepianka, *E.*, and *L.* **Marchlewski**, absorption of [ultra-]violet light by organic substances, ii, 179.

Kerb, *J.*, and *E.* **Kerb-Etzdorf**, glucosane, i, 233.

Kerb-Etzdorf, *E.* See *J.* **Kerb**.

Kermack, *W. O.*, syntheses in the indole group. I., i, 67.

Kermack, *W. O.*, and *P.* **MacCullum**, colloidal properties of Wassermann antigens, i, 197.

influence of gelatin on the stability of a colloidal solution of cholesterol and on the charge on the particles, ii, 525.

Kermack, *W. O.*, and *C. I. B.* **Voge**, action of salts with multivalent cations on colloidal solutions of gold and gum benzoin, ii, 523.

Kermack, *W. O.*, and *W. T. H.* **Williamson**, stability of suspensions. I. Rate of sedimentation of kaolin suspensions, ii, 523.

Kern, *J. W.*, *R. L.* **Shriner**, and *R.* **Adams**, platinum and palladium oxides as catalysts in the reduction of organic compounds. IX. Reduction of olefines, i, 625.

Kern, *W.* See *F.* **Fichter**.

Kernbach, *M.*, protein in exhumed bone tissue and its antigenic properties, i, 326.

Kerr, *C. A.* See *J. M.* **Robertson**.

Kerr, *R. W.* See *W. H.* **Eddy**.

Kerridge, *P. T.*, use of the glass electrode in biochemistry, i, 1201.

Keschan, *A.*, separation of phosphoric acid in qualitative analysis by means of basic bismuth nitrate, ii, 328.

precipitation of oxalic acid with basic bismuth nitrate in qualitative analysis, ii, 1008.

Kesting, production of ethylene for the preparation of ethylene bromide from alcohol by the contact process, i, 625.

Ketchum, *P. W.*, extension of Bohr's correspondence principle to small quantum numbers, ii, 1.

Keuffel, *C. W.*, direct reading spectrophotometer, ii, 1193.

Keunecke, *E.* See *W.* **Biltz**.

Keyes, *F. G.*, and *F. W.* **Sears**, recent measurements of the Joule effect for carbon dioxide, ii, 275.

Keyworth, *C. M.*, arylamine salts of some sulphonic acids of the benzene series. I. Benzenemonosulphonic acid, i, 124.

Keyworth, *C. M.* See also *R. B.* **Forster**.

Kharasch, *M. S.*, and *M. W.* **Grafflin**, preparation and decomposition of unsymmetrical mercuri-organic compounds; a method of establishing the relative degree of negativity of organic radicals, i, 1107.

Kharasch, *M. S.*, and *B.* **Sher**, electronic conception of valency and heats of combustion of organic compounds, ii, 636.

Khastgir, *S. R.*, and *W. H.* **Watson**, spectroscopic evidence of *J*-transformation of *X*-rays, ii, 336, 727.

Khastgir, *S. R.* See also *C. G.* **Barkla**.

Khotinska, *E.*, and (*Mme.*) *T.* **Epifanova**, mucic acid, i, 783.

Kidd, *J. D.* See *K. C.* **Bailey**.

Kidner, *C. A.* See *S.* **Dushman**.

Kieferle, *F.*, *J.* **Schwaibold**, and *C.* **Haekmann**, concentration of citric acid in cow's milk and its relation to the chlorine : sugar ratio, i, 855.

Kieniger, *O.* See *E.* **Wilke**.

Kienzl, *H.* See *R.* **Kremann**.

Kieper, *K.*, volumetric determination of zinc, ii, 70.

Kierzek, *L.* See *A.* **Korczynski**.

Kiesel, *A.*, m.p. of cerotic acid, i, 1035.

Kiesel, *K.*, stalagmometric investigations on urine, in particular that of the large herbivora. I. Methods. II. Nature of the capillary-active substance of urine. III. Adsorption of the capillary-active substance of urine, i, 98.

Kiess, *C. C.*, series regularities in the spark spectrum of nitrogen, ii, 4.

series in the arc spectrum of nitrogen, ii, 911.

Kiess, *C. C.* See also *W. F.* **Meggers**.

Kijner, *N.*, action of hydrazine on dimethylpyrone, i, 1105.

Kijukwin, *N.* See *V.* **Ipatiev**.

Kikuchi, *K.*, comparative urea determinations on human and animal urines, i, 609.

Kilby, *W.* See *J. I. M.* **Jones**.

Kimura, *K.* See *G. von* **Hevesy**.

Kimura, *M.*, classification of enhanced lines of various elements. II. Spectra of intermittent arc shunted by a condenser, ii, 726.

Kimura, *M.*, and *G.* **Nakamura**, cathode spectra of metals and their salts, ii, 166.
cathode spectra of metals, ii, 167.
classification of enhanced lines of various elements. I., ii, 726.
Kindler, *K.*, preparation of primary, secondary, and tertiary amines, i, 387.
Kindler, *W.* See *R.* **Willstätter.**
Kindscher, *E.* See *V.* **Rodt.**
Kindt, *G.* See *D.* **Bigiavi.**
King, *A. S.*, electric furnace spectra of vanadium and chromium in the ultra-violet, ii, 453.
...ing, *C. V.* See *J. N.* **Brönsted**, and *J.* **Kendall.**
King, *H.*, and *W. O.* **Murch**, trypanocidal action and chemical constitution. I. Arylamides of *p*-aminophenylarsinic acid, i, 319.
King, *J. F.*, and *S. P.* **Smedley**, vaporisation of liquid mixtures, ii, 101.
King, *W. B.* See *H.* **Gilman.**
King, *W. J.*, volumetric determination of small quantities of carbon in tungsten, ii, 435.
Kingdon, *K. H.*, electron emission from adsorbed films on tungsten, ii, 9.
Kingdon, *K. H.* See also *I.* **Langmuir.**
Kingsbury, *F. L.* See *C. S.* **Marvel.**
Kingslake, *R.*, new type of nephelometer, ii, 821.
Kingston, *H. L.*, and *S. B.* **Schryver**, gelatin. III. Separation of the products of hydrolysis of gelatin by the carbamate method, i, 89.
Kinkel, *E.* See *E.* **Sauer.**
Kinnersley, *H. W.*, and *R. A.* **Peters**, antineuritic yeast concentrates. I., i, 1516.
Kinnersley, *H. W.*, *R. A.* **Peters**, and *B. T.* **Squires**, animal quinoidine, i, 997.
Kipping, *F. B.*, and (*Sir*) *W. J.* **Pope**, resolution of *dl*-diphenylpropylenediamine and *dl*-1:4-diphenyl-2-methylpiperazine, i, 22.
Kipping, *F. S.*, organic derivatives of silicon. XXX. Complex silicohydrocarbons $[SiPh_2]_n$, i, 87.
Kipping, *F. S.*, and *T.* **Greasley**, isomeric benzoyl derivatives from vinyldiacetonamine, i, 144.
Kipping, *F. S.* See also *L. R.* **Vyle.**
Kircher, *A.*, and *F. von* **Ruppert**, determination of arsenic in "salvarsan" and its congeners, ii, 240.
Kirchoff, *P.* See *M.* **Volmer.**
Kirchrath, *H.* See *A.* **Schönberg.**
Kirner, *W. R.* See *J. B.* **Conant.**
Kirpal, *A.*, 2-pyridone-1-acetic acid, i, 66.
Kirpal, *A.*, and *E.* **Reiter**, 3-nitropyridine and its derivatives, i, 697.
Kirsch, *G.*, radioactive methods for the age determination of minerals, ii, 320.
retrograde H-particles from disintegrating atoms, ii, 621.
atomic disintegration by α-particles, ii, 923.
Kirsch, *G.* See also *H.* **Pettersson.**
Kistiakovski, *G.* See *M.* **Bodenstein.**
Kitahara, *Y.*, excretion of chlorophyll derivatives in the urine. III., i, 460.
Kitasato, *T.* See *K.* **Takahashi.**
Kitasato, *Z.*, biochemical study of phycoerythrin and phycocyanine, i, 1111.
Kitchen, *F. N.* See *I. M.* **Heilbron.**
Kitran, *B. E.*, equilibrium diagrams and the heats of formation in some binary organic systems. I., ii, 533.
Klamer, *C. E.*, effect of chemicals on various kinds of glass, ii, 427.
Klander, *F.*, weathering of sandstone by circulating solutions, ii, 821.
...larer, *J.* See *Hans* **Fischer.**
Klarer, *W.* See *P.* **Karrer.**
Klarmann, *E.* See *E.* **Abderhalden.**
Klason, *P.*, constitution of pine lignin. IV. and V., i, 371, 1246.
cuprous hydroxide, ii, 318.
sugar analysis by Fehling's method, ii, 881.
Klauer, *H.* See *R.* **Lorenz.**
Kleeberg, *J.*, beryllium compounds as adsorption media, ii, 956.
Kleeman, *R. D.*, nature of the constant of mass action, ii, 1170.
Kleeman, *R. D.*, and *C. R.* **Pitts**, sign of the electrical layer furthest away from the surface of a solution in contact with air or metal, ii, 659.
Kleiber, *M.*, action of electric current on micro-organisms, i, 1509.
Klein, (*Mlle.*) *A.*, reactions of benzoic acid at the boundary of two liquid phases, ii, 802.
relation between rapidity of stirring and velocity of reaction in heterogeneous systems, ii, 802.
reactions between liquid amalgams and aqueous solutions, ii, 802.
Klein, (*Mlle.*) *A.* See also *K.* **Jabłczyński.**
Klein, *G.*, and *O.* **Werner**, physiology and distribution of flavones, i, 870.
micro- and histo-chemical demonstration of free and bound oxalic, succinic, malic, tartaric, and citric acids, i, 871.
Klein, *L.*, bitter principles in hops and beer, ii, 248.
Klein, *L.* See also *O. L.* **Brady.**

Klein, *W.*, formation of methæmoglobin, i, 709.
Kleine, *H.*, change of resistance of platinum and iron wires in a high vacuum due to absorbed gas, ii, 947.
Kleinicke, *W.* See *G.* **Heller.**
Kleinmann, *H.*, nephelometry, ii, 389.
Kleinmann, *H.* See also *P.* **Rona.**
Klemenc, *A.*, nitric oxide reaction, ii, 407.
sensitive glass manometer for gases which attack mercury, ii, 995.
Klemenc, *A.*, and *R.* **Schöller**, nitric acid. I. Behaviour as a nitrating agent, ii, 212.
Klemenc, *A.*, and *A.* **Schroth**, action of nitrogen peroxide on metallic copper and its adsorption by cuprous oxide, ii, 228.
Klemensiewicz, *Z.*, conductivity of chlorides in fused antimony trichloride and Ghosh's theory, ii, 40.
Klemm, *D.* See *W.* **Eller.**
Klemm, *W.* See *W.* **Biltz.**
Klenk, *E.*, new cerebroside, i, 1346.
Klenk, *E.* See also *H.* **Thierfelder.**
Klever, *H. W.* See *H.* **Staudinger.**
Klimone, *J.* [with *C. B. von* **Moltini**, and (*Miss*) *I.* **Benedik**], configuration of the higher unsaturated fatty acids and their salts, i, 505.
Kling, *A.*, and (*Mme.*) *A.* **Lassieur**, separation of zinc and nickel by hydrogen sulphide, ii, 439.
Klingstedt, *F. W.* determination of pentosan, ii, 720.
ultra-violet absorption spectra of mono- and di-derivatives of benzene, ii, 929.
Klinke, *K.*, volumetric determination of sulphate in minute amounts, ii, 239.
Klissiunis, *N.*, antiseptic action of cupric chloride in solvents of different dielectric constants, i, 1500.
Klissiunis, *N.* See also *G.* **Joachimoglu** and *L.* **Pincussen.**
Klobusitzky, *D. von*, rate of sinking of erythrocytes with reference to the Hofmeister ionic series, i, 710.
Klobusitzky, *D. von.* See also *J.* **Csapó.**
Klockmann, *P.* See *R.* **Stoermer.**
Kloppers, *R. K.* See *G.* **Hertz.**
Klopstock, *A.* See *H.* **Sachs.**
Klopstock, *E.* See *J.* **Wohlgemuth.**
Klopstock, *F.*, nature of the specific hæmolysins, i, 1345.
Klosky, *S.*, and *C.* **Marano**, titania jellies, ii, 1057.
Kloss, *J.* See *G.* **Heller.**
Kluyver, *A. J.*, and *H. J. L.* **Donker**, formation of acetylmethylcarbinol and 2:3-butyleneglycol in the fermentation of sugars by alcohol yeasts and true lactic acid bacteria, i, 1215.
the unity in the chemistry of the fermentative sugar dissimilation processes of microbes, i, 1215.
catalytic transference of hydrogen as the basis of the chemistry of decomposition processes, ii, 1173.
Knaggs, *I. E.*, crystalline structure of pentaerythritol tetranitrate, ii, 748.
Knaggs, *J.*, and *S. B.* **Schryver**, gelatin. IV. Purification of gelatin by flocculation in an electric field, i, 90.
gelatin. VI. Influence of the treatment of the precursor on the character of the gelatin, i, 90.
gelatin. VII. Non-amino nitrogen of gelatin, i, 90.
Knaus, *W.* See *Robert* **Müller.**
Knecht, *E.*, and *E.* **Hibbert**, constituents of French and American resins. II., i, 1420.
interaction of dextrose and methylene-blue in an alkaline medium, ii, 605.
Knecht, *E.*, and *E. F.* **Muller**, action of heat on cotton cellulose, i, 370.
Knecht, *E.*, and *J. H.* **Platt**, alkali-cellulose, i, 370.
Knehans, *K.* See *F.* **Sauerwald.**
Knehe, *E.* See *M.* **Bergmann.**
Knickmann, *E.*, and *M.* **Helbig**, "Hager" soils, i, 1528.
Kniphorst, *L. C. E.*, nitration of symmetrical arylalkylcarbamides, i, 905.
Knipping, *H. W.*, I. Determination of the carbon dioxide tension in alveolar air. II. Acetylene narcosis, i, 176.
Knobel, *M.*, commutator measurements on polarised electrodes, ii, 211.
effect of pressure on overvoltage, ii, 212.
effect of surface condition on overvoltage, ii, 547.
porous electrode for oxidations or reductions, ii, 1092.
Knoll, *W.* See *H.* **Pringsheim.**
Knoll & Co., preparation of salts of dimethylxanthine with organic acids, i, 828.
Knoop, *F.*, and *J. G.* **Blanco**, acetylation of amino-acids in the animal body, i, 1208.
Knoop, *F.*, and *M.* **Gehrke**, oxidation of acetic acid, acetone, and toluene, i, 1131.

Knoop, *F.*, and *H.* **Jost**, influence of some aliphatic substances on the level of lactic acid and sugar in the blood, i, 180.
Knoop, *F.*, and *H.* **Oesterlin**, natural synthesis of amino-acids and its experimental reproduction, i, 1493.
Knuth, *C. A.* See *A. S.* **Richardson.**
Kobel, *M.* See *C.* **Neuberg.**
Koberne, *M.* See *B.* **Emmert.**
Kobiliansky, *R.* See *F.* **Feigl.**
Kobliansky, *G. G.* See *S. V.* **Lebedev.**
Koblic, *O.*, oxidimetric titration of uranium, ii, 331.
Koch, *C.* See *H.* **Remy.**
Koch, *E. M.*, and *F. C.* **Koch**, presence of trehalose in yeast, i, 1508.
Koch, *F. C.* See *E. M.* **Koch.**
Koch, *H.* See *A.* **Sieglitz.**
Koch, *J. A.* See *L. H.* **Cretcher.**
Koch, *L.* See *G.* **Masing.**
Koch, *P. P.*, and *B.* **Kreiss**, change of mass of silver halides on intense illumination, ii, 810.
Koch, *P. P.*, and *H.* **Vogler**, separation of silver from silver halides through intense irradiation, ii, 941.
Koch, *P. P.* See also *R.* **Blunck.**
Koch, *W.* See *W.* **Mund.**
Kochinki, *K. L.* See *H.* **Reinwein.**
Kochmann, *R.*, auxoureases; mechanism of the action of calcium, i, 200.
Kockel, *L.*, dependence of dielectric constant of aqueous solutions on temperature, ii, 932.
Kodama, *S.* See *K.* **Linderström-Lang.**
Köberle, *K.* See *H.* **Lecher.**
Kögl, *F.*, and *J. J.* **Postowsky**, colouring matters of fungi. I. and III. Atromentin, i, 50, 1439.
colouring matters of fungi. II. Dyes from *Dermocybe sanguinea*, Wulf, i, 1083.
Kögl, *F.*, and *G. von* **Taeuffenbach**, colouring matters of fungi. IV. Xylindein, the colouring matter of the green mould of decayed wood, i, 1440.
Kögler, *F.* See *H. P.* **Kaufmann.**
Köhl, *A.* See *W. D.* **Treadwell.**
Koehler, *A. E.*, acidosis of operative anæsthesia, i, 195.
Köhler, *B.*, modified Soxhlet extraction apparatus, ii, 708.
Köhler, *K.* See *E.* **Koenigs.**
Koehler, *M. G. A.* See *M.* **Marqueyrol.**
Köhler, *W.* See *G.* **Heller.**
König, *F.*, adsorption capacities of different charcoal powders, ii, 1054.
König, *J.* See *W.* **Manchot.**
König, *W.* See *F.* **Dehnert.**
König, *Walter*, homologous "vinylene-" indole and pyrrole dyes, i, 1184.
König, *Walter*, and *W.* **Meier**, thio- and oxa-cyanines, i, 705.
König, *Walter.* See also *D.* **Vörlander.**
Koenigs, *E.*, and *H.* **Geissler**, 3-hydroxy-4:5-pyridothiophen, i, 166.
Koenigs, *E.*, and *F. K.* **Hoffmann**, synthesis of 4-methyl-3-ethylpyridine and a new parvoline [2:6-dimethyl-3-ethylpyridine], i, 298.
Koenigs, *E.*, and *O.* **Jungfer**, sulphonation of 4-amino- and 4-hydroxypyridine, i, 154.
Koenigs, *E.*, *K.* **Köhler**, and *K.* **Blindow**, pyridonemethides [methylenedihydropyridines], i, 833.
Köpke, *O.*, Winkler's method for determining the iodine-bromine number without potassium bromide, ii, 246.
Koernicke, *E.*, determination of the heat of dissociation of mercury molecules from the band spectrum of mercury vapour, ii, 848.
Kötz, *A.*, and *W.* **Hoffmann**, hydroaromatic 1:2-oxides and 3-keto-1:2-oxides, i, 910.
Kofler, *L.*, and *W.* **Schrutka**, toxicity of saponins and detoxication by cholesterol, i, 1501.
Kofler, *L.*, and *A.* **Wolkenberg**, behaviour of saponins on dialysis, i, 1519.
Kohlhaas, *W.* See *K. von* **Auwers.**
Kohlrausch, *A.* See *F. B.* **Hofmann.**
Kohlschütter, *V.*, and *C.* **Egg**, "somatoid" forms, ii, 1035.
alterations of the habit and of the modification of calcium carbonate by substances in solution, ii, 1036.
Kohman, *G. T.*, solubility relations of isomeric organic compounds. IV. Mutual solubility of *o*-, *m*-, and *p*-nitroanilines and of *o*-, *m*-, and *p*-chloronitrobenzenes, ii, 1052.
Kohman, *G. T.*, and *D. H.* **Andrews**, solubility relations of isomeric organic compounds. V. Construction of the ideal ternary solubility diagram, and its use in analysis, ii, 1053.
Kohman, *G. T.* See also *D. H.* **Andrews.**
Kohn, *H.*, and *M.* **Guckel**, experiments on the carbon arc; vapour pressures of carbon, ii, 100.
Kohn, *M.*, and *A.* **Fink**, bromophenols. III. Bromo derivatives of phenol and the mobility of their bromine atoms, i, 133.
Kohn, *M.*, and *S.* **Grün**, bromophenols. XI. Bromination of quinol monomethyl ether and of nitroquinol dimethyl ether, i, 1265.

Kohn, *M.*, and *L. W.* **Guttmann**, bromophenols. VII. Bromine substitution products of quinol, i, 1263.

Kohn, *M.*, and *M.* **Jawetz**, bromophenols. IV. Bromo derivatives of *o*-cresol and the mobility of their bromine atoms, i, 135.

Kohn, *M.*, and *R.* **Lakner**, compounds obtained by the action of magnesium phenyl bromide on β-bromoethylphthalimide and γ-bromopropylphthalimide, i, 1276.

Kohn, *M.*, and *G.* **Löff**, bromophenols. VIII. Bromo- and bromonitroresorcinols, i, 1264.

monomethyl styphnate and a new trinitroguaiacol, 3:4:5-trinitro-2-hydroxyanisole, i, 1265.

Kohn, *M.*, and *R.* **Marberger**, bromophenols. X. Ethers of chloronitro and bromonitro derivatives of quinol and toluquinol and the mobility of the halogen atoms therein, i, 1264.

Kohn, *M.*, and *S.* **Strassmann**, bromophenols. IX. Bromo- and bromonitro-phenols, i, 1264.

Kohn, *M.*, and *M.* **Weissberg**, bromophenols. VI. *m*-Bromophenols, i, 655.

Kohn, *M.*, and *J.* **Wiesen**, bromophenols. V. Some bromo derivatives of *p*-cresol and the mobility of their bromine atoms, i, 539.

Kohn-Abrest, *E.*, detection of gaseous poisons in blood, i, 451.

gases in fresh, putrefied, and frozen blood, i, 604.

progress in chemical toxicology, i, 1116.

Koidzumi, *S.*, electrolytic oxidation of alcohols. II. Electrolytic chlorination of ethyl alcohol, ii, 808.

Kolker, *I.*, and *A.* **Lapworth**, direct combination of ethylenic hydrocarbons with hydrogen sulphites, i, 353.

Kolkmeijer, *N. H.*, *J. M.* **Bijvoet**, and *A.* **Karssen**, crystal structure of mercuric sulphide. I. and II., ii, 93, 484.

Koll, *W.* See *O.* **Diels**.

Koller, *G.* See *E.* **Späth**.

Koller, *L. R.*, electron emission from oxide-coated filaments, ii, 617.

Kollo, (*Mrs.*) *C.*, and *N.* **Georgian**, separation of aluminium from calcium by means of hexamethylenetetramine, ii, 330.

Kolosovski, *N. de*, entropy of perfect gases at absolute zero, ii, 496.

partition phenomena, ii, 506.

applications of the kinetic theory of gases, ii, 531.

heats of solution of glycerol, ii, 540.

heats of solution of barium chloride in aqueous alcohol, ii, 540.

Kolosovski, *N. de*, relation between the critical temperature and the expansion of liquids, ii, 646.

influence of the variation of the coefficient of viscosity with temperature on the specific heat of solutions, ii, 653.

viscosity of solutions, ii, 765.

theory of specific heats of solutions, ii, 791.

viscosity of acetic acid solutions, ii, 859.

work of viscosity and apparent molecular heat of substances in solution, ii, 870.

apparent molecular heat and viscosity of solutions of naphthalene in organic solvents ii, 1163.

Kolosovski, *N. de*, and *A.* **Kraeff**, heats of solution of phenols in water, ii, 540.

Kolthoff, *I. M.*, colour reaction for glycerol, ii, 161.

condition of methyl-orange in its transition interval, ii, 296.

condition of methyl-red in its transition interval, ii, 296.

adsorption of electrolytes on charcoal, ii, 383.

buffer mixtures prepared without standard acid as base, ii, 396.

salt errors of indicators in solutions poor in electrolytes, ii, 596.

trustworthiness of the quinhydrone electrode for the measurement of hydrogen-ion concentration in various solutions, ii, 671.

standard values in the calculation of the hydrogen exponent from measurements with the hydrogen and quinhydrone electrodes, ii, 794.

ionisation and catalysis experiments suitable for lecture demonstrations, ii, 819.

titration of iodides with iodate, ii, 1000.

albumin solutions, ii, 1055.

sodium rhodizonate as a reagent for barium, strontium, and lead, ii, 1095.

Kolthoff, *I. M.*, and *B. D.* **Hartong**, antimony electrode as an indicator for hydrogen ions and its application in potentiometric titrations of acids and bases, ii, 325.

Kolthoff, *I. M.*, and *O.* **Tomiček**, potentiometric determination of vanadium, chromium, and iron in presence of each other and its application to steel analysis, ii, 72.

Koltschin, *N. J.*, equation of state and its relation to the laws of thermodynamics, ii, 1061.

Komatsu, *S.*, and *C.* **Fujio**, camphor series. IV., i, 564.
Komatsu, *S.*, and *T.* **Hiraidzumi**, Beckmann rearrangement. XIV. Distillation of the sodium salts of oximes under reduced pressure, i, 934.
Komatsu, *S.*, and *M.* **Ishimasa**, ripening of the kaki-fruit. VII., i, 759.
Komatsu, *S.*, and *M.* **Kurata**, catalytic action. XI. and XV. Catalytic activity of reduced copper. I. and II., i, 687, 942.
camphor series. VII. Catalytic formation of menthols and menthones from *l*-menthol, i, 943.
camphor series. V., i, 1290.
Komatsu, *S.*, and *B.* **Masumoto**, catalytic action. X. Comparative study of the catalytic activity of reduced copper, reduced nickel, and thoria. I., ii, 1071.
Komatsu, *S.*, and *N.* **Matsunami**, kakishibu. III. Constitution of shibuol. II., i, 950.
Komatsu, *S.*, *N.* **Matsunami**, and *M.* **Ishimasa**, kakishibu. II., i, 759.
Komatsu, *S.*, and *R.* **Nodzu**, synthesis of phosphoric acid esters. II. Synthesis of some glucose monophosphoric acid esters and their behaviour towards yeast, i, 515.
chemistry of Japanese plants. VII. Phyto-chemical study of yamamomo-fruit, i, 1025.
Komatsu, *S.*, and *C.* **Tanaka**, catalytic action. XIV. Comparative study of the catalytic activity of reduced copper, reduced nickel, and thoria. II., i, 905.
chemistry of Japanese plants. III. Chemical development in the growth of bamboo shoots, i, 1369.
Komatsu, *S.*, and *H.* **Ueda**, chemistry of Japanese plants. V. Chemical composition of *Hydrangea paniculata*, Sieb. I., i, 762.
constitution of polysaccharides. III. Plant mucilage. I., i, 762.
Komatsu, *S.*, and *S.* **Yamada**, chemistry of Japanese plants. IV. Saturated fatty acids in camphor seed fat, i, 881.
Komatsu, *S.*, and *T.* **Yukitomo**, camphor series. V. Catalytic action of reduced copper and reduced nickel on *l*-menthol, i, 687.
Komatsu, *S.* See also *T.* **Hara**.
Komiyama, *J.* See *F.* **Haffner**.
Komm, *E.*, the tryptophan–aldehyde reaction, ii, 164.
Komm, *E.* See also *E.* **Abderhalden**, and *A.* **Heiduschka**.
Komori, *K.* See *M.* **Horii**.
Kon, *G. A. R.*, and *R. P.* **Linstead**, three-carbon system. III. $\alpha\beta$–$\beta\gamma$ Change in unsaturated acids, i, 506.
three-carbon system. IV. A case of retarded mobility, i, 633.
Kon, *G. A. R.*, *L. F.* **Smith**, and *J. F.* **Thorpe**, ring-chain tautomerism. XII. Derivatives of $\beta\beta$-dimethyl-α-ethylglutaric acid, i, 509.
Kon, *S.*, and *C.* **Funk**, unusual type of fatty compound in a product of animal origin [caseinogen], i, 230.
Kon, *S.* See also *C.* **Funk**.
Kondakov, *I. L.*, and *S.* **Saprikin**, pinene. I. Action of the pinenes on certain compounds capable of yielding hydrogen halides, i, 1080.
terpenes. II. Synthesis of diterpenes, i, 1163.
terpenes. III. Synthetic diterpenes and polyterpenes, i, 1292.
Kondo, *K.*, casein, ii, 518.
Kondo, *M.*, transformation of glucal into deoxyglucose in the rabbit, i, 99.
Kondo, *S.*, metabolism of acid-fast bacteria. III. Nutritional needs of the bacillus of avian tuberculosis; utilisation of simple chemical substances for its growth, i, 206.
metabolism of acid-fast bacteria. IV. Metabolism of the human and bovine types of tubercle bacillus, i, 477.
Kondratéev, *V.*, ionisation of salt vapours. II., ii, 615.
Kondyrev, *N. V.*, electrolytic properties of magnesium organic compounds, i, 529.
Kondyrev, *N. V.*, and *D. P.* **Manojev**, electrolytic properties of magnesium organic compounds. II. Electrical conductivity of magnesium ethyl bromide in ethereal solutions, i, 529.
Konermann, *E.* See *P.* **Pfeiffer**.
Konetschnigg, *A.* See *Robert* **Müller**.
Konishi, *M.*, fate of urocanic (glyoxalineacrylic) acid in the animal body, i, 731.
urocanic acid formation from the optical isomerides of histidine, i, 731.
Konishi, *M.*, and *Y.* **Tani**, fate of glyoxalinepropionic acid (and iminazolelactic acid) in the dog, i, 731.
Konovalova, *R. A.* See *A. E.* **Tschitschibabin**.
Konrich, *F.*, and *E.* **Scheller**, effect of *X*-rays on cholesterol content, hydrogen-ion concentration, freezing-point depression, and surface tension of blood, i, 1356.
Kontníková, *Z.*, and *M.* **Shikata**, abnormal ionic activities in concentrated alkoxide solutions, ii, 672.

Kopaczewski, *W.*, coagulation of pectin, i, 872.
effects of dilution on colloids, ii, 111.
physical-chemical studies of synthetic colouring matters, ii, 529.
electrocapillary analysis of colloidal colouring matters, ii, 828.
turgoelectricity, ii, 978.
Kopaczewski, *W.* See also *E.* **Henrijean.**
Kopecky, *R.* See *C.* **Kranz.**
Kopfermann, *H.* See *R.* **Ladenburg.**
Kopler, *L.*, and *M.* **Brauner**, unpleasant taste of *Radix primulæ*, i, 1224.
Kopp, *E.* See *H.* **Rupe.**
Koppenhöfer, *S.* See *W.* **Küster.**
Kořán, *V.*, effect of vapours of some organic liquids on the surface tension of water, ii, 659.
Korczynski, *A.*, and *L.* **Kierzek**, catalysts for the Fischer synthesis of indoles, i, 973, 1097.
Kordysch, *L.*, the Epstein–Sommerfeld quantum rule, ii, 836.
Koref, *F.*, crystal tempering; softening of hard-drawn tungsten single-crystal wire, ii, 846.
Koref, *F.* See also *H.* **Alterthum.**
Korenchevski, *V.*, effect of excess of calcium on the skeleton, i, 1355.
Korenchevski, *V.*, and *M.* **Carr**, influence of the parents' diet on the young. I. Influence of the father's diet, i, 210.
influence of the parents' diet on the young. II. Influence on the young of an excessive amount of fat-soluble factor and calcium in the mother's diet during pregnancy, i, 210.
comparison of the values of yeast and of orange juice with those of marmite and of decitrated lemon juice, respectively, in the calcification of the skeleton, i, 211.
influence of the parents' diet on the young. III. Influence on the young of an excessive amount of calcium in the mother's diet during pregnancy, i, 463.
effects of calcium glycerophosphate, sodium glycerophosphate, and sodium dihydrogen phosphate on the skeleton of rats kept on a diet deficient only in fat-soluble factor, i, 464.
sexual glands and metabolism. IV. Influence of injections of emulsions of testes and prostate and of insulin-like testicular extracts on the nitrogen metabolism of normal, castrated, and thyroidectomised rabbits, i, 1513.
Korezyn, *J.* See *R.* **Weiss.**
Kores, *H. J.* See *H.* **Freundlich.**
Korn, *A.*, force of attraction and repulsion in atoms, ii, 1112.
Kornfeld, *G.*, and *H.* **Müller**, photochemical formation of hydrogen chloride, ii, 984.
Kornfeld, *H.*, influence of the deformation of ions on optical and chemical constants. III., ii, 12.
Korschun, *G.*, and (*Mme.*) *C.* **Roll**, absorption spectra of pyrrole and its derivatives. III. Influence of amino and carbamido groups on the absorption spectra of pyrrole derivatives, ii, 258.
Kortschagin, *M. W.*, pigment metabolism in the living organism. I. Action of gastric juice on chlorophyll, i, 200.
Koser, *S. A.*, and *R. H.* **Galt**, oxalic acid test for indole, i, 1510.
Kossel, *A.*, and *F.* **Curtius**, bacterial arginase, i, 1505.
Kostytschev, *S.*, and *M.* **Afanasieva**, respiration of lactic bacteria, i, 1118.
Kostytschev, *S.*, and *L.* **Frey**, alcoholic fermentation. XI. Acids resulting from yeast fermentation in presence of calcium carbonate, i, 1214.
Kostytschev, *S.*, and *A.* **Ryskaltchouk**, products of atmospheric nitrogen fixation by *Azotobacter agile*, i, 1014.
Kotake, *M.* See *R.* **Majima**, and *H.* **Wieland.**
Kotake, *Y.*, deamination of amino-acids and transformation of resulting products in the animal organism, i, 730.
Kotake, *Y.*, *M.* **Chikano**, and *K.* **Ichihara**, action of *Oidium lactis* on tyrosine and related compounds, i, 746.
Koten, *I. A.*, and *R.* **Adams**, reactions of the alkyl- and aryl-mercuric hydroxides, i, 236.
Kotko, *L.* See *E.* **Grischkevitsch-Trochimovski.**
Koulen, *K.* See *F.* **Speyer.**
Koumans, *A. K.*, standard solution for Sahli's hæmometer, i, 851.
Kourilsky, *R.* See *H.* **Bierry.**
Kovache, *A.*, and *E.* **Tricot**, attempts to synthesise benzene by condensation of acetylene at a high temperature, i, 799.
Kozakevitsch, *P. P.*, absorption of arsenic and oxalic acids by certain calcined oxides, ii, 855.
Kraeff, *A.* See *N. de* **Kolosovski.**
Kraemer, *E. O.*, second isoelectric point of gelatin, ii, 519.
kino-ultramicroscope, ii, 1156.

Kraemer, *E. O.*, and *J. R.* **Fanselow**, optical activity of gelatin systems, ii, 1057.
Kraemer, *E. O.*, and *A. J.* **Stamm**, determination of distribution of size of particles in emulsions, ii, 202.
Kraft, *F.* See *H.* **Finger**.
Krajewski, *A.* See *G. F.* **Hüttig**.
Kramer, *B.*, and *I.* **Gittleman**, iodometric determination of sodium in small amounts of serum, i, 180.
Kramers, *H. A.*, chemical properties of atoms according to the Bohr theory, ii, 835.
Kranlpuhl, *E.* See *R.* **Lesser**.
Kranz, *C.*, and *R.* **Kopecky**, laboratory apparatus for high-temperature nitrations, ii, 319.
Krasnikov, *A.* See *N.* **Seljakov**.
Kratinova, *K.* See *A.* **Palladin**.
Kratzer, *A.*, band spectra and molecular properties, ii, 836.
Kratzer, *A.*, and *E.* **Sudholt**, regularities in the resonance spectrum of iodine vapour and the determination of the moment of inertia, ii, 839.
Kraul, *R.* See *K. von* **Auwers**.
Kraus, *C. A.*, and *W. N.* **Greer**, tin dimethyl group and some of its reactions, i, 1394.
Kraus, *C. A.*, and *T.* **Harada**, compounds formed between tin trimethyl hydroxide and tin trimethyl halides, i, 1254.
Kraus, *C. A.*, and *W. C.* **Johnson**, so-called "metal ammoniums"; vapour pressure of solutions of lithium in liquid ammonia, ii, 389.
Kraus, *C. A.*, and *H. F.* **Kurtz**, reduction of metals from their salts by means of other metals in liquid ammonia solution, ii, 577.
Kraus, *C. A.*, and *W. V.* **Sessions**, chemistry of the tin trimethyl group, i, 1253.
Kraus, *E. J.*, logarithmic tables for volumetric analysis, ii, 323.
Kraus, *F.*, *S. G.* **Zondek**, *W.* **Arnoldi**, and *E.* **Wollheim**, position of electrolytes in the organism, i, 198.
Kraus, *I.*, colorimetric determination of tryptophan and its separation from indole and skatole, ii, 448.
Krause, *A.*, reaction between ferric sulphate and alkali, ii, 1192.
Krause, *A. C.*, and *F. C.* **Krauskopf**, substituted ammonium molybdates and tungstates, i, 908.
Krause, *E.*, and *A. von* **Grosse** fluorides of organo-metallic compounds. III. Thallium alkyl and aryl fluorides, i, 378.
alkyl compounds of thallium, i, 1252.
Krause, *E.*, and *O.* **Schlöttig**, preparation of a crystalline, organic lead compound with four different groups, i, 449.
Krause, *E.* See also *H.* **Wieland**.
Krauskopf, *F. C.* See *A. C.* **Krause**.
Krauss, *F.*, and *H.* **Deneke**, separation of palladium from platinum, ii, 1005.
Krauss, *F.*, and *H.* **Gerlach**, beryllium. I. Beryllium sulphate and its hydrates, ii, 314.
iridium tetroxide, ii, 424.
iridium halides, ii, 1089.
Krauss, *F.*, and *H.* **Kükenthal**, ruthenium tetroxide. III. Valency of ruthenium in the tetroxide, ii, 480.
Krauss, *F.*, and *D.* **Wilken**, osmium tetroxide. II. Compounds of osmium tetroxide, ii, 894.
Krauss, *G.* See *F.* **Feigl**.
Kraut, *H.* See *R.* **Willstätter**.
Kranz, *C.*, and *O.* **Turek**, decomposition of [2:4:6-]trinitrotoluene by the action of sunlight, i, 646.
Kraybill, *H. R.*, and *T. O.* **Smith** [metabolism of the tomato], i, 1122.
Krebs, *H. A.*, precipitation of colloidal gold by proteins, ii, 1155.
Krefft, *H.*, Döppler effect in canal rays from hydrogen, oxygen, and nitrogen, ii, 3.
Döppler effect of arc and spark lines, ii, 78.
Döppler effect in canal rays of hydrogen, ii, 78.
Kreis, *W.* See *H.* **Staudinger**.
Kreiss, *B.* See *P. P.* **Koch**.
Kreiss, *S.* See *D.* **Vorländer**.
Kremann, *R.*, and *O.* **Baukovac**, electrolysis of molten alloys. VIII. Tin–zinc alloys, ii, 679.
Kremann, *R.*, and *O.* **Benda**, electrolysis of molten alloys. VII. Silver–lead alloys, ii, 679.
Kremann, *R.*, and *J.* **Dellacher**, electrolysis of molten alloys. IX. Tin–aluminium alloys, ii, 679.
Kremann, *R.*, and *H.* **Drazil**, influence of substitution in the components on equilibria in binary solutions. XLV. Binary systems of benzhydrol with phenols and amines, ii, 649.
Kremann, *R.*, and *R.* **Gruber-Rehenburg**, electrolysis of molten alloys. VI. Copper alloys (Cu–Zn, Cu–Sn, Cu–Ag, Cu–Al), ii, 678.
Kremann, *R.*, and *A.* **Kapaun** [with **Budan**], electrolysis of molten amalgams of lead, tin, and bismuth, ii, 313.
Kremann, *R.*, *H.* **Kienzl**, and *R.* **Markl**, electrolysis of molten alloys. III. Lead–cadmium and lead–sodium alloys, ii, 132.

Kremann, *R.*, *Robert* **Müller**, and *H.* **Kienzl**, electrolysis of molten alloys. IV. Sodium–mercury alloys, ii, 132.

Kremann, *R.*, *Robert* **Müller**, and *H.* **Ortner**, electrolysis of molten alloys. V. Potassium, calcium, and cadmium amalgams, ii, 132.

Kremann, *R.*, and *P. G. von* **Rehenburg**, electrolysis of some tin alloys, ii, 312.

Kremann, *R.*, and *R. G. von* **Rehenburg**, electrolysis of potassium–sodium alloys, ii, 132.

Kremann, *R.*, *E.* **Zechner**, and *H.* **Drazil**, influence of substitution in the components on equilibria in binary solutions. XLVII. Binary systems of acids or esters with phenols, ii, 650.

Kremann, *R.*, *K.* **Zechner**, and *G.* **Weber**, influence of substitution in the components on equilibria in binary solutions. XLVI. Binary systems of azobenzene with phenols, ii, 650.

Kremers, *F.* See *L.* **Claisen**.

Kremers, *H. C.*, laboratory circulating pump for corrosive vapours, ii, 427.

rare earths. XX. Preparation and properties of metallic neodymium, ii, 588.

Kremers, *H. C.*, and *H.* **Beuker**, rare earths. XIX. Preparation and some properties of metallic cerium, ii, 581.

Kremers, *H. C.* See also *A. P.* **Thompson**, and *J.* **Wierda**.

Křepelka, *H.*, and *N.* **Nikolić**, revision of the atomic weight of aluminium. III. Analysis of aluminium chloride, ii, 620.

Křepelka, *H.*, and *W.* **Podrouzek**, precipitation of ferric salts with ammonium sulphide, ii, 703.

Křepelka, *H.*, and *F.* **Toul**, solubility of silver in water. I., ii, 697.

Krethlow, *A.*, optical and magnetic rotation dispersion, dispersion, density, and absorption spectra of chemically homologous compounds, ii, 1029.

Kreuder, *A.* See *K. von* **Auwers**.

Kreulen, *D. J. W.* [analysis of coal]; three point method with rapid cooling, ii, 240.

Krey, *W.* See *K.* **Brand**.

Kriegesmann, *L.* See *L.* **Grebe**.

Kriesel, *F. W.*, analysis of the new germanium–gallium mineral germanite, ii, 153.

Krige, *G. J. R.* See *G.* **Tammann**.

Krings, *W.* See *G.* **Tammann**.

Krishnan, *K. S.*, molecular scattering of light in liquids, ii, 1030.

Krishnan, *M. S.*, cordierite from Madras, India, ii, 822.

Kriss, *L.*, nephelometric determination of calcium and magnesium, i, 852.

Krizenecky, *J.*, and *J.* **Podhradsky**, function of water-soluble nutrients in the metabolism of aquatic animals. IV. Significance of carbamide in modifying the growth-promoting effect of dissolved nutrients on tadpoles, i, 612.

Kröger, *M.* See *M.* **Le Blanc**.

Kroetz, *C.*, biochemistry of irradiation. II. Influence of ultra-violet and Röntgen rays on the water, salt, and protein content of serum, i, 178.

biochemistry of irradiation. III. Effect of radiant heat on the reaction, the alkali reserve, and the salt equilibrium of the blood, i, 178.

adsorption of hydrogen and hydroxyl ions by charcoal, ii, 191.

Kroetz, *C.* See also *K.* **Gollwitzer-Meier**.

Krohn, *I. F. M.* See *O.* **Aschan**.

Krollpfeiffer, *F.*, spectrochemistry of thiochromans, Δ^3-thiochromens, and thiochromanones, ii, 1028.

Krollpfeiffer, *F.* [with *H.* **Schultze**, *H.* **Schlumbohm**, and *E.* **Sommermeyer**], thiochromanones and their transformation products. II., i, 1305.

Krone, *F.* See *R.* **Anschütz**.

Kronig, *R. de L.*, intensity of multiplets and their Zeeman components. I. and II., ii, 458, 917.

theory of the influence of magnetic fields on the stopping power of gases for α-particles, ii, 834.

Kronig, *R. de L.* See also *S.* **Goudsmit**.

Kroon, (*Miss*) *R.* See *A.* **Smits**.

Kruber, *O.*, aromatic hydrocarbons in low-temperature tar, i, 1137.

Krueger, *A. P.* See *F.* **Proescher**.

Krüll, *H.* See *A.* **Schönberg**.

Krug, *R.* See *R.* **Dietzel**.

Kruger, *A.*, normal and basic copper sulphate, ii, 58.

Kruger, *F.*, and *A.* **Sacklovsky**, *X*-ray investigation of palladium–silver alloys containing hydrogen, ii, 1125.

Kruyt, *H. R.*, lyophile colloids and Poiseuille's law, ii, 515.

albumin solutions, ii, 1056.

Kruyt, *H. R.*, and *J.* **Postma**, silicic acid sol, ii, 861.

Kruyt, *H. R.*, and *C.* **Robinson**, lyophile colloids and Poiseuille's law, ii, 391.

Kruyt, *H. R.*, and *H. J. C.* **Tendeloo**, determination of the size of invisible particles in emulsoid sols, ii, 113.

limited significance of hydrogen-ion concentration as a factor in determining the condition of lyophilic sols, ii, 1059.

Krzywanek, *W.*, calorific value and elementary analysis of animal fats, i, 1496.
Kubel, *K.* See *F.* **Foerster**.
Kubisch, *G.* See *T.* **Sabalitschka**.
Kubota, *B.*, *Y.* **Fujimura**, and *K.* **Akashi**, formation of a new dihydroxydiphenyl from resorcinol, i, 809.
Kubota, *B.*, and *K.* **Yoshikawa**, poisoning of nickel catalyst by thiophen and action of a copper catalyst, i, 805.
composition of reduced nickel as a catalyst, ii, 1174.
Kubota, *O.*, and *A. G.* **Perkin**, wandering of the acetyl group during methylation, i, 1159.
Kuckertz, *H.* See *R.* **Anschütz**.
Kudar, *J.*, quantum theory of red displacement of spectral lines, ii, 467.
Kudrjavzeva, *A.*, influence of polyneuritis on the creatine content of the muscle, i, 329.
Kudrjavzeva, *A.* See also *N. V.* **Kultaschev**, and *A.* **Palladin**.
Kühl, *F.*, rapid determination of sulphur, ii, 156.
Kühn, *R.* See *H.* **Baur**.
Kühnl, *N.*, and *W.* **Pauli**, general colloid chemistry. XIV. Constitution and stability of iron oxide sols. IV., ii, 776.
general colloid chemistry. XIV. Structure of heteropeptoids. I. Aluminium-iron oxide sols, ii, 776.
Kükenthal, *H.* See *G. F.* **Hüttig**, and *F.* **Krauss**.
Kürschner, *K.*, sublimation of "unsublimable" substances, i, 890.
lignin, i, 1387.
Kürthy, *L.*, chemistry and physiology of bismuth. V. Excretion of subcutaneously and intra-muscularly administered bismuth, i, 101.
Kürthy, *L.*, and *Hans* **Müller**, chemistry and physiology of bismuth. III. Determination of bismuth in urine, i, 100.
chemisty and physiology of bismuth. IV. Excretion of orally administered bismuth, i, 100.
chemistry and physiology of bismuth. I. Determination of bismuth, ii, 73.
Kürthy, *L.* See also *E. A.* **Hafner**, and *Hans* **Müller**.
Küster, *W.*, attempts to prepare a methylhydroxyethylmaleic acid. II. Derivatives of acetyl*cyclo*propanecarboxylic acid, i, 922.
Küster, *W.*, *E.* **Brudi**, and *S.* **Koppenhöfer**, 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl-$\omega\omega$-dicarboxylic acid and -5-vinyl-ω-carboxylic acid, i, 972.
Küster, *W.*, and *F.* **Grassner**, attempts to prepare a methylhydroxyethylmaleic acid. I. Derivatives of *cyclo*propanedicarboxylic acid, i, 922.
Küster, *W.*, and *R.* **Haas**, bile pigments. XIV. Treatment of ox gallstones, i, 722.
Küster, *W.*, *R.* **Haas**, and *H.* **Maurer**, bile pigments. XV. Bilirubin dimethyl ester, i, 307.
Küster, *W.*, and *W.* **Heess**, prosthetic group of blood pigments, i, 992.
Küster, *W.*, and *R.* **Huttenlocher**, porphyrins. VIII. Formation of porphyrin from hæmin, i, 845.
additive product of chlorine and a monomethyl(chloro)hæmin, i, 992.
Küster, *W.*, and *F.* **Schoder**, formation of sorbose by condensation of formaldehyde, i, 366.
Kuhlmann, *A.* See *H.* **Remy**.
Kuhlmann, *W. H. F.* [ultra-balance], ii, 706.
Kuhlmann, *W. H. F.* See also *F.* **Holtz**.
Kuhn, *A.*, water fixation in colloids, ii, 36.
Kuhn, *A.*, and *H.* **Pirsch**, peptisation of bismuth hydroxide, ii, 525.
Kuhn, *A.* See also *W.* **Ostwald**.
Kuhn, *H.* See *E.* **Wilke**.
Kuhn, *M.* See *J. von* **Braun**.
Kuhn, *P.* See *B.* **Stuber**.
Kuhn, *R.*, constitution of starch and different modes of action of the amylases, i, 11, 636.
theory of the isoelectric point, ii, 117.
Kuhn, *R.*, and *H.* **Baur** [with *R.* **Heckscher**], insulin and its action. IV. Influence of insulin on the lactic acid content and hydrogen-ion concentration of the blood, i, 843.
Kuhn, *R.*, and *F.* **Ebel**, stereochemistry of the tetrahedral carbon atom. I. Inversion phenomena, i, 780.
action of yeast on glycidic acids, i, 1237.
fission of ring systems, i, 1378.
Kuhn, *R.*, and *G. E. von* **Grundherr**, influence of acidity on the action of yeast extracts on concentrated solutions of dextrose, i, 203.
Kuhn, *R.*, and *P.* **Jacob**, mutarotation, ii, 49.
stereochemistry of aromatic compounds; isomerism of the 9-aminofluorenes, i, 1260, 1404.

Kuhn, *R.*, and *H. H.* **Schlubach**, behaviour of polymethylated sugars towards emulsin, i, 863.
Kuhn, *R.*, and *T.* **Wagner-Jauregg**, rate of oxidation of sugars by permanganate, i, 1241.
Kuhn, *R.*, and *A.* **Wassermann**, "fluorenone hydrate," i, 1398.
Kuhn, *R.*, and *F.* **Zumstein**, stereochemistry of the tetrahedral carbon atom. II. Configuration of the diaminosuccinic acids, i, 1249.
Kuhn, *R.* See also *B.* **Emmert**.
Kuhrmann, *F.* See *H.* **Stobbe**.
Kuindshi, *B. M.* See *A. E.* **Tschitschibabin**.
Kulenkampff, *H.*, reflection of *X*-rays in potassium bromide crystals, ii, 1033.
Kulkarni, *D. A.* See *P. S.* **Varma**.
Kultaschev, *N. V.*, and *A.* **Kudrjavzeva**, catalytic decomposition of acetic acid by wood charcoal, ii, 881.
Kumagawa, *H.* See *R.* **Willstätter**.
Kunz, *A.* See *C. S.* **Hudson**.
Kunz, *E.* See *E.* **Späth**.
Kunz, *R.*, and *K.* **Sehrbundt**, complex metallic derivatives of chlorophyll. I., i, 1297.
Kunz, *R.*, and *W.* **Stählinger**, complex metallic compounds of indigotin. III., i, 1318.
Kunze, *J.* See *E.* **Schill**.
Kunze, *K.* See *D.* **Vorländer**.
Kurata, *M.* See *S.* **Komatsu**.
Kurckmann, *E.*, soil acidity, i, 1032.
Kurnakov, *N. S.*, solid solutions of water and oxygen, ii, 767.
singular points in chemical diagrams, ii, 868.
Kurnakov, *N. S.*, and *K. F.* **Beloglazov**, copper–antimony alloys, ii, 787.
Kurnakov, *N. S.*, and *S. F.* **Shemtschushni**, equilibrium of the reciprocal salt system, sodium chloride–magnesium sulphate with reference to natural salt solutions, ii, 299.
Kurtenacker, *A.*, and *K.* **Bittner**, iodometric analysis of a mixture of sulphide, sulphite, and thiosulphate, ii, 239.
determination of sulphur in polysulphides, ii, 433.
determination of polythionic acids in presence of one another, ii, 434.
Kurtenacker, *A.*, and *M.* **Kauffmann**, polythionates. I. Decomposition of polythionates in aqueous solution, ii, 1189.
polythionates. II. Influence of thiosulphate and sulphite on the stability of polythionates, ii, 1190.
Kurtenacker, *A.*, and *M.* **Kauffmann**, polythionates. III. Action of hydrogen sulphide on polythionates, ii, 1190.
polythionates. IV. Action of alkali on polythionates, ii, 1190.
Kurtenacker, *A.*, and *F.* **Wengefeld**, oxidation of hydroxylamine. II., ii, 224.
catalysis of hydroxylamine, ii, 308.
Kurtz, *H. F.* See *C. A.* **Kraus**.
Kusnetzov, *S. J.*, significance of calcium for the genus *Citromyces*, i, 746.
Kutscher, *F.* See *O.* **Flössner**.
Kutscher, *G.* See *K. H.* **Bauer**.
Kutter, *F.*, colour reaction for lactic acid, ii, 1210.
Kvapil, *K.*, and *A.* **Němec**, relation between the "absolute air capacity" and degree of acidity of forest soils, i, 221.
Kylin, *E.*, and *B.* **Silfversvärd**, blood calcium. I. Calcium content of blood. II. Serum calcium during menstruation. III. Blood calcium during hypertonia. IV. Effect on blood calcium of administration of atropine–calcium, i, 852.

L.

Laar, *J. J. van*, structure of benzene, i, 799, 894.
theories of strong electrolytes and their history, ii, 152.
liquid densities at various temperatures, ii, 278.
equation of state of liquids and solids at high and low temperatures, ii, 495.
Van der Waals' equation of state, ii, 647.
simple formula for determining the critical temperature from the coefficient of expansion of the liquid phase, and the cause of its non-applicability for many molten salts, ii, 950.
additivity of boiling points, ii, 1141.
value of $\sqrt{a}$ calculated from the vapour tensions of alkali metals and halides in relation to the additive nature of this quantity, ii, 1141.
Laar, *J. J. van*, and *R.* **Lorenz**, ratio melting point: critical temperature, ii, 374.
derivation of the fundamental equation from the law of mass action for condensed and heterogeneous systems, ii, 866.
heat of mixture of condensed systems, ii, 870.

Labaune, *L.* See *J.* **Dupont.**
Labbé, *H.*, and *F.* **Lavagna**, action of acetoacetic acid on nitrogen metabolism, i, 191.
chemical constitution of crystalline lens of eye under normal and pathological conditions, i, 724.
Labes, *R.*, specific electro-kinetic effects between solid phases and dissolved electrolytes, ii, 796.
Lachmann, *A.*, Beckmann rearrangement. II., i, 678.
Lacrenier, *A.*, and *P.* **Gilard**, fusibility and viscosity of glass, ii, 379.
measurement of the surface tension of molten glass, ii, 387.
Lacroix, *A.*, new type of eruptive, mesocratic alkaline rock, ii, 429.
Lacroix, *J.*, electrolytic reduction of *mm'*-dinitrodiphenylsulphone to *mm'*-diaminodiphenylsulphone, i, 156.
Ladenburg, *R.*, inverse Stark effect in sodium vapour, ii, 79.
Ladenburg, *R.*, and *H.* **Kopfermann**, anomalous electrical double refraction of sodium vapour, ii, 917.
Laer, *J. A. van.* See *L. de* **Hoop.**
Lätt, *B.*, reactions of *p*-phenylenediamine with formaldehyde and hydrogen peroxide (comparison with the reactions of natural peroxydases), i, 1457.
La Face, *F.*, properties of some ethereal oils in Calabria, i, 564.
Laffay, *J.*, spark spectrum of mercury in the extreme red, ii, 384.
Laffitte, *P.*, propagation of the explosion wave, ii, 135.
Lafontaine, *G. H.*, equilibrium conditions of magnesium carbonate in ammoniacal solutions, ii, 785.
Lafontaine, *L.* See *V.* **Auger.**
Lafortune, *F.* See *P.* **Bruylants.**
Lafuma, *H.*, corresponding temperatures of solids, ii, 26.
Lagatu, *H.*, and *L.* **Maume**, linear relationship between the amounts of phosphoric acid and of nitrogen in the leaves of the adequately nourished vine, i, 756.
Lagrave, *R.* See *J.* **Lévy.**
Laing, *M. E.*, composition of soap films, ii, 960.
Lakner, *R.* See *M.* **Kohn.**
Lamb, *A. B.*, and *W. E.* **Vail**, effect of water and of carbon dioxide on the catalytic oxidations of carbon monoxide and hydrogen by oxygen, ii, 567.
Lambert, *B.*, and *S. F.* **Gates**, relationships existing between hydrogen and palladium, ii, 785.
Lambert, *R. H.*, and *E. P.* **Wightman**, automatic recorder for measuring size-frequency distribution of grains, ii, 1194.
La Mer, *V. K.* See *L. E.* **Holt**, *jun.*
Lamparter, *W.* See *J.* **Meisenheimer.**
Lamy, *R.* See *L.* **Bert.**
Landa, *S.*, new derivatives of pentadecaldehyde, i, 1038.
Landau, *M.* See *E.* **Philippi.**
Landé, *A.*, "dashed" and displaced spectral terms, ii, 249.
Zeeman effect in multiplets of higher grade, ii, 340.
Landrieu, *P.*, and *H.* **Blatt**, thermochemical study of triphenylpropargyl alcohol and its derivatives, i, 137.
Landrieu, *P.* See also *C.* **Mouren.**
Landsberg, *G.*, and *A.* **Predvoditelev**, absorption of light by ammonia, ii, 352.
Lane, *J. H.*, and *L.* **Eynon**, preparation of Fehling's solution for the volumetric determination of reducing sugars, ii, 445.
Lane, *L. B.*, freezing points of glycerol and its aqueous solutions, ii, 971.
Lang, *H.* See *A.* **Löwenbein.**
Lang, *L.*, lipoids of the ovaries of cows during the œstrous cycle, i, 457.
Lang, *R.*, iodometric methods based on the formation of cyanogen iodide. II., III., and IV., ii, 597, 713.
iodometric determination of cyanogen compounds, ii, 1009.
Lang, *R. J.*, ultra-violet spark spectra of some elements, ii, 609.
Lang, *R. J.*, and *S.* **Smith**, doublet separation in C II and Si IV, ii, 829.
Langdon, *G. M.* See *J. W.* **McBain.**
Lange, *E.*, lattice energies, heats of hydration, and heats of solution, ii, 847.
Lange, *E.* See also *J.* **Wüst.**
Lange, *F.*, investigations of specific heat at low temperatures, ii, 96.
Lange, *H.*, simple *X*-ray apparatus for the examination of powdered crystals by the Seemann–Bohlin method, giving higher resolution with shorter exposure, ii, 482.
X-ray spectroscopic examination of some alloys by the Seemann–Bohlin method, ii, 482.
Lange, *Hans.* See *J.* **Meisenheimer.**
Lange, *Hermann*, and *M. E.* **Mayer**, significance of ions in muscular function. VI. Effect of various anions on the formation of phosphoric acid in surviving frog's muscle, i, 729.

Lange, *Hermann*, and *M. E.* **Mayer**, narcosis. III. Influence of general narcosis on the chemical processes in the striped muscle of the frog, i, 735.

Lange, *Hermann*. See also *G.* **Embden**, and *C.* **Emmrich**.

Lange, *L.*, dielectric constant and molecular association of some liquids, ii, 840.

Lange, *N. A.*, and *L. A.* **Ward**, determination of small amounts of iodine as iodide and iodate, ii, 598.

Lange, *W.* See *W.* **Traube**.

Langedijk, *S. L.*, absorption spectra of some ketones, ii, 1116.

Langedijk, *S. L.* See also *J.* **Böeseken**.

Langenbeck, *W.*, isomerism between pilocarpine and *iso*pilocarpine, i, 151.

degradation of histidine to *l*-aspartic acid, i, 306.

Langfeldt, *E.*, and *J.* **Holmsen**, excretion of purine derivatives in dogs, i, 1205.

"uricolytic index" of diabetic dogs, i, 1207.

determination of allantoin in presence of uric acid, creatinine, and amino-acids, ii, 1010.

Langmuir, *I.*, *C. G.* **Found**, and *A. F.* **Dittmer**, new type of electric discharge; streamer discharge, ii, 341.

Langmuir, *I.*, and *H. A.* **Jones**, simple method for quantitative studies of ionisation phenomena in gases, ii, 162.

Langmuir, *I.*, and *K. H.* **Kingdon**, thermionic effects caused by vapours of alkali metals, ii, 254.

Lankelma, *H. P.* See *L. C.* **Raiford**.

Lantz, *R.*, and *A.* **Wahl**, β-naphthaquinone-1-arylimines, i, 820.

action of aromatic amines on naphthaquinonearylimines, i, 820.

arylaminonaphtholsulphonic acids, i, 910.

preparation and properties of naphthaquinonearylimines, i, 1159.

Lantz, *R.* See also **Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis**.

Laporte, *G.*, primed terms in the spectra of the lighter elements, ii, 1104.

Laporte, *O.*, structure of the iron spectrum. II., ii, 4.

Laporte, *O.* See also *W. F.* **Meggers**.

Lapparent, *J. de*, relations between hydrocarbons and carbonates in silex and phtanites, ii, 821.

Lapschin, *M. I.* See *A. E.* **Tschitschibabin**.

Lapworth, *A.*, induction of alternate polarities, especially in relation to the extent and intensity of transmission, ii, 636.

Lapworth, *A.*, and *E. N.* **Mottram**, oxidation products of oleic acid. I. Conversion of oleic acid into dihydroxystearic acid and the determination of higher saturated acids in mixed acids from natural sources, i, 1129.

oxidation products of oleic acid. II. Degradation of dihydroxystearic acid, i, 1234.

Lapworth, *A.*, *L. K.* **Pearson**, and *E. M.* **Mottram**, preparation and properties of purified oleic acid and some of its salts, i, 355.

Lapworth, *A.* See also *W.* **Baker**, *G. N.* **Burkhardt**, (*Miss*) *L.* **Higginbotham**, and *I.* **Kolker**.

Laqueur, *E.*, and *A.* **Sluyters**, adsorption of poisons by a new plant charcoal "supra-norit," i, 736.

Laqueur, *E.* See also *E.* **Dingemanse**.

Laquer, *F.*, lactic acid content of blood in high altitudes. II. Influence of muscular work, i, 324.

Lardy, *G. C.*, ultra-violet absorption spectra of ketens and of their dimerides. I. and II., ii, 87.

Larsen, *E. S.* See *E. V.* **Shannon**.

Larson, *A. T.*, and *C. A.* **Black**, concentration of ammonia in a compressed mixture of hydrogen and nitrogen over liquid ammonia, ii, 501.

solubility of mixtures of hydrogen and nitrogen in liquid ammonia, ii, 852.

Larson, *A. T.*, and *F. E.* **Smith**, synthesis of water over nickel and copper catalysts, ii, 563.

Larsson, *E.*, electrolytic dissociation of dibasic acids. II. Second dissociation constants, ii, 294.

Lasarev, *P.*, kinetics of colloidal processes in the stimulation of tissues, i, 1499.

theory of electrodeless discharge in gases, ii, 1107.

molecular physics. I. Relationship between elastic limit and atomic concentration, ii, 1134.

theory of [solid] solutions, ii, 1144.

Lasch, *F.*, cholesterol in the cerebrospinal fluid, i, 456.

Lasnitzki, *A.* See *P.* **Rona**.

Lassé, *R.* See *W. A.* **Roth**.

Lasseur, *P.*, *F.* **Girardet**, and *H.* **Vermelin**, physico-chemical constants of sera. I. Variations of the electrical conductivity with dilution, i, 853.

Lassieur, *A.*, economic anode for rapid electro-analysis, ii, 154.
electrolytic separation of copper, antimony, and bismuth from lead, ii, 159.
electrolytic separation of copper, antimony, lead, and tin, ii, 328.
rapid electroanalysis; separations by graded potentials, ii, 711.
Lassieur, (*Mme.*) *A.* See *A.* **Kling.**
Lászlo, *D.* See *F.* **Lieben.**
Lászlő, *H. de*, absorption of ultra-violet rays by methyl derivatives of naphthalene, ii, 179.
Latham, *O.*, Folin and Wu's method of blood analysis, i, 1343.
Latimer, *W. M.*, *R. M.* **Buffington**, and *H. D.* **Hoenshel**, hydrogen liquefying cycle and cryostat for the maintenance of low temperatures, ii, 818.
Latshaw, *M.*, simple tangentimeter, ii, 428.
Latshaw, *M.*, and *W. A.* **Patrick**, rate of oxidation of nitric oxide. I. Method of measuring the velocity of a rapid gaseous reaction, ii, 681.
Latshaw, *M.*, and *L. H.* **Reyerson**, reducing action of hydrogen adsorbed in silica gel, ii, 412.
Lattès, (*Mme.*) *J. S.*, separation of the total radiation of radium into groups by absorption in platinum, ii, 465.
method of analysis by absorption of radioactive radiations, ii, 623.
Lattey, *R. T.*, passage of an alternating current through sulphuric acid, ii, 979.
Lau, *E.*, excitation maxima for spectral lines in the striæ of the positive column of hydrogen, ii, 721.
Lau, *E.* See also *E.* **Gehrcke.**
Laubengayer, *A. W.* See *R. B.* **Corey**, and *L. M.* **Dennis.**
Laude. See **Pariselle.**
Lauder, *P. E.*, and *B.* **Ali**, nitrogen fixation in the Punjab, i, 1524.
Laue, *M. von*, and *N.* **Sen**, calculation of the fall of potential in the ion and electron gas emitted from glowing metals, ii, 7.
Laun, *F.* See *P.* **Walden.**
Laurent, (*Mlle.*) *Y.* See *P.* **Freundler.**
Laurie, *A. P.*, magnetic theory of valency, ii, 16.
expansion of water while freezing, ii, 762.
Lavagna, *F.* See *H.* **Labbé.**
Lavrov, *B. A.*, *O. P.* **Moltschanova**, and *A. J.* **Ochotnikova**, efficiency of urea as a source of nitrogen in a young ruminant (kid), i, 464.
Lawn, *L.*, and *C. G. L.* **Wolf**, early action of insulin in the diabetic, i, 483.
Lawrence, *E. O.*, the photo-electric effect in potassium vapour as a function of the frequency of the light, ii, 831.
Lawrence, *J. V.* See *J. A.* **Harris.**
Lawrence, *Z. W.* See *J. A.* **Harris.**
Lawson, *W.* See *E. C.* **Dodds.**
Lawson, *W. E.*, and *W. O.* **Scott**, electrolytic modification of the Gutzeit method for determination of arsenic in body-tissues, i, 996.
Lazier, *W. A.*, and *H.* **Adkins**, dehydrogenation and dehydration of alcohols over a zinc oxide catalyst, i, 878.
Lazier, *W. A.* See also *C. S.* **Marvel.**
Lazzarini, *G.* See *G.* **Minunni.**
Lea, *F. M.* See *S. R.* **Carter.**
Leake, *C. D.*, effect of ethylene anæsthesia on the acid-base balance of blood, i, 862.
Leavenworth, *C. S.* See *H. B.* **Vickery.**
Lebeau, *P.*, and *P.* **Marmasse**, determination of carbon dioxide and carbon monoxide, ii, 824.
Lebeau, *P.*, and *M.* **Picon**, transformation of diamond in a vacuum at high temperatures, ii, 136.
Lebedev, *A.*, mechanism of alcoholic fermentation, i, 204.
Lebedev, *S. V.*, and *E. P.* **Filonenko**, polymerisation. X. Action of certain silicates on unsaturated compounds, i, 225.
Lebedev, *S. V.*, *G. G.* **Kobliansky**, and *A. O.* **Yakubchik**, relative rates of catalytic hydrogenation of different types of unsaturated compounds. I. Aliphatic ethylenic derivatives, i, 350.
Lebermann, *F.*, simple clinical method for determining small amounts of potassium in blood-serum and other fluids, i, 96.
simple clinical micro-method for determining sodium in blood-serum, i, 324.
micro determination of potassium in blood-serum and other fluids, i, 714.
Le Blanc, *M.*, and *M.* **Kröger**, migration of ions in solid electrolytes, ii, 41, 977.
Le Blanc, *M.*, and *A.* **Rössler**, dissolution of mixed crystals of (Na,Ag)Cl and Tammann's *n*/8 mol. law, ii, 365.
Le Breton, *E.*, and *C.* **Kayser**, purine metabolism in *Diabetes insipidus*, i, 610.

Le Chatelier, *H.*, allotropy of glass, ii, 190.
viscosity and allotropy of glass, ii, 280.
theoretical force of explosives, ii, 558.
Lecher, *H.* [with *F.* **Graf**, *C.* **Heuck**, *K.* **Köberle**, *F.* **Gnädinger**, and *F.* **Heydweiler**], constitution of thiocarbamide and of thiuronium salts. II., i, 1390.
Lecher, *H.* [with *F.* **Holschneider**], valency problem of sulphur. VIII., i, 390.
Lecher, *H.* [with *F.* **Holschneider**, *K.* **Köberle**, *W.* **Speer**, and *P.* **Stöcklin**], sulphur phenyl chloride [chlorothiolbenzene]. II., i, 390.
Lecher, *H.*, and *F.* **Graf** [with *F.* **Gnädinger**], peralkylated guanidines. III., i, 1392.
Lecher, *H.*, and *F.* **Heydweiler**, constitution of thiocarbamide and of thiuronium salts. III., i, 1392.
Lecher, *H.*, *K.* **Köberle**, and *P.* **Stöcklin**, valency problem of sulphur. IX. New class of organic radicals, i, 391.
Lechner, *M.* See *K. von* **Auwers**.
Lecomte, *J.*, infra-red absorption spectra of alcohols, ii, 351.
infra-red absorption spectra of aldehydes and ketones, ii, 627.
Lecoq, *R.*, variability of the optimum temperature for the diastatic action of germinated barley on cooked and uncooked starchy materials, i, 470.
Ledbury, *W.* See *E. W.* **Blair**.
Lederer, *F. L.* See *F.* **Feigl**.
Ledig, *P. G.*, absorption of carbon dioxide and ammonia from gas bubbles, ii, 106.
Leduc, *A.*, molecular association and the gas equation of state, ii, 376.
Leduc, *S.*, action of magnesium *p*-anisyl and *p*-tolyl bromides on camphor, i, 821.
Lee, *S.* See *B.* **Stuber**.
Leendertz, *G.*, serum proteins, i, 96.
Lees, *N. D.* See *J. A.* **Aeschlimann**.
Le Fèvre, *A. J.* See *W. C. de* **Graaff**.
Leffmann, *H.*, and *M.* **Trumper**, tests for ethyl phthalate, ii, 1008.
Legagneur, *F. S.* See *A.* **Haller**.
Legendre, *R.*, determination of dissolved carbon dioxide, ii, 714.
Legg, *V. H.*, and *R. V.* **Wheeler**, plant cuticles. I. Modern plant cuticles; composition of coal, i, 1025.
Le Guyon, *R. F.*, and *R. M.* **May**, rapid determination of phosphates, ii, 1202.
Le Heux, *J. W.*, permanence of choline solutions in ampoules, i, 374.
Lehmann, *E.* See *C.* **Räth**.
Lehmann, *F.* See *A.* **Rosenheim**.
Lehmann, *J. F.*, and *T. H.* **Osgood**, ionisation produced in air during the complete absorption of slow electrons, ii, 832.
Lehmstedt, *K.*, formation of salts from glyoxaline-4:5-dicarboxylic acid, i, 1103.
Lehmstedt, *K.*, and *O.* **Zumstein**, determination of nitroamino and nitroimino groups, ii, 1201.
Lehne, *A.*, and *W.* **Schepmann**, cellulose of jute, i, 518.
Leibowitz, *J.* See *H.* **Pringsheim**.
Leide, *A.*, *K*-series of *X*-rays, ii, 457.
Leineweber, *F.* See *R.* **Kautsky**.
Leiss, *C.*, new spectrum apparatus, monochromator, and quartz spectrograph with crossed prisms to secure highest spectral purity in the region 200 $\mu\mu$ to 2 μ, ii, 341.
Leiter, *L.*, metabolism of glyoxalines, i, 1003.
Leites, *S.*, endocrine glands and blood calcium, i, 95.
Lejeune, *G.* See *C.* **Marie**.
Lelesz, *E.* See *L.* **Randoin**.
Lelièvre, *J.*, and *V.* **Ménager**, application to *Laminaria flexicaulis* of the combustion method of analysis, i, 619.
Lely, *C. W. A.*, structure of the dihydrobenzenes and some related compounds, i, 1396.
Lemarchand, *M.*, occlusion of magnesium [oxalate] by calcium oxalate, ii, 385.
Lemarchands, qualitative separation of cobalt, nickel, zinc, and manganese, ii, 242.
Lematte, *L.*, and *L.* **Beauchamp**, composition of human brain, i, 1487.
Lemay, *P.*, and *L.* **Jaloustre**, comparative action of bismuth on *Staphylococcus*, *Streptococcus*, and *Bacillus coli*, i, 206.
Lemay, *P.* See also *A.* **Maubert**.
Lemmermann, *O.*, action of silica in increasing the yield [of plants] in sand cultures with insufficient phosphoric acid, i, 767.
Lemmermann, *O.*, and *H.* **Wiessmann**, carbon dioxide production in soils, i, 348.
Lemmermann, *O.*, *H.* **Wiessmann**, and *K.* **Eckl**, from what depth in the soil can plants usefully obtain nutrients? i, 1029.
Lemmermann, *O.*, *H.* **Wiessmann**, and *K.* **Sammet**, action of silica in increasing the yield [of plants], i, 766.
Lemoigne, *M.*, bacterial autolysis; acidification due to the formation of β-hydroxybutyric acid, i, 478.

Lemoigne, *M.*, origin of β-hydroxybutyric acid obtained by microbial processes, i, 867.
chemical mechanism of the principal fermentations of dextrose, i, 1361.
Lemon, *H. B.*, comet tail spectrum and Deslandres' first negative group, ii, 249.
spark spectrum of tungsten in a helium vacuum arc, ii, 454.
spectrum of "nebulium," ii, 1099.
Lendle, *L.*, standardisation of certain glucosides which affect the heart, by oral administration to frogs, i, 1501.
Lenher, *S.* See *I. R.* **McHaffie**.
Lenher, *V.*, and *C. H.* **Kao**, preparation of selenium monochloride and monobromide, ii, 426.
[quantitative] separation of selenium and tellurium by sulphur dioxide in hydrochloric acid solution, ii, 434.
preparation of selenic acid and of certain selenates, ii, 817.
separation of selenium and tellurium, ii, 1199.
Lenher, *V.*, and *E. J.* **Wechter**, selenic acid and the selenates, ii, 815.
Lenher, *V.* See also *C. W.* **Muehlberger**.
Lennon, *J. J.* See *H.* **Ryan**.
Lennox, *W. G.*, and *M. F.* **O'Connor**, uric acid in blood, i, 711.
Lenoble, *E.*, electrolysis of a colloidal solution of hemicellulose, i, 793.
Lenz, *H.*, passage of electrons through photo-electrically active crystals, ii, 920.
electronic conduction in crystals, ii, 1019.
Léon, *A.* See *J.* **Ranedo**.
Leonard, *C. S.*, synthesis of β-phenylethyl alcohol, i, 913.
Leonard, *C. S.* See also *C.* **Voegtlin**.
Leone, *P.*, organo-metallic compounds of aluminium. I., i, 529.
organo-metallic compounds of aluminium. III. Action of ammonia and amines, i, 530.
organo-metallic compounds of aluminium. IV. Action of acid chlorides, i, 937.
separation of aliphatic amines from ammonia, ii, 907.
Leone, *P.*, and *A.* **Braicovic**, organo-metallic compounds of aluminium. II. Action of ketones, i, 677.
Leone, *P.*, and *G. B.* **Tafuri**, determination of acetaldehyde in the determination of lactic acid, ii, 907.
Leone, *P.* See also *G.* **Bargellini**.
Leontovicz, *M.*, equilibrium principle of G. N. Lewis, ii, 926.
Lepeschkin, *W. W.*, starch-swelling in living and dead cells, i, 1004.
Lepouse, *H.*, action of sulphuric acid and sulphuric anhydride on acetylene dichlorides, i, 784.
Lepper, *E. H.*, and *C. J.* **Martin**, micromethod for titrating the bicarbonate in plasma, i, 1201.
Lepper, *E. H.*, and *S. S.* **Zilva**, hydrogen carbonate of the plasma and hydrogen-ion concentration of the blood of guinea-pigs suffering from scurvy, i, 1208.
Lerner-Steinberg. See *H. von* **Wartenberg**.
Leroux, *P.*, determination of the coefficient of viscosity of water, ii, 1048.
Lescœur, *L.* See *A.* **Desgrez**.
Les Établissements Poulenc Frères, preparation of *p*-β-carbamido-β-acetoxy-*n*-propylaminophenylarsinic acid, i, 601.
Les Établissements Poulenc Frères, *E.* **Fourneau**, and *A.* **Madinaveitia**, *p*-dimethylaminomethylphenylarsinic acid, i, 990.
Les Établissements Poulenc Frères, and *C.* **Oechslin**, preparation of hydroxylated aliphatic arsinic acids, i, 122.
Leslie, *E. H.*, and *A. R.* **Carr**, vapour pressure of organic solutions and application of Dühring's rule to calculation of equilibrium diagrams, ii, 1050.
Leslie, *E. H.* See also *G. G.* **Brown**.
Lespieau, *R.*, true acetylenic compounds from mixed magnesium derivatives of acetylene, i, 225.
αβ-dihydroxy-Δγ-butinene, i, 351.
acetylenic derivatives of glycerol, i, 1375.
Lespieau, *R.*, and *C.* **Prévost**, diacetylene, i, 493.
diacetylene hexabromide, i, 626.
Lesser, *E. J.*, influence of homologous alcohols on sugar formation in the liver of the frog. II., i, 613.
Lesser, *E. J.* See also *E.* **Bissinger**.
Lesser, *R.*, *E.* **Kranlpuhl**, and *S.* **Sad**, constitution of naphthalene and its derivatives, i, 1424.
Lessing, *R.*, and *M. A. L.* **Banks**, influence of catalysts on carbonisation, i, 9.
Lessing, *R.* See also *L.* **Moser**.
Leuchs, *H.*, constitutional formulæ of anthranil and anthroxanic acid, i, 1335.
Leuchs, *H.* [with *K.* **Taube**], strychnos alkaloids. LXV. Oxidation of Hanssen's acid, i, 1314.
Leuchs, *H.*, and *S.* **Kanao**, strychnos alkaloids. XLIV. The hydrazone of brucinonic acid, i, 61.

Leuchs, *H.*, and *P.* **Sander**, isomerism of the *N*-carbalkoxy derivatives of dipeptides which contain a β-amino-acid, i, 1248.
spirans. XII. Preparation of dibenzo-Δ^{6}-suberen-1-one-2:2′-spiran, i, 1432.
Leuchs, *H.*, and *K.* **Winzer**, reaction of 2-benzylhydrindonephenylhydrazone with phenylhydrazine, i, 1281.
Leulier, *A.* See *G.* **Mourignand**, and *A.* **Policard**.
Levaditi, *C.*, curative action of basic bismuth 3-acetamido-4-hydroxyphenylarsinate in experimental syphilis, i, 1005.
Levaditi, *C.*, *A.* **Girard**, and *S.* **Nicolau**, trypanocidal action of gold and platinum, i, 1117.
Levaditi, *C.*, *S.* **Nicolau**, *J.* **Salgue**, and *R.* **Schoen**, mechanism of the action of bismuth in syphilis, i, 463.
Levaltier, *H.* See *P.* **Fleury**.
Levene, *P. A.*, configuration of α-aminohexonic acids and of α-aminohexoses, i, 523.
phenylhydrazino derivatives of pyrimidines, i, 979.
configurational relationships of the sugars, hydroxy-acids, amino-acids, and halogen acids, i, 1241.
Levene, *P. A.*, and *H. L.* **Haller**, sphingosine. V. Synthesis of 1-amino-2-hydroxy-*n*-heptadecane, i, 890.
configurational relationships between β-hydroxy-acids and α-hydroxy-acids and between the latter and secondary alcohols, i, 1375.
Levene, *P. A.*, and *B. J. C. van der* **Hoeven**, concentration of vitamin-*B*. II., i, 1516.
Levene, *P. A.*, and *G. M.* **Meyer**, monoacetonegalactose [galactose *iso*propylidene ether], i, 1043.
Levene, *P. A.*, and *L. A.* **Mikeska**, Walden inversion. III. Oxidation of optically active thiolsuccinic acid and thiolsuccinamic acid to the corresponding sulpho acids, i, 5.
oxidation of *d*-β-thiolbutane to *d*-butane-β-sulphonic acid; rotations of thio- and sulpho-carboxylic acids and their salts, i, 512.
Levene, *P. A.*, and *M. H.* **Pfaltz**, racemisation; action of alkali on *d*-alanyl-*d*-alanine anhydride, i, 795.
action of alkalis on peptides and on ketopiperazines, i, 1474.
Levene, *P. A.*, and *I. P.* **Rolf**, synthetic lecithins, i, 92.
Levene, *P. A.*, and *I. P.* **Rolf**, plant phosphatides. I. Lecithin and cephalin of the soya bean, i, 487.
bromolecithins. I. Fractionation of brominated soya-bean lecithins, i, 1520.
Levene, *P. A.*, and *H. S.* **Simms**, relation of chemical structure to rate of hydrolysis of peptides. II. Hydrolysis with erepsin, i, 473.
stereochemistry of αδ-anhydrotetrahydroxyadipic acids, i, 782.
lactone formation from mono- and di-carboxylic sugar acids, i, 1380.
dissociation constants of plant nucleotides and nucleosides and their relation to nucleic acid structure, i, 1478.
Levene, *P. A.*, and *H.* **Sobotka**, synthetic nucleosides. I. Theophylline pentosides. II. Substituted uracil xylosides, i, 1463.
Levene, *P. A.*, and *R.* **Ulpts**, condensation of monosaccharides by dilute mineral acid, i, 1042.
Levi, *G. R.*, varying tendency of the principal aromatic nuclei to couple with diazo compounds, i, 436.
different coupling tendencies of the principal aromatic nuclei with diazo compounds, i, 1186.
Levi, *G. R.*, and *M.* **Faldino**, reactions of diazo compounds with secondary aromatic amines, i, 171.
Levi, *G. R.*, and *G.* **Natta**, crystalline structure of perowskite, ii, 1036.
Levi, *G. R.*, and *G.* **Tacchini**, non-existence of nickel suboxide, ii, 424.
Levi, *G. R.* See also *G.* **Bruni**.
Levi, (*Miss*) *M.*, characteristic *X*-rays from light elements, ii, 456.
Levi, *R. G.* See *F.* **Zambonini**.
Levi, *T. G.*, reactions of various arylthiocarbamides with sulphur and aromatic amines, i, 445.
Levina, *L.* See *H.* **Bierry**.
Levine, *S. Z.* See *H. B.* **Richardson**.
Levine, *V. E.*, Jendrassik reaction for vitamin-*B*, i, 108, 1220.
Levinson, *S.*, detection of ethyl phthalate, ii, 1008.
Levschin, *W. L.*, polarisation of fluorescence from dye solutions. III., IV., and VI., ii, 13, 629, 1117.
Levtschenko, *V.* See *V.* **Palladin**.
Lévy, *J.*, and *R.* **Lagrave**, comparison of migratory tendencies of hydrogen and some acyclic radicals, i, 679.
Lévy, *J.* See also *M.* **Tiffeneau**.
Levy-Lajeunesse, *S.* See *M.* **Javillier**.
Lewcock, *W.*, formation of azoaniline-sulphonic acids, i, 597.

Lewicki, *J.* See *J. A.* **Collazo.**
Lewis, *G. N.*, and *D. F.* **Smith**, theory of reaction rate, ii, 799.
Lewis, *G. N.* See also *N. W.* **Taylor.**
Lewis, *H. B.*, metabolism of sulphur. IX. Effect of repeated administration of small amounts of cystine, i, 1354.
Lewis, *H. B.* See also *D. A.* **McGinty.**
Lewis, *H. F.*, and *S.* **Shaffer**, decomposition of anthraquinone by heat, i, 45.
Lewis, *H. H.*, *M.* **Nierenstein**, and *E. M.* **Rich**, action of diazomethane on some aromatic acyl chlorides. III. Mechanism of the reaction, i, 935.
Lewis, *H. P.*, determination of anthracene in anthraquinone, ii, 74.
Lewis, *J.* See *J.* **Moir.**
Lewis, *J. E.*, viscosity of liquids containing dissolved gases, ii, 377.
Lewis, *W. C. M.* See *F.* **Bradley**, and *J. W.* **Corran.**
Lewis, *W. K.*, and *W. G.* **Whitman**, principles of gas absorption, ii, 106.
Lewis, *W. L.*, and *H. W.* **Stiegler**, β-chlorovinylarsines and their derivatives, i, 1470.
Lewis-Dale, *P.*, liquid hydrocarbons obtained in the compression of oil gas, i, 769.
Lewitsky, *M.* See *A.* **Joffé.**
Ley, *H.*, and *R.* **Grau** [with *W.* **Emmerich**], dissociation constants of organic complexes, ii, 1159.
Ley, *H.*, and *F.* **Volbert**, absorption measurement in the ultra-violet by photographic photometry, ii, 78.
Liana, *F.*, transparence of varieties of glass in the infra-red, ii, 357.
Licht, *H.*, action of bacteria on bile acids, i, 478.
Lichtenecker, *K.*, calculation of refractive indices by the logarithmic rule of mixtures, ii, 632.
Lieb, *H.*, storage of cerebrosides in splenomegaly (Gaucher's type), i, 189.
Lieben, *F.*, combination of chloral hydrate with protein, i, 91.
Lieben, *F.*, and *D.* **László**, iodine absorption of caseinogen, i, 1476.
Liebl, *F.* See *L.* **Ruzicka.**
Liebreich, *E.*, and *W.* **Wiederholt**, passivity phenomena and cathodic overvoltage, ii, 44.
current-potential curves for nickel and aluminium, ii, 404.
Liebreich, *E.* See also *E.* **Maass.**
Liempt, *J. A. M. van*, hafnium oxide in tungsten filaments, ii, 233.
Liempt, *J. A. M. van*, binary systems, sodium and lithium tungstates, potassium and lithium tungstates, lithium tungstate–tungsten trioxide, sodium tungstate–tungsten trioxide and potassium tungstate–tungsten trioxide, ii, 421.
electrolytic deposition of tungsten, ii, 694.
Liempt, *J. A. M. van.* See also *W.* **Geiss.**
Liepatov, *S.*, adsorption, ii, 385.
kinetics of swelling and shrinking of gels. I. and II., ii, 685, 968.
adsorption [of alkali from alcoholic solutions by cellulose]. II., ii, 957.
action of electrolytes on colloidal nitroalizarin, ii, 1059.
Liepe, *J.* See *H. P.* **Kaufmann.**
Liepus, *T.* See *W.* **Guertler.**
Lier, *H.* See *P.* **Karrer.**
Liesegang, *R. E.*, calcium chemistry of teeth, i, 607.
Lifschitz, *I.*, relatively asymmetric synthesis in the case of complex salts of heavy metals, i, 522.
rotation dispersion. II., ii, 264.
Lifschütz, *I.*, wool-fat. VIII. Instability of wool-fat, i, 327.
Lignac, *G. O. E.*, disturbances of cystine metabolism in children, i, 610.
Liljestrand, *S. H.*, and *D. W.* **Wilson**, excretion of lactic acid in the urine after muscular exercise, i, 1115.
Lilley, *H. S.* See *C. E.* **Wood.**
Linck, *G.*, and *W.* **Becker**, chalk and flint, ii, 820.
Linck, *G.*, and *H.* **Jung**, *X*-ray investigation of black ("metallic") phosphorus, ii, 1035.
Linckh, *E.* See *W.* **Manchot.**
Lind, *S. C.*, and *D. C.* **Bardwell**, direct synthesis of higher from lower hydrocarbons, i, 493.
mercury and ionised helium, ii, 1181.
Lindau, *P.*, structure of the second positive group of nitrogen bands, ii, 11, 625.
Linde, *E.*, conductivity of aqueous perchloric acid, ii, 39.
Lindegren, *C. C.* See *J. C.* **Walker.**
Lindemann, *F. A.*, temperature coefficient of the mobility of ions in liquids, ii, 127.
Lindemann, *H.*, and *W.* **Wessel**, carbazole, i, 1098.
Lindenfeld, *K.* See *J.* **Zaleski.**
Linder, *E. G.*, thermo-electric effect in single crystal zinc wires, ii, 1136.
Linder, *G. C.* See *A.* **Hiller.**

Linderstrøm-Lang, *K.*, the salting-out effect, ii, 30.
ionisation of proteins, ii, 203.
is casein a homogeneous substance? ii, 1056.
Linderstrøm-Lang, *K.*, and *S.* Kodama, solubility of casein in hydrochloric acid, ii, 1056.
Lindet, *L.*, coagulation of caseinogen in acid solution in presence of calcium salts, i, 846.
Lindgren, *W.*, gel replacement; a new aspect of metasomatism, ii, 392.
Lindner, *F.* See *Hans* Fischer.
Lindner, *J.*, volumetric determination of carbon and hydrogen in elementary organic analysis, ii, 901.
Lindner, *K.*, and *H.* Helwig, so-called molybdenum dibromide and some of its derivatives, ii, 421.
Lindow, *W.* See *R.* Seeliger.
Lindsay, *R. B.*, quantum numbers of the Bohr orbits in the alkali atoms, ii, 467.
quantum number relations in series spectra, ii, 915.
Lindsley, *L. C.*, and *L. M.* Dennis, double selenates of thallous selenate and the selenates of bivalent metals, ii, 584.
Ling, *A. R.*, and *D. R.* Nanji, starch. II. Constitution of polymerised amylose, amylopectin, and their derivatives, i, 516.
starch. III. Nature and genesis of the stable dextrin and of the maltodextrins, i, 516.
starch. IV. Nature of the amylohemicellulose constituent of certain starches, i, 517.
Ling, *A. R.*, *D. R.* Nanji, and *F. J.* Paton, glycogen. I. Nature of yeast glycogen, its preparation, determination, and rôle in yeast metabolism, i, 1011.
Lingelsheim, *A. von*, green colouring matter, related to chlorophyll, from flowers of *Primulaceæ*, i, 601.
Link, *K. P.*, effects of the method of desiccation on the carbohydrates of plant tissue, i, 618.
Linnell, *W. H.*, and *W. H.* Perkin, *jun.*, derivatives of acridone and tetrahydrocarbazole, i, 62.
Linner, *F.* See *A.* Zinke.
Linsert, *O.* See *A.* Windaus.
Linstead, *R. P.* See *G. A. R.* Kon.
Linton, *C. S.*, Voges-Proskauer reaction [for *Bacillus coli aerogenes*], i, 867.
Lintzel, *W.*, metabolism of iron. I. Behaviour of blood pigment in artificial digestion, i, 1482.
Lions, *F.*, *W. H.* Perkin, *jun.*, and *R.* Robinson, strychnine and berberine. III. Position of the methoxyl groups in brucine, i, 831.
Liot, *A.*, variations in the p_H of solutions of cocaine hydrochloride subjected to sterilisation, i, 862.
Liotta, *D.*, scurvy and the antiscorbutic value of orange and lemon juices, i, 1365.
Lipman, *C. B.*, and *L. J. H.* Teakle, fixation of nitrogen by *Azotobacter* in a displaced solution and in the soil residue therefrom, i, 491.
symbiosis between *Chlorella* sp. and *Azotobacter chroococcum* and nitrogen fixation, i, 748.
Lipmann, *F.*, and *J.* Planelles, blood-sugar curves after intravenous injection of α-, β-, and αβ-glucose in rabbits, i, 179.
Lipp, *P.*, pinane, i, 1080.
Lipp, *P.*, and *F.* Caspers, synthesis of 1-aryl-2-pyrrolidones, i, 963.
Lippmann, *E. O. von*, occurrence of a rhamnosan, i, 366.
Lipschitz, *W.*, catalysis of oxido-reductions by blood pigments, ii, 1070.
Lipschitz, *W.*, and *Paul* Meyer, anaërobic production of carbon dioxide by muscle-cells in the presence of hydrogen acceptors, i, 603.
Lipschitz, *W.*, and *J.* Osterroth, pharmacological effects of combined camphor, i, 1005.
Liquier, (*Mlle.*) *J.*, variation of rotatory power of solutions of asparagine as a function of hydrogen-ion concentration, ii, 743.
Lisbonne, *M.*, activation of pancreatic juice by acidification, i, 615.
Lissievici-Draganescu, (*Mme.*) *A.*, fixation of bismuth in the organs after administration of soluble and insoluble salts of the metal, i, 465.
Lissievici-Draganescu, (*Mme.*) *A.* See also *S.* Draganescu.
Listwa, *L.* See *F.* Kehrmann.
Littauer, *F.*, decomposition of urea in soil, i, 218.
Litterscheid, *F. M.*, and *H.* Löwenheim, qualitative and quantitative analysis of sodium dithionate, ii, 68.
Littmann, *E. R.*, preparation of 3-nitrophthalic acid, i, 1066.
Liu, *S. H.*, influence of cod-liver oil on the calcium and phosphorus metabolism in tetany, i, 725.
Livens, *G. H.* See *E. L.* Davies.
Livingston, *R. S.*, and *W. C.* Bray, catalytic decomposition of hydrogen peroxide in acid chlorine–chloride solution, ii, 981.

Ljubitsch, *N.* See *K.* **Hess.**
Lochte, *H. L.* See *H. D.* **Wilde**, *jun.*
Locke, *A. P.* See *E. R.* **Main.**
Lockrow, *L. L.*, low-voltage arc in oxygen, ii, 1099.
Locquin, *R.*, and *R.* **Heilmann**, new bases: carbamides of pyrazolines, i, 837.
decomposition of pyrazolines by spontaneous oxidation, i, 1185.
Lodge, *A.*, quantum radiation, ii, 624.
Lodge, (*Sir*) *O.*, quantum radiation, ii, 465.
Loeb, *L. B.*, gas ion mobilities, ii, 461.
ionic mobilities in ethyl ether as a function of pressure, ii, 832.
Loeb, *L. B.*, and *M. F.* **Ashley**, ionic mobilities in gaseous mixtures, ii, 7.
Loeb, *L. F.* See *H.* **Freundlich.**
Loeb, *S.* See *G. M.* **Schwab.**
Loebenstein, *F.*, swelling-promoting effect of alcohol, ii, 520.
Löff, *G.* See *M.* **Kohn.**
Loehr, *O.* See *K.* **Brand.**
Loele, *W.*, naphthol reaction of red blood-corpuscles, i, 1342.
Loeper, *M.*, *R.* **Schulmann**, and *J.* **Tounet**, transformation of calcium oxalate into calcium carbonate in animal tissues, i, 1497.
Lövenskiold, *H.* See *H.* **Wieland.**
Lövgren, *T.* See *H. von* **Euler.**
Loew, *O.*, calcium requirements of algæ and fungi, i, 1218.
Löwenbein, *A.* [with *W.* **Folberth**], radical dissociation of arylated succinic acid derivatives. I. Radical dissociation of 2:2-dihydroxytetraphenylsuccinodilactones [2:2′-diketo-3:3′-diphenyl-3:3′-dicoumaranyls], i, 552.
Löwenbein, *A.*, and *W.* **Folberth**, lactonic–enolic tautomerism of *o*-hydroxydiphenylacetolactone, i, 546.
Löwenbein, *A.*, and *H.* **Simonis** [with *H.* **Lang**, and *W.* **Jacobus**], enolates of *o*-hydroxydiphenylacetolactone, i, 147.
Löwenheim, *H.* See *F. M.* **Litterscheid.**
Löwensohn, *V.* See *F.* **Arndt.**
Löwenstein, *L.*, automatic gas analysis, ii, 154.
Loewi, *O.* See *H.* **Häusler.**
Lohmann, *K.* See *O.* **Meyerhof.**
Lohmann, *W.* See *E.* **Blanck.**
Lohr, *A.* See *K. von* **Auwers.**
Loiseau, *G.* See *G.* **Abt.**
Loiseleur, *J.*, mechanism of the therapeutic action of suspensoids, i, 197.
Loiseleur, *J.* See also *E.* **Hugounenq.**
Lomanitz, *S.* See *S. A.* **Waksman.**
London, *F.* See *H.* **Hönl.**
Long, *C. N. H.* See *K.* **Furusawa.**
Long, *E. R.* See *F. B.* **Seibert.**
Long, *J. S.* See *W. A.* **Patrick.**
Long, *R. G.* See *W. E.* **Curtis.**
Long, *W. L.* See *D. W.* **Wilson.**
Longchambon, *L.*, polymorphic transformations of silica, ii, 752.
cristobalite, ii, 1131.
Longinescu, *G. G.*, and *G.* **Chaborski**, detection of calcium in the presence of barium and strontium, ii, 1202.
Longinescu, *G. G.*, and *E.* **Petrescu**, detection of iron, chromium, and manganese without the use of nitric acid, ii, 1206.
Loomis, *A. G.* See *J. E.* **Walters.**
Lorah, *J. R.* See *H. V.* **Tartar.**
Lorber, *L.*, simple micro method for determination of sugar or of reducing substance in blood, i, 852.
Lorber, *N.* See *A.* **Zinke.**
Lorenz, *R.*, and *W.* **Herz**, thermal expansion of fused salts, ii, 950.
Lorentz-Zienkovska, *H.* See *K.* **Jabiczyński.**
Lorenz, *L.* See *K. H.* **Slotta.**
Lorenz, *R.*, equilibria between metals and fused salts, ii, 536.
molten electrolytes, ii, 537.
Lorenz, *R.*, and *E.* **Bergheimer**, detection of silicic acid, ii, 600.
Lorenz, *R.*, *E.* **Grau**, and *E.* **Bergheimer**, test for bromine, ii, 597.
Lorenz, *R.*, and *W.* **Herz**, relation between the volume of a substance at absolute zero and its critical temperature, ii, 25.
volume in liquid mixtures, ii, 101.
relation between the critical temperature and the molecular volume at absolute zero, ii, 185.
free-space numbers. I., ii, 185.
boiling point relations for fused salts, ii, 276.
molecular volume and molecular refraction, ii, 356.
vapour-pressure curves of salts, ii, 493.
molecular volume of salts at the m. p., ii, 840.
Lorenz, *R.*, and *H.* **Klauer**, theory of electrolytic ions. XXIX. Method of measuring conductivity by the use of an amplifying tube, ii, 541.
Lorenz, *R.*, and *A.* **Magnus**, separation of gas mixtures by diffusion, ii, 501.
Lorenz, *R.*, and *A.* **Voigt**, conductivity of potassium and sodium chloride in aqueous solution, ii, 871.

Lorenz, *R.*, and *E.* **Wiedbrauck**, influence of temperature on the evolution of gases from an "adsorber," ii, 382.
adsorption equilibria in presence of two gases, ii, 382.
influence of rate of flow on the adsorption of gases, ii, 507.
Lorenz, *R.* See also *J. J. van* **Laar**.
Lorenz, *V.* See *W.* **Eller**.
Loriette, *P.* See *M.* **Marqueyrol**.
Loring, *F. H.*, valency relations: an element of atomic number zero with an atomic weight of unity, ii, 841.
Loring, *F. H.*, and *J. G. F.* **Druce**, eka-cæsium, ii, 1124.
eka-cæsium and eka-iodine, ii, 1124.
Loris, *K.* See *F.* **Jirsa**.
Lormand, *C.* See *M.* **François**.
Lorriman, *F. R.*, derivatives of acenaphthene, i, 672.
Lošan, *J.*, ammoniation of ions in aqueous solutions, ii, 654.
Losana, *L.*, ferric acid and ferrates, ii, 1088.
Lotte, *P.* See *C.* **Moureu**.
Lotter, *P.* See *F.* **Fichter**.
Lottermoser, *A.* [with *F.* **Friedrich**, *H. M.* **Hübner**, and *A.* **Szabó**], physico-chemical analysis of oxide sols, ii, 521.
Lottermoser, *A.*, and *M.* **Grützner**, reactions in the lead accumulator, ii, 312.
Lottermoser, *A.*, *W.* **Seifert**, and *W.* **Forstmann**, silver iodide hydrosol; method of formation of hydrosols and gels. IV., ii, 514.
Lovell, *W. G.* See *R. T.* **Haslam**.
Lovtschinovskaja, *E.* See *V.* **Palladin**.
Lowe, *G. M.* See *F. D.* **Farrow**.
Lowe, *P.*, and *D. C.* **Rose**, intensities in the argon spectrum, ii, 452.
Lowery, *H.*, pole lines occurring in the interrupted arc spectra of silver, gold, and copper, ii, 4.
broadening of lines in arc spectra and the Stark effect, ii, 614.
Lowry, *C. D.*, *jun.* See *R.* **Willstätter**.
Lowry, *H. H.*, and *S. O.* **Morgan**, vapour pressures of Rochelle salt, the hydrates of sodium and potassium tartrates, and their saturated solutions, ii, 26.
adsorption of gases by graphitic carbon, ii, 1053.
Lowry, *T. M.*, dynamic isomerism. XVIII. Mechanism of mutarotation, i, 886.
electronic theory of valency. IV. Origin of acidity, ii, 15.
graphitic conduction in conjugated chains of carbon atoms, ii, 299.
Lowry, *T. M.*, and *J. O.* **Cutter**, rotatory dispersive power of organic compounds. XV. Borneol, camphor, and camphorquinone; origin of complex and anomalous rotatory dispersion, ii, 356.
Lowry, *T. M.*, and *E. M.* **Richards**, dynamic isomerism. XIX. Arrest of mutarotation of tetramethylglucose, i, 886.
rotatory dispersive power of organic compounds. XIII. Significance of simple rotatory dispersion; rotatory dispersion of camphorquinone and of sucrose, ii, 265.
Lowry, *T. M.* See also *H.* **Burgess**, *J. O.* **Cutter**, *I. J.* **Faulkner**, and *E. M.* **Richards**.
Lozinsky, *E.* See *R. L.* **Stehle**.
Lubimenko, *V.*, quantity of chlorophyll in marine algæ, i, 216.
Lublin, *A.*, ratio of the amounts of acetone and of β-hydroxybutyric acid excreted in the urine, i, 459.
Lubman, *N.* See *P.* **Petrenko-Kritschenko**.
Lucarini, *C.* See *R. R.* **Read**.
Lucas, *H. J.*, and *A. Y.* **Jameson**, electron displacement in carbon compounds. I. Electron displacement *versus* alternate polarity in aliphatic compounds, i, 2.
Lucas, *H. J.*, and *H. W.* **Moyse**, electron displacement in carbon compounds. II. Hydrogen bromide and Δβ-pentene, i, 770.
Lucas, *H. J.*, *T. P.* **Simpson**, and *J. M.* **Carter**, electron displacement in carbon compounds. III. Polarity differences in carbon–hydrogen unions, i, 769.
Lucas, *R.*, influence of solvents on rotatory power, ii, 742.
Lucas, *R.* See also *A.* **Haller**.
Lucasse, *W. W.*, activity coefficients and transference numbers of the alkaline-earth chlorides, ii, 399.
Luce, *E.*, migration of the α-naphthyl radical, i, 263.
Luce, *E. M.*, influence of sunlight on the growth-promoting and antirachitic properties of cow's milk, i, 211.
Luce, *E. M.*, and (*Mrs.*) *I. S.* **Maclean**, presence of vitamin-*A* in yeast fat, i, 483.
Luciano, *M.*, crystallographic investigation of diopside from Saulera (Val d'Ala), ii, 1037.
Luck, *J. M.*, and *T. N.* **Seth**, gastric urease, i, 200.
physiology of gastric urease, i, 1010.
Luck, *J. M.* See also *T. N.* **Seth**.

Ludewig, *P.*, and *F.* **Reuther**, coloration of rock salt by radium, ii, 21.
Ludlam, *A. E.* See *S.* **Chapman**.
Ludlam, *E. B.*, Budde effect in bromine, ii, 470.
electron affinity of the halogens, ii, 1018.
Ludlam, *E. B.*, and *W.* **West**, ultra-violet emission spectra of the halogens, ii, 350.
Ludlam, *E. B.* See also *W.* **West**.
Ludloff, *H.*, terms of the mercury hydride bands, ii, 1113.
Ludwig, *H.* See *K.* **Brand**.
Ludwig, *O.* See *A.* **Rippel**.
Lüde, *K. von*. See *R.* **Suhrmann**.
Lüdtke, *M.*, proteins. IV. Hydrolytic fission of 2:5-diketopiperazines and dipeptides, i, 450.
oxidation of 2:5-diketopiperazines by hydrogen peroxide, i, 837.
Lüers, *H.*, and *G.* **Nowak**, zymocasein from yeast, i, 338.
Lüers, *H.*, and *E.* **Sellner**, purification of malt amylase, i, 737.
Lüppo-Cramer, [photographic] ripening process. III., IV., and V., ii, 574, 810, 986.
history and theory of the latent image. II. and III., ii, 575, 811.
silver in photography, ii, 985.
Lüthy, *M.* See *H.* **Staudinger**.
Lütkemeyer, *H.* See *M.* **Bodenstein**.
Luff, *G.*, separation of cadmium from zinc by means of hydrogen sulphide, ii, 159.
oxalate separation of calcium and magnesium, ii, 438.
use of potassium ferrocyanide in gravimetric analysis; [determination of cadmium], ii, 826.
Lukacs, *M.* See *H.* **Kappen**.
Lukas, *J.*, and *A.* **Jilek**, determination of copper by rapid electrolysis in the presence of tin, antimony, and lead, ii, 241.
Lukas, *J.* See also *A.* **Jilek**.
Lukes, *R.* See *E.* **Votoček**.
Lukirsky, *P.*, *S.* **Sčukarev**, and *O.* **Trapesnikov**, electrolysis of crystals ii, 369.
Lumière, *A.*, regularity of lactic fermentation in the presence of mercuric chloride, i, 106.
new chemical anti-coagulants, i, 606.
Lumière, *A.*, and *R.* **Courjon**, influence of time of coagulation of blood on toxicity of serum, i, 853.
Lumière, *A.*, and *H.* **Couturier**, anti-coagulating action of zinc salts, i, 717.
Lumière, *A.*, *L.* **Lumière**, and *A.* **Seyewetz**, fluorescence of the principal photographic developers, i, 1060.
Lumière, *L.* See *A.* **Lumière**.
Lund, *E. J.*, electrodes for the measurement of small bioelectric potentials, ii, 897.
Lund, *G. S.*, and *C. G. L.* **Wolf**, glucose [dextrose] content of normal urine, i, 1205.
Lund, *W.* See *O.* **Mumm**.
Lunde, *G.*, crystal structure of thallium chloride and thallium bromide, ii, 941.
Lundegårdh, *H.*, and *V.* **Morávek**, absorption of salts by plants. I. Mutual influence of ions, i, 214.
Lundquist, *O.*, $K\beta$ lines in the *X*-ray emission spectra of phosphorus and potassium, ii, 1014.
Lundsgaard, *C.*, and *S. A.* **Holbøll**, effect of insulin and muscle-tissue on dextrose *in vitro*, i, 208.
nature of dextrose in the blood of healthy men, i, 1206.
nature of dextrose in the blood of diabetics before and after injection of insulin, i, 1207.
nature of dextrose in different physiological fluids, i, 1207.
carbohydrate metabolism. II. Mutarotation of β-glucose. III. Nature of the dextrose of the blood of normal individuals. IV. Nature of the dextrose of the blood of patients with diabetes mellitus and with benign glycosuria. V. Form of dextrose in body fluids, i, 1494.
Lunn, *E. G.* See *T. R.* **Hogness**.
Lunn, *J. W.* See *R.* **Campbell**.
Lunt, *J.*, spectrum of germanium, ii, 611.
large line-displacement in the spectra of germanium and chlorine under different conditions of temperature, ii, 611.
Lunt, *R. W.*, interaction of carbon dioxide and hydrogen in the corona due to alternating currents of high frequency, ii, 579.
behaviour of hydrogen in the discharge due to alternating electric fields of high frequency, ii, 616.
Lunt, *R. W.* See also *M.* **Crespi**.
Lupton, *H.* See *K.* **Furusawa**.
Lush, *E. J.*, kinetics of hydrogenation. II. Stationary films, ii, 411.
Lutz, *R. E.*, determination of small quantities of zinc in materials of organic nature; microchemical method based on the fluorescence of zinc salts with urobilin, ii, 825.

Lutz, *R. E.* See also *J. B.* **Conant.**
L'vov, *S.*, dependence of the reduction processes of yeast on fermentation, i, 1508.
fermentation of mannitol by yeasts, i, 1509.
Lyman, *T.*, and *F. A.* **Saunders**, spectra of neon and argon in the extreme ultra-violet, ii, 911.
Lynch, *D. F. J.* See *J. A.* **Ambler.**
Lyon, *N.*, electrical double refraction of gases, ii, 266.
Lyon, *T. L.*, *J. A.* **Bizzell**, and *B. D.* **Wilson**, accumulation of nitrates in soil following the growth of clover or lucerne, i, 347.
Lyons, *E.*, mercury derivatives of some imides, i, 645.
Lythgoe, *R. J.*, and *J. R.* **Pereira**, muscular exercise, lactic acid, and the supply and utilisation of oxygen. XI. Pulse rate and oxygen intake during the early stages of recovery from severe exercise, i, 1341.

M.

Maass, *E.*, and *E.* **Liebreich**, corrosion of metals, ii, 140.
Maass, *E.*, and *W.* **Wiederholt**, corrosion phenomena in aluminium, ii, 560.
, *O.*, and *P. G.* **Hiebert**, properties of pure hydrogen peroxide. V. Vapour pressure, ii, 188.
Maass, *O.*, and *D. M.* **Morrison**, effect of molecular attractions on the total pressure of a gas, ii, 500.
Maass, *O.*, and *L. J.* **Waldbauer**, specific heats and latent heats of fusion of ice and of several organic compounds, ii, 492.
Maass, *O.*, and *C. H.* **Wright**, molecular attraction and velocity of reactions at low temperatures of unsaturated hydrocarbons, ii, 214.
Macallum, *A. B.* See *D. W.* **MacKenzie.**
Macallum, *A. D.*, and *G. S.* **Whitby**, molecular refraction of natural and of methyl-rubber, ii, 478.
McAulay, *J.* See *P.* **Debye.**
McBain, *J. W.*, and *G. M.* **Langdon**, system, sodium palmitate–sodium chloride–water, ii, 537.
McBain, *J. W.* See also *A. M.* **Bakr.**
Macbeth, *A. K.*, and *J.* **Craik**, condensation reactions of oxindole and 3-oxythionaphthen, i, 1315.
Macbeth, *A. K.*, and *D.* **Traill**, labile nature of the halogen atom in organic compounds. X. Action of hydrazine hydrate on the halogen derivatives of α-nitro-fatty acids, i, 628.
labile nature of the halogen atom in organic compounds. XI. Halogenation of ethyl acetylsuccinate, i, 782.
Macbeth, *A. K.* See also *J.* **Craik**, and *E. L.* **Hirst.**
MacCallum, *P.* See *W. O.* **Kermack.**
McCallum, *S. P.*, and *C. M.* **Focken**, electrical properties of neon, hydrogen, and nitrogen, ii, 641.
McCance, *R. A.*, influence of oxygen on the production of urea by enzymes of the liver and spleen, i, 472.
McCance, *R. A.* See also *M. E.* **Robinson.**
McCandless, *J. M.*, and *J. Q.* **Burton**, sources of error in the determination of phosphoric acid by the molybdate–magnesia method, ii, 157.
McCleland, *N. P.* See *J. A.* **Aeschlimann.**
McClosky, *W. T.* See *M. I.* **Smith.**
McCluskey, *K. L.*, modification of Bloor's method for the determination of blood phosphates, i, 605.
McCollum, *E. V.*, *N.* **Simmonds**, *J. E.* **Becker**, and *R. W.* **Bunting**, effect of addition of fluorine to the diet of the rat on the quality of the teeth, i, 861.
McCollum, *E. V.*, *N.* **Simmonds**, *J. E.* **Becker**, and *P. G.* **Shipley**, experimental rickets. XXVI. Diet of purified foodstuffs for use in vitamin-*D* studies, i, 1366.
McCombie, *H.*, *H. M.* **Roberts**, and *H. A.* **Scarborough**, velocity of reaction in mixed solvents. VIII. Velocity of formation of certain quaternary ammonium salts, ii, 554.
McCombie, *H.* See also *W. I.* **Jones.**
McCool, *M. M.*, and *A. W.* **Weidemann**, moisture relationships of soils, i, 1527.
McCorkle, *P.*, anhysteretic magnetostrictive effects in iron, nickel, and cobalt, ii, 487.
McCormick, *N. A.*, insulin from fish. VII., i, 754.
McCormick, *N. A.*, and *J. J. R.* **Macleod**, effect on the blood-sugar of fish of various conditions, including removal of the principal islets (isletectomy), i, 856.
McCormick, *N. A.*, and *E. C.* **Noble**, yield of insulin from fish, i, 754.
MacCorquodale, *D. W.* See *C. S.* **Marvel.**

McCulloch, *L.*, rapid corrosion of metals by acids within capillaries, ii, 879.
McCurdy, *W. H.*, *L. A.* **Turner**, and *K. T.* **Compton**, excited atoms in the striated glow discharge in mercury vapour, ii, 1102.
McCurdy, *W. H.* See also *L. A.* **Turner**.
MacDougal, *D. T.*, and *B. L.* **Clarke**, hydrophilic effect of ions on agar and protoplasmic components, ii, 1156.
McDowall, *F. H.*, constituents of *Myoporum laetum*, Forst. (the "ngaio"). I., i, 1521.
McDowall, *F. H.*, and *H. J.* **Finlay**, essential oil of the "rimu" (*Dacrydium cupressinum*), i, 418.
McElroy, *C. H.* See *V. G.* **Heller**.
McEnery, *E. I.*, *A. C.* **Ivy**, and *C. E.* **Pechous**, presence of isoagglutinins in the blood of dogs, i, 1344.
McGeorge, *W. T.*, soil analysis, i, 348.
McGill, *W. J.* See *M.* **Gomberg**.
McGinty, *D. A.*, *H. B.* **Lewis**, and *C. S.* **Marvel**, amino-acid synthesis in the animal organism; availability of caproic [*n*-hexoic] acid derivatives for synthesis of lysine, i, 100.
McGrath, *P. C.* See *G. L.* **Clark**.
McHaffie, *I. R.*, and *S.* **Lenher**, adsorption of water from the gas phase on plane surfaces of glass and platinum, ii, 854.
McHaffie, *I. R.* See also *J. W.* **Shipley**.
McHargue, *J. S.*, occurrence of copper, manganese, zinc, nickel, and cobalt in soils, plants, and animals, and their possible functions as vital factors, i, 1023.
association of copper with substances containing the fat-soluble vitamin-*A*, i, 1515.
Mâcheboeuf, *M.* See *G.* **Bertrand**.
Macht, *D. I.*, *A.* **Grollman**, and *O. R.* **Hyndman**, relation between the chemical structure of bile acids and their effects on animal and plant tissues, i, 1355.
McIlvaine, *L.* See *L. S.* **Weatherby**.
MacInnes, *D. A.*, transference numbers of solutions of mixed chlorides, ii, 872.
MacInnes, *D. A.*, and *T. B.* **Brighton**, transport numbers by the moving-boundary method. III. Novel form of apparatus, ii, 542.
MacInnes, *D. A.* See also *E. R.* **Smith**.
McIntyre, *G. H.* See *A. F. O.* **Germann**.
MacIntyre, *W. H.*, and *W. M.* **Shaw**, ternary systems, CaO–Fe_2O_3–$CaSO_4$ and CaO–Al_2O_3–$CaSO_4$, as explaining the retention of sulphates by heavily-limed soil, i, 490.
Mack, *E.* See *T. H.* **Swan**.
Mack, *E.*, *jun.*, average cross-sectional areas of molecules by gaseous diffusion methods, ii, 1124.
Mack, *E.*, *jun.* See also *R. J.* **Havighurst**.
McKeehan, *L. W.*, theory of ferromagnetism, ii, 944.
McKeehan, *L. W.* See also *O. E.* **Buckley**.
McKenzie, *A.*, and *W. S.* **Dennler**, elimination of the amino group of tertiary amino-alcohols. II. The semipinacolinic deamination of β-hydroxy-αβ-diphenyl-β-naphthylethyl amine, i, 26.
McKenzie, *A.*, and *R.* **Roger**, dehydration of the optically active methyl- and ethyl-hydrobenzoins, i, 25.
McKenzie, *A.*, and *I. A.* **Smith**, asymmetric catalytic racemisation, i, 822.
McKenzie, *A.*, and *R. C.* **Strathern**, reactions of displacement in the tropic acid group. I., i, 401.
McKenzie, *A.*, and *T. M. A.* **Tudhope**, Walden inversion. XI. Substitution by halogen of the hydroxyl group of secondary octyl alcohols, i, 226.
McKenzie, *A.*, and *G. O.* **Wills**, conversion of amino-acids into tertiary amino-alcohols, i, 395.
McKenzie, *D. W.*, and *M. I.* **Séng** [with *A. B.* **Macallum**], tuberculosis and calcification of prostate, i, 330.
Mackenzie, *G. I.* See *C. G.* **Barkla**.
Mackenzie, *G. M.* See *L.* **Bauman**.
McKeown, *A.* See *R. O.* **Griffith**.
McKinley, *E. B.* See *N. F.* **Fisher**.
McKinney, *A. E.* See *F.* **Wilcoxon**.
McLaughlin, *H. M.*, simple automatic mercury pump, ii, 428.
McLaughlin, *H. M.* See also *W. D.* **Harkins**.
McLay, *A. B.* See *J. C.* **McLennan**.
McLean, *F. T.* See *F. R.* **Pember**.
McLean, *H. C.* See *J. S.* **Joffe**.
Maclean, (*Mrs.*) *I. S.*, and *D.* **Hoffert**, carbohydrate and fat metabolism of yeast. II. Influence of phosphates on the storage of fat and carbohydrate in the cell, i, 204.
Maclean, (*Mrs.*) *I. S.* See also *E. M.* **Luce**.
MacLean, *W.*, and *G. W.* **Robinson**, determination of ammoniacal nitrogen in soils, i, 224.

McLennan, *J. C.*, luminescence of solid nitrogen and argon, ii, 88.
auroral green line, ii, 249, 339.
McLennan, *J. C.*, and *A. B.* **McLay**, series spectrum of gold, ii, 913.
McLennan, *J. C.*, and *W. W.* **Shaver**, series, ultra-violet, and infra-red spectra of silicon, ii, 452.
McLennan, *J. C.*, and *G. M.* **Shrum**, secondary spectrum of hydrogen at very low temperatures, ii, 468.
origin of the auroral green line 5577 Å., and other spectra associated with the aurora borealis, ii, 723.
McLennan, *J. C.*, *J. F. T.* **Young**, and *A. B.* **McLay**, absorption and series spectra of tin, ii, 454.
absorption and series spectra of lead, ii, 455.
Macleod, *D. B.*, viscosity of binary mixtures, ii, 280.
relation between the viscosities of liquids and their molecular weights, ii, 498.
physical properties of water, ii, 498.
kinetic theory of evaporation, ii, 784.
viscosities of liquids at their b. p., ii, 1049.
Macleod, *F. L.* See *H. C.* **Sherman**.
Macleod, *J. J. R.* See *G. S.* **Eadie**, and *N. A.* **McCormick**.
McLeod, *J. W.*, and *J.* **Gordon**, production of peroxide by anaërobes in presence of oxygen, i, 1362.
relations between the reducing powers of bacteria and their capacity for forming peroxide, i, 1362.
McMath, *A. M.* See *J.* **Read**.
McMillan, *A.*, and *W. C.* **Ferguson**, electrometric titrations; use of titanous chloride for ore analysis, ii, 441.
McMillan, *A.* See also *T. S.* **Patterson**.
McMillin, *H. R.*, automatic burette and flask for standard alkali solutions, ii, 711.
McMullin, *R. B.* See *M. C.* **Taylor**.
McQuarrie, *W. C.*, spectra of silicon and aluminium, ii, 1013.
McTaggart, *H. A.*, property of very small bubbles of gas in water, ii, 509.
McVicker, *W. H.*, *J. K.* **Marsh**, and *A. W.* **Stewart**, Tesla-luminescence spectra. IV. Hydrocarbons containing a single benzene nucleus, ii, 12.
new variety of spectra, ii, 86.
Tesla-luminescence spectra. V. Polynuclear hydrocarbons, ii, 630.
Macy, *R.*, ternary system, silver perchlorate, pyridine, and water, ii, 536.
Maddison, *R. E. W.* See *A. J.* **Allmand**, and *R. G.* **Franklin**.
Madelung, *W.*, coloured salts of the di- and tri-phenylmethane series, i, 1459.
Madinaveitia, *A.*, and *I.* **Ribas**, isomerism of the diphenylsuccinic acids, i, 671.
Madinaveitia, *A.* See also **Les Établissements Poulenc Frères**.
Madsen, *E.* See *G. von* **Hevesy**.
Madsen, *S. T.*, distribution of the residual nitrogen in the organism, i, 718.
Maeser, *S.* See *T. D.* **Stewart**.
Magath, *T. B.* See *J. L.* **Bollmann**.
Magee, *H. E.* See *J. B.* **Orr**.
Magidson, *O. I.*, closure of the fluorene ring in the di-α-naphthylmethane series, i, 384.
Magidson, *O. I.*, and *G.* **Menschikov**, iodination of 2-aminopyridine, i, 301.
Magistad, *O. C.*, aluminium content of the soil solution and its relation to soil reaction and plant growth, i, 1371.
Magnin, *G.*, destruction of organic matter by hydrogen peroxide; its use in toxicology, ii, 594.
toxicological detection of hydrocyanic acid by Chelle's reaction, ii, 607.
Magnus, *A.*, and *A.* **Hodler**, atomic heat of silver at high temperatures, ii, 95.
Magnus, *A.* See also *R.* **Lorenz**.
Magnus-Levy, *A.*, cystinuria, i, 610.
Magnuson, *H. P.* See *W. M.* **Gibbs**.
Mahnert, *P.* See *M.* **Volmer**.
Mahood, *S. A.*, and *C. R.* **Harris**, chemistry of furfuraldehyde; preparation of the furan analogue of benzoflavine or dimethyldiaminofurylacridine hydrochloride, i, 302.
Maier, *C. G.*, vapour pressures of common metallic chlorides and a static method for high temperatures, ii, 850.
Maige, *A.*, regeneration of amylogenous excitability of plastids during hydrolysis, i, 486.
carbohydrate utilisation by the cell and variations in the nucleus and nucleolus, i, 1493.
Maignon, *F.*, electrolysis of enzymes and their phosphoric acid and silica content, i, 1116.
Maiho, *P.* See *E.* **Rupp**.
Mailhe, *A.*, decomposition of acids in the presence of metallic chlorides, i, 503.
catalytic decomposition of acid chlorides, i, 629.

Mailhe, *A.*, separation of carbon monoxide in organic molecules, i, 1232.
Main, *E. R.*, and *A. P.* **Locke**, determination of small amounts of protein nitrogen, i, 997.
Majima, *R.*, and *T.* **Hoshino**, synthetic experiments in the indole group. VI. New synthesis of 3-aminoalkylindoles, i, 1450.
Majima, *R.*, and *M.* **Kotake**, synthetic experiments in the indole group. V. Synthesis of 3-β-amino-α-hydroxyethylindole, i, 1450.
Majima, *R.*, and *H.* **Suginome**, aconite alkaloids. IV. Oxonitin and some new derivatives thereof, i, 1447.
Major, *R. H.*, and *R. C.* **Davis**, high blood-sugar with absence of sugar in the urine in diabetes treated with insulin, i, 1491.
Major, *R. T.* See *C. S.* **Hamilton**.
Majumder, *K.*, and *N. K.* **Swe**, absorption spectrum of aluminium, ii, 338.
Makamiya, *Z.* See *K.* **Takahashi**.
Maki, *S.*, skin secretion of *Triton tæniatus* (small water newt), i, 327.
Malandkar, *M. A.*, chemical constitution of the gum from *Boswellia serrata*, i, 1438.
Malandkar, *M. A.* See also *G. J.* **Fowler**.
Malchow, *W.* See *H.* **Freundlich**.
Malcolm, *A. M.*, magnetic quality of pure nickel, ii, 371.
Mali, *S.*, and *J.* **Ghosh**, vapour pressure and chemical constant of formaldehyde, i, 116.
Mali, *S. B.*, calculation of the vapour pressure of a solution of a non-volatile solute, ii, 850.
Malik, *K. S.* See *N. A.* **Yajnik**.
Malinowski, *A. E.*, ionisation in the wave of propagation of explosions, ii, 182.
Malischeva, *V. T.* See *A.* **Kablukov**.
Malkin, *T.*, and *R.* **Robinson**, phenyl benzyl diketone and some derivatives, i, 559.
synthesis of pyrylium salts of anthocyanidin type. VIII. Synthesis of pelargonidin chloride and of galanginidin chloride, i, 827.
Mallemann, *R. de*, electrical birefringence of limonene, ii, 642.
calculation of rotatory power from molecular structure, ii, 840.
calculation of rotatory power of a tetrahedral molecule, ii, 935.
theory of rotatory polarisation, ii, 1029.
diffusion of light by active and inactive molecules, ii, 1030.
Malm, *I. L.* See *F. B.* **Dains**.
Malquori, *G.*, electrolytic preparation of ozone with an alternating superposed on a continuous current, ii, 62.
mixed basic silver–copper salts, ii, 696.
thermal behaviour of hydrated barium aluminate, ii, 813.
Malquori, *G.* See also *N.* **Parravano**.
Malyoth, *G.* See *E.* **Schmidt**.
Mameli, *E.*, and *E.* **Filippi**, hyperthermic action of the phenoxyacetic acids, i, 466.
Manchot, *W.*, method of determining the solubility of gases in liquids, ii, 233.
Manchot, *W.* [with *H.* **Haunschild**], dissociation equilibria of compounds of ferrous salts with nitric oxide, ii, 298.
Manchot, *W.* [with *M.* **Jahrstorper**, and *H.* **Zepter**], gas solubility and hydration, ii, 282.
Manchot, *W.*, and *H.* **Gall**, dehydrogenation and autoxidation and their mutual relationship, i, 561.
metal–carbon monoxide salts. IX. Compound of carbon monoxide with iridium chloride, ii, 232.
compounds of gold with carbon monoxide, ii, 1182.
Manchot, *W.*, and *K.* **König**, compounds of carbon monoxide with ruthenium salts, ii, 149.
compounds of carbon monoxide with osmium chloride, ii, 232.
compound of rhodium with carbon monoxide, ii, 1193.
Manchot, *W.*, and *E.* **Linckh**, preparation of crystalline compounds of ferrous salts and nitric oxide. III., ii, 317.
Manchot, *W.*, and *F.* **Oberhauser** [with *H.* **Wettstein**], bromometric determinations, ii, 161.
Manchot, *W.*, and *A.* **Wirzmüller**, preparation of selenic acid, ii, 319.
Manchot, *W.* See also *H.* **Gall**.
Mandell, *W.*, and *J.* **West**, temperature gradient in gases at various pressures, ii, 99.
Manegold, *E.*, electrolyte threads. I. Behaviour of electrolyte threads and their deflection in a magnetic field, ii, 873.
Maneval, *R. V.* See *F. B.* **Dains**.
Manfredi, *M.* See *M.* **Francesconi**.
Mange, *C. E.*, and *O.* **Ehler**, solubilities of vanillin, ii, 119.
Mangold, *E.*, digestion of carbohydrates and proteins in pigeons and hens, and the penetration of digestive enzymes through plant cell membranes, i, 615.

Manière, (*Mme.*) *Y.* See *A.* **Boutaric.**
Manley, *J. J.*, mercury and helium, ii, 57.
mercury helide, ii, 314, 696.
Mann, *A.*, and *P. M.* **Paulson**, electrochemical oxidation of toluene to benzaldehyde, i, 556.
Mann, *C. E. T.*, antagonism between dyes and inorganic salts in their absorption by storage tissue, ii, 35.
Mann, *F. C.* See *J. L.* **Bollmann.**
Mann, *F. G.*, and (*Sir*) *W. J.* **Pope**, $\alpha\beta\gamma$-triaminopropane and its complex metallic compounds, i, 373.
Mannich, *C.*, preparation of β-ketobases, i, 374.
Mannich, *C.*, and *K.* **Sutter**, lactone formation and intramolecular alkylation with brominated aminomethylallylmalonic acids, i, 1037.
Manning, *A. B.*, gelatin. V. Properties of a gelatin purified by flocculation in an electric field, i, 90.
Manojev, *D. P.* See *N. W.* **Kondyrev.**
Mansfield, *G.*, and *E.* **Geiger**, mechanism of action of insulin, i, 1016.
Maplethorpe, *C. W.*, and *N.* **Evers**, picrates of the opium alkaloids, i, 1166.
Maracineanu, (*Mlle.*) *S.*, effect of the sun on radioactivity, ii, 348.
Marano, *C.* See *S.* **Klosky.**
Marberger, *R.* See *M.* **Kohn.**
Marbeukel, *E.* See *H.* **Scheibler.**
Marcelin, *A.*, superficial solutions and the law of Gay-Lussac, ii, 772.
March, *A.*, continuous *X*-ray spectrum and Planck's radiation law, ii, 614.
Marchal, (*Mlle.*) *G.*, thermal decomposition of metallic sulphates. I. and II., ii, 870, 1162.
Marchal, (*Mlle.*) *G.* See also *C.* **Matignon.**
Marchet, *A.*, amphibolites from Austria, ii, 997.
Marchlewski, *L.*, chemical parent of blood pigment and chlorophyll, i, 604.
Marchlewski, *L.*, and *A.* **Moroz**, ultraviolet absorption spectra of organic compounds. VI., ii, 353.
Marchlewski, *L.* See also *E.* **Kepianka.**
Marckwald, *W.*, and *H.* **Gebhardt**, gravimetric determination of zinc by means of cyanamide, ii, 1002.
Marcus, *E.* See *E.* **Günzel.**
Marcusson, *J.*, formation of fatty acids from "protoparaffin," i, 349.
polymerisation of fatty oils. III. and IV., i, 356, 1234.
Marcusson, *J.*, structure of humic acids and coal, i, 793.
Mardles, *E. W. J.*, dissolution of substances in mixed liquids with special reference to colloids, ii, 34.
Mareeuw, *W. P. H. van den D.*, identification of *Secale cornutum* preparations; [detection of ergotinine], ii, 1010.
Margosches, *B. M.*, *L.* **Friedmann**, and *W.* **Tschörner**, chemical nature of fats. I. Iodine super-value of fatty oils and unsaturated fatty acids, i, 629.
Margosches, *B. M.*, *L.* **Friedmann**, *E.* **Scheinost**, and *W.* **Tschörner**, chemical nature of fats. II. Iodine supernumber of fatty oils and unsaturated fatty acids of similar iodine number, i, 883.
Margosches, *B. M.*, and *E.* **Scheinost**, replacement of monohydric by dihydric phenols in the kjeldahlisation of nitrates, ii, 1094.
Margosches, *B. M.*, and *E.* **Scheinost** [with *M.* **Frischer**], remarkable behaviour of alkali sulphate in the kjeldahlisation of the nitroanilines, ii, 1200.
Margosches, *B. M.*, and *E.* **Scheinost** [with *V.* **Woynar**], quantitative kjeldahlisation of nitrates with phenolsulphonic acid and potassium sulphate, ii, 1094.
Margulies, *C.* See *L. J.* **Curtman.**
Margulies, *O.*, preparation of aromatic carbonyl compounds containing tervalent arsenic, i, 447.
preparation of derivatives of organic arseno compounds, i, 447.
preparation of arsenious oxides and arseno compounds of the aromatic series, i, 448.
Marian, *J.*, behaviour of oxygenated yeast to β-hydroxybutyric acid, i, 105.
assimilation of glycerol by oxygenated yeast, i, 105.
Marie, *C.*, and *G.* **Lejeune**, influence of colloids on the cathodic overvoltage of hydrogen and metals, ii, 115.
electrolytic reduction of pyridine; preparation of piperidine, i, 577.
Marie, *S. U.* See *J. T.* **Raleigh.**
Mark, *H.*, application of Röntgen crystal analysis to questions of structure of organic compounds, i, 1.
crystal structure of some simple inorganic substances (condensed gases, sulphates, etc.), ii, 1130.

Mark, *H.*, and *S.* **Tolksdorf**, refractive power of atoms for *X*-rays, ii, 933.
Mark, *H.* See also *J. R.* **Katz**.
Mark, *J. van der.* See *D.* **Gouldsmit**.
Mark, *R. E.*, biological oxygen transport by sulphydryl groups, i, 332.
Marker, *R. E.*, and *N. E.* **Gordon**, effect of hydrogen-ion concentration on compound formation and adsorption of dyes by mordants, ii, 31.
Markert, *L.* See *K.* **Freudenberg**.
Markl, *R.* See *R.* **Kremann**.
Markley, *K. S.*, and *R. M.* **Hann**, Gunning–Arnold and Winkler boric acid modifications of the Kjeldahl method for the determination of nitrogen, ii, 824.
Markov, *V.* See *G.* **Povarnin**.
Markowitz, *J.* See *F. N.* **Allan**.
Marks, *E.* See *R. W.* **Seuffert**.
Markwood, *L. N.*, alkaloids and oil of larkspur seed (*Delphinium consolida*), i, 762.
Marmasse, *P.* See *P.* **Lebeau**.
Marqueyrol, *M.* [with *L.* **Chenel**, **Friederich**, *D.* **Florentin**, **Koehler**, and *P.* **Loriette**], determination of nitrogen [in explosives], ii, 599.
Marqueyrol, *M.*, and *H.* **Muraour**, reactions of diphenylamine; preparation of diphenylbenzidine; action of acids on diphenylnitrosoamine in aqueous-alcoholic solution, i, 387.
Marquina, *M.* See *E.* **Moles**.
Marquis, (*Mlle.*) *M.*, *P.* **Urbain**, and *G.* **Urbain**, treatment of malacon; separation of celtium [hafnium] from *zirconium*, ii, 699.
Marsh, *J. K.*, emission band spectra of aromatic compounds. I. Their connexion with infra-red absorption bands and a classification, ii, 470.
emission band spectra of aromatic compounds. II. Their origin, ii, 625.
Marsh, *J. K.* See also *W. H.* **McVicker**, and *T. H.* **Nunan**.
Marsh, *J. T.*, and *H.* **Stephen**, hydroxybenzils, i, 1158.
Marshall, *A. L.*, electrodeposition of zinc from sulphate solutions, ii, 808.
mechanism of the photochemical reaction between hydrogen and chlorine, ii, 883.
Marshall, *A. L.*, and *B.* **Bruzs**, heat of formation of lead carbonate, ii, 1040.
Marshall, *A. L.* See also *H. S.* **Taylor**.
Marshall, *J.*, action of aldehydes on Grignard's reagent. III., i, 1428.
Marshall, *M.*, metastable states in low-voltage mercury arcs, ii, 339.
Marston, *H. R.*, colorimetric method for determination of guanidine and methylguanidine, i, 97.
sterol of *Boletus granulatus*, i, 346.
colorimetric method for the determination of guanidine and methylguanidine. II. Distinction between guanidine and its methyl derivatives, i, 1047.
Martin, *C. J.* See *E. H.* **Lepper**.
Martin, *E.* See *W.* **Herz**.
Martin, *E. J.* See *R. A.* **Sawyer**.
Martin, *F.*, measurements of viscosity by the Ostwald viscosimeter, ii, 499.
Martin, *F. J.* See *A. F.* **Joseph**.
Martin, *J. C.*, and *J. S.* **Burd**, composition of the soil solution as indicated by the displacement method, i, 1526.
concentration of phosphate in the soil solution according to the displacement method, i, 1527.
Martin, *J. H.* See *G. D.* **Buckner**.
Martin, *L. H.* See *E. C.* **Stoner**.
Martin, *R. E.*, effect of light on the thermal conductivity of selenium, ii, 1117.
Martin, *T. L.*, effect of straw on accumulation of nitrates [in soil] and crop growth, i, 1372.
Martin, *W. H.*, relation between the depolarisation of the scattered light and the Kerr effect in liquids, ii, 90.
Martin, *W. S.* See *E. M.* **Crowther**.
Martini, *A.* See *J.* **Holluta**.
Martini, *M.*, and *A.* **Nourisson**, determination of alcohol, ii, 719.
Martland, *M.*, phosphoric esterase of blood at various hydrogen-ion concentrations, i, 454.
Martland, *M.*, and *R.* **Robison**, possible significance of the hexosephosphoric esters in ossification. V. The enzyme in the early stages at bone development, i, 201.
Marton, *L.*, infra-red absorption spectra, ii, 1025.
Martz, *E.* See *H.* **Wieland**.
Marvel, *C. S.*, *F. L.* **Kingsbury**, and *F. E.* **Smith**, identification of amines. II. *m*-Nitrobenzenesulphonamides, i, 244.
Marvel, *C. S.*, *D. W.* **MacCorquodale**, *F. E.* **Kendall**, and *W. A.* **Lazier**, synthesis of some possible precursors of lysine, i, 234.
Marvel, *C. S.*, and *V. du* **Vigneaud**, detection of nitrates and perchlorates, ii, 240.
Marvel, *C. S.* See also *D. A.* **McGinty**.
Marza, *V.* See *C. J.* **Parhon**.

Maschmann, *E.*, bismuth compounds, i, 527.
Masing, *G.*, cause of inverse segregation [in alloys], ii, 1146.
Masing, *G.*, and *L.* **Koch**, constitution of aluminium–copper alloys, ii, 787.
Masing, *G.*, and *M.* **Pólányi**, tensile strength of zinc and cold working, ii, 370.
Mason, *C. W.*, temper colours, ii, 108.
Mason, *F. A.*, derivatives of 1:8-naphthalic acid. II. Preparation and properties of 8-benzoyl-α-naphthoic acid and its derivatives, i, 33.
derivatives of 1:8-naphthalic acid. I. Preparation and properties of 1:8-naphthalyl chloride, i, 34.
synthesis of 1:2-dihydroquinaldine, i, 834.
Mason, *F. A.* [with *H.* **Jenkinson**], nitration of the carbonate and ethyl carbonate of *m*-hydroxybenzaldehyde, i, 931.
Mason, *R. B.*, and *J. H.* **Mathews**, equilibrium in the systems, zinc chloride–pyridine and cadmium chloride–pyridine, ii, 1063.
Massa, *G.* See *G.* **Cusmano**.
Masson, *I.* See *G. A.* **Elliott**.
Mastin, *H.* See *F.* **Fairbrother**.
Masuda, *S.*, oxygen-combining capacity of hæmoglobin determined by the ferricyanide method, i, 604.
Masumizu, *Y.*, cetacea. XVIII. Sugar content of the blood, i, 1349.
Masumoto, *B.* See *S.* **Komatsu**.
Masumoto, *H.*, thermal and electric conductivities of some aluminium alloys, ii, 503.
Matheson, *G. L.* See *G. S.* **Whitby**.
Mathews, *J. H.* See *B. H.* **Carroll**, *R. B.* **Mason**, and *R. V.* **Williamson**.
Matievic, *A.* See *A.* **Skrabal**.
Matignon, *C.*, law of volatility, ii, 670.
physico-chemical study of some organic syntheses, ii, 1063.
Matignon, *C.*, and (*Mlle.*) *G.* **Marchal**, measurements of radioactivity, ii, 1110.
Matignon, *C.* See also *H.* **Copaux**.
Matlin, *D.* See *L. S.* **Weatherby**.
Matscher, *J.* See *A.* **Zinke**.
Matsumiya, *K.*, organic compounds of arsenic. III. Reaction between arsenic trichloride and α-naphthyl compounds of mercury, i, 1339.
organic compounds of antimony. I. Reaction between magnesium-α-naphthyl bromide and inorganic antimony compounds; tri-α-naphthylstibine and some of its derivatives, i, 1472.
Matsumiya, *K.*, and *M.* **Naka**, organic compounds of arsenic. II. Reaction between the Grignard reagent and arsenic trioxide, i, 1339.
Matsunami, *N.* See *S.* **Komatsu**.
Matsuoka, *Z.*, *S.* **Takemura**, and *N.* **Yoshimatsu**, kynurenic acid formation in the animal body, i, 731.
Matsuoka, *Z.*, and *N.* **Yoshimatsu**, new substance formed from tryptophan in the animal body, i, 731.
Matthäus, *K.*, relationship between Ostwald's viscosity equation and Poiseuille's law, ii, 663.
Matthew, *C. W.* See *E. D.* **Plass**.
Matthews, *M. A.* See *E. de B.* **Barnett**.
Matthias, *E.*, *C. A.* **Crommelin**, *H. K.* **Onnes**, and *J. C.* **Swallow**, rectilinear diameter of helium, ii, 468.
Matula, *V.* See *J.* **Sterba-Boehm**.
Matveev, *W.* See *W.* **Rodionov**.
Matz, *P. P.*, calcium content of blood of normal and tuberculous subjects, i, 1492.
Mau, *C.* See *W.* **Biltz**.
Maubert, *A.*, *L.* **Jaloustre**, and *P.* **Lemay**, influence of radium on the catalase of the liver, i, 737.
Maubert, *A.*, *L.* **Jaloustre**, *P.* **Lemay**, and *G.* **Andreoly**, catalytic properties of bismuthoxyl, i, 614.
Maume, *L.* See *H.* **Lagatu**.
Maurer, *H.* See *W.* **Küster**.
Maurer, *K.* See *H. H.* **Schlubach**.
Mauss, *H.* See *K. von* **Auwers**.
Mauthner, *F.*, synthesis of divarinol, i, 25.
synthesis of 3:5-dihydroxycinnamic acid, i, 926.
synthesis of androsin, i, 950.
Mautner, *P.* See *F.* **Straus**.
Maverick, *G.* See *T.* **Batuecas**.
Maw, *W.* See *C. F.* **Allpress**.
Maxted, *E. B.*, absorption of catalytically poisonous metals by platinum. I. Absorption of lead and mercury, ii, 384.
Maxymowicz, *W.* See *L.* **Moser**.
May, *O. E.* See *J. F. T.* **Berliner**.
May, *R.* See *G. D.* **Bengough**.
May, *R. M.* See *R. F.* **Le Guyon**.
Mayer, *A.*, and *L.* **Plantefol**, equilibrium of cell constituents and mode of oxidation in the cell; imbibition and respiratory types in reviviscent plants, i, 1120.
Mayer, *F.*, and *W.* **Fischbach**, anthrone series, i, 1076.
Mayer, *F.*, and *R.* **Schulze**, 4- and 6-methylisatin, i, 1315.
Mayer, *H.*, absorption spectrum and specific heat of chlorine dioxide, ii, 12.

Mayer, *M. E.* See *H.* **Lange.**
Mayer, *N.* See *G.* **Weissenberger.**
Mayer, *P.*, behaviour of oxalacetic acid to animal organs, i, 736.
Mayer-Bugström, *C.* See *A.* **Schaarschmidt.**
Mayneord, *W. V.* See *F. L.* **Hopwood.**
Mazé, *P.*, plurality of the products of photosynthesis deduced from a study of the gaseous exchanges between the atmosphere and the whole plant, i, 485.
influence of fluorine and iodine on reproductive power of rats and on the growth of the young, i, 870.
Maze-Sencier, *J.* See *P.* **Jolibois.**
Mazourevitsch, *H.*, action of aromatic amines on thiosemicarbazide, i, 984.
hydrogenation of cyclic and acyclic aldazines and ketazines by aluminium amalgam, i, 1240.
preparation of alicylic primary amines by reduction of oximes with active aluminium, i, 1247.
Mazzetti, *C.*, cobalt chloride solutions. I., ii, 209.
cobalt chloride solutions. II. Solutions of barium chloride and of barium and cobalt chlorides, ii, 210.
Mazzocco, *P.*, and *V.* **Morera**, effect of insulin on the composition of the blood, i, 482.
Mazzucchelli, *A.*, perchlorate ion as catalyst in the electrolytic preparation of persulphuric acid, ii, 214.
Mazzucchelli, *A.*, and *A.* **Vercillo**, preparation of intermetallic compounds by the wet method, ii, 582.
refractive indices of perchlorates in aqueous solution, ii, 963.
Mecke, *R.*, theory of band spectra, ii, 259.
structure of a class of band spectra, ii, 351.
anomalies of intensity in band spectra, ii, 626.
formation of band spectra, ii, 736.
Mecklenburg, *M.* See *L.* **Dünner.**
Mecklenburg, *W.*, methylene-blue test; evaluation of active charcoals, ii, 530.
Medici, *M.* See *U.* **Sborgi.**
Meeker, *D. O.* See *R. S.* **Hubbard.**
Meerwein, *H.*, and *Rudolf* **Schmidt**, reduction of aldehydes and ketones, i, 1239.
Meerwein, *H.*, and *J.* **Weber**, transformation of maleic esters into fumaric esters, i, 1038.
Meester, *W. A. T. de.* See *E.* **Cohen.**
Meggers, *W. F.*, spectrum regularities for scandium and yttrium, ii, 77.
regularities in the arc spectrum of niobium, ii, 167.
Meggers, *W. F.*, periodic structural regularities in spectra as related to the periodic law of the chemical elements, ii, 258.
platinum metals. VII. Arc spectra of the platinum metals (4500—9000 Å.), ii, 454.
multiplets in the spectrum of ionised vanadium, ii, 913.
Meggers, *W. F.*, *C. C.* **Kiess**, and *F. M.* **Walters**, *jun.*, the displacement law of arc and spark spectra, ii, 77.
Meggers, *W. F.*, and *O.* **Laporte**, arc spectrum regularities for ruthenium, ii, 1101.
Meggers, *W. F.*, and *B. E.* **Moore**, quartet-system multiplets in the arc spectrum of yttrium, ii, 612.
Meggers, *W. F.* See also *P. D.* **Foote.**
Mehl, *R. F.*, and *D. P.* **Smith**, vacuum door, ii, 707.
Mehrer, *M.* See *S.* **Fränkel.**
Mehrotra, *M. R.* See *K. C.* **Sen.**
Mehta, *R. P.* See *O. L.* **Brady.**
Meidinger, *W.*, photographic blackening curve, ii, 143.
Meier, *R.*, formation of methæmoglobin. VI. Ferricyanide and *p*-benzoquinone, i, 1476.
Meier, *R.*, and *O.* **Meyerhof**, heat of combustion of glycogen, ii, 92.
Meier, *R.* See also *O.* **Meyerhof.**
Meier, *W.* See *Walter* **König.**
Meijer, *G.*, system, copper nitrate–ammonium nitrate–water, ii, 123.
Meininger, *H.* See *F.* **Hein.**
Meisenburg, *K.* See *L.* **Taub.**
Meisenheimer, *J.*, constitution of Grignard's magnesium compounds. II., i, 527.
fission of ring systems, i, 1335.
Meisenheimer, *J.*, *Hans* **Lange**, and *W.* **Lamparter**, Beckmann transformation. V. Oximes of *p*-methoxybenzil, i, 1073.
Meisenheimer, *J.*, *E.* **Piper**, and *H.* **Lange**, etherates of the magnesium halides, i, 1252.
Meissner, *K. W.*, absorption in excited neon, ii, 337.
absorption in excited gases, ii, 1099.
plant for liquefaction of helium; some measurements made with the aid of liquid helium, ii, 1135.
Meissner, *O.* See *D.* **Vorländer.**
Meitner, *L.*, γ-rays and atomic disintegration, ii, 10.
Meitner, *L.* See also *O.* **Hahn.**
Meldrum, *A. N.*, and *R. L.* **Alimchandani**, reduction of the group $-CH(OH)\cdot CCl_3$. I., i, 1272.

Melin, *E.*, and *K.* **Helleberg**, activity of the proteolytic and related enzymes of certain *Hymenomycetæ* known as *Mycorrhyza*, i, 745.
Mellon, *M. G.*, and *V. M.* **Morris**, borax as a standardising agent for acids and bases, ii, 325.
Mellor, *J. W.*, and *A.* **Scott**, action of heat on kaolinite and other clays. I., ii, 698.
Melly, *J.*, and *A. von* **Rötth**, animal calorimetry. IV. Specific dynamic action of completely hydrolysed protein, with a note on method of evaluation, i, 193.
animal calorimetry. V. Specific dynamic action of fat, i, 332.
Mélon, *L.*, effect of amino-acids on the metabolism of isolated organs of dogs, i, 190.
Memmen, *F.* See *R.* **Willstätter**.
Ménager, *Y.* See *J.* **Lelièvre**.
Menchikovski, *F.*, composition of Palestine olives and their oil, i, 1521.
Mendeléev, *P.*, and *A.* **Slosse**, rôle of calcium and potassium ions in the development of embryos, i, 456.
Menke, *J. B.*, nitration with nitrates. I. and II., i, 386, 655.
Menner, *E.* See *R.* **Schwarz**.
Menschikov, *G.* See *O. I.* **Magidson**, and *A. E.* **Tschitschibabin**.
Menzies, *A. C.*, optical separations and atomic numbers, ii, 2.
optical screening-constant regularities, ii, 831.
Menzies, *A. W. C.*, isotopic composition and atomic weight of chlorine in meteorites, ii, 1109.
Menzies, *A. W. C.*, *E. M.* **Collins**, and *P. L.* **Tyson**, simple circulation pump for gases, ii, 818.
Mercier, *P.* See *C. E.* **Guye**.
Merck & Co., quinine compounds [quinine salicylosalicylate], i, 1448.
Merck, *E.*, **Chemische Fabrik**, preparation of oxycodeinones, i, 1315.
acetopyrocatechol dibenzyl ether, i, 1431.
Merck, *E.*, *O.* **Wolfes**, and *A.* **Dützmann**, preparation of polyalkylhydroxyarylaminopropanes or their *N*-monoalkyl derivatives, i, 393.
Merejkovski, *B. K.*, partial dehalogenation of polyhalogen derivatives, i, 878.
action of bromine on hydrocarbons; bromination of β-methylbutane, i, 1033.
relations between organic ring systems and unsaturation properties. II., i, 1291.
Merkenschlager, *F.* See *F.* **Boas**.
Merrill, *A. T.* See *W. M.* **Clark**, and *H. C.* **Sherman**.
Merrill, *H. B.*, hydrolysis of skin and hair, i, 92.
Merton, *T. R.*, ultra-violet spectrophotometry, ii, 78.
Merton, *T. R.*, and *J. E. G.* **Pilley**, spectrum of nitrogen, ii, 333.
extension of the negative band spectrum of nitrogen, ii, 737.
excitation of the band spectrum of helium, ii, 1024.
Merwin, *H. E.* See *R. E.* **Gibson**, and *R. W. G.* **Wyckoff**.
Messenger, *W. G.* See *E.* **Vanstone**.
Messerknecht, *C.*, and *W.* **Biltz**, density of beryllium halides, ii, 1141.
Messerknecht, *C.* See also *W.* **Biltz**.
Messmer, *E.* See *K.* **Hess**.
Mestrezat, *W.*, and (*Mlle.*) *Y.* **Garreau**, transport of electrolytes; mobilisation of ions by intermolecular exchanges, ii, 543.
transport of electrolytes; velocity of diffusion through a membrane and ionic selection, ii, 543.
Mestrezat, *W.*, and (*Mlle.*) *M.* **Janet**, dispersion of colloidal electrolytes in relation to mineral exchanges in cells, i, 198.
Metcalfe, *E. P.*, and *B.* **Venkatesachar**, origin of the satellites of mercury lines, ii, 82.
Métin, *M.* See *A.* **Goris**.
Metz, *L.* See *L.* **Wöhler**.
Meulen, *H. ter*, determination of nitrogen in organic compounds by catalytic hydrogenation, ii, 66.
determination of oxygen in organic compounds. II., ii, 156.
colorimetric determination of molybdenum, ii, 330.
dithiomolybdates, ii, 584.
determination of nitrogen in oil, coke, and proteins, ii, 599.
Meulen, *P. A. van der.* See *W.* **Rieman**.
Meulenhoff, *J.*, complex compounds of boric acid. I. Dipyrocatecholboric acid, some salts and derivatives. II. Salts of borosalicylic acid, i, 541.
optically active boron, i, 920.
Meunier, *L.*, and *A.* **Bonnet**, fluorescence of vegetable colouring matters, i, 1439.
fluorescence of fisetin in the ultra-violet light of the wood lamp, ii, 738.
Meunier, *L.*, and *A.* **Breguet**, relations between age of cellulose and the properties of nitrocellulose prepared from it, i, 119.

Meunier, *L.*, and *M.* **Queroix**, reactions in solutions of quinone, i, 412.
Meurice, *R.*, determination of potassium, ii, 825.
Meuwissen, *J. C.* See *W. P.* **Jorissen.**
Meyer, *A.* See *W.* **Autenrieth.**
Meyer, *E.* See *R.* **Wintgen.**
Meyer, *F.*, apparatus for ferrous oxide determinations, ii, 898.
Meyer, *G. M.* See *P. A.* **Levene.**
Meyer, *H.*, new derivatives of the pyridinecarboxylic acids, i, 836.
Meyer, *H. O.* See *A.* **Gutbier.**
Meyer, *J.*, reaction between diazodeoxybenzoin and carbon disulphide, i, 424.
substitute for cobalt glass, ii, 601.
Meyer, *J.*, *G.* **Dirska**, and *F.* **Clemens**, complex cobaltic selenates, ii, 422
Meyer, *J.* See also *F.* **Fichter**, and *L.* **Ruzicka.**
Meyer, *K. F.* See *E.* **Wagner.**
Meyer, *P.* See *H.* **Staudinger.**
Meyer, *Paul.* See *W.* **Lipschitz.**
Meyer, *M.*, laboratory preparation of zinc diethyl and lead tetraethyl, i, 893.
Meyer, *R. J.*, and *H.* **Nachod**, sulphates of quadrivalent uranium, ii, 230.
Meyer, *R. J.*, and *W.* **Schulz**, detection and determination of small quantities of fluorine, ii, 598.
Meyer, *S.*, magnetisation numbers of the rare earths, ii, 173, 944.
Meyer, *W.* See *W.* **Autenrieth**, and *A.* **Sonn.**
Meyer-Bisch, *R.*, and *F.* **Günther**, mineral metabolism in diabetics. II. Disturbances in intermediate calcium and chloride metabolism, i, 328.
Meyerfeld, *J.*, ammonium oxalate as a reagent for distinguishing sodium from potassium salts, ii, 1202.
Meyerhof, *O.*, determination of lactic acid in animal organs, i, 719.
relation between processes of fission and respiration in the cell, i, 993.
methylglyoxalase, i, 1507.
Meyerhof, *O.*, *K.* **Lohmann**, and *R.* **Meier**, synthesis of carbohydrate in muscle, i, 727.
Meyerhof, *O.*, and *R.* **Meier**, lactic acid metabolism in the living animal, i, 612.
Meyerhof, *O.* See also *R.* **Meier.**
Michaelis, *L.*, theory of permeability of membranes for electrolytes, ii, 1150.
general principles of ion effects on colloids, ii, 1154.
Michaelis, *L.*, and *S.* **Dokan**, electric charge on sparingly soluble substances, ii, 963.
Michaelis, *L.*, and *A.* **Fujita**, phase boundary potentials, ii, 131.
Michaelis, *L.*, and *M.* **Mizutani**, influence of neutral salts on the potential of the hydrogen electrode in contact with a hydrochloric acid solution, ii, 130.
dissociation of weak electrolytes in water–alcohol solutions, ii, 793.
Michailov, *A. K.* See *W. S.* **Sadikov.**
Michalek, *J. C.* See *W. H.* **Rodebush.**
Michaud, *F.*, general character and electrical properties of gels, ii, 292.
Michaux, *A.* See *L.* **Randoin.**
Michel, *P.* See *G.* **Mourignand.**
Michetti, *A.* See *L.* **Vecchiotti.**
Michlin, *D.* See *B.* **Sbarsky.**
Mickwitz, *A.*, phosphors of boric acid, ii, 476.
Mie, *G.*, impulse radiation and Compton's scattered radiation, ii, 844, 1128.
Miekeley, *A.* See *M.* **Bergmann.**
Mijs, *J. A.* See *J.* **Böeseken.**
Mikeska, *L. A.* See *P. A.* **Levene.**
Milan, *E. F.* See *W. A.* **Patrick.**
Milas, *N. A.*, and *E. M.* **Terry**, oxidation of fumaric and of maleic acid to tartaric acid, i, 780.
Miller, *A. L.* See *C. H.* **Viol.**
Miller, *A. W.* See *F. B.* **Dains.**
Miller, (*Miss*) *C. C.*, Stokes–Einstein law for diffusion in solution, ii, 28.
Miller, *C. J.*, and *S.* **Smiles**, constitution of disulphoxides. II., i, 391.
Miller, *C. J.* See also *D. T.* **Gibson.**
Miller, *E. J.*, adsorption by activated sugar charcoal. II. Adsorbability of hydrogen and hydroxyl ions, ii, 656.
Miller, *H.* See *G.* **Piness.**
Miller, *H. G.*, and *W. W.* **Yates**, relation of treatment of natural foodstuffs to their effect on growth and reproduction, i, 108.
Miller, *H. G.*, *W. W.* **Yates**, *R. C.* **Jones**, and *P. M.* **Brandt**, mineral metabolism with dairy cattle; mineral equilibrium after prolonged lactation, i, 1498.
Miller, *H. R.*, use of acetylene for the determination of hæmoglobin, i, 1112.
Miller, *L. B.*, adsorption by aluminium hydroxide considered as a solid solution phenomenon, ii, 192.
Miller, *M.* See *E.* **Wedekind.**
Miller, *R. C.* See *W. D.* **Ramage.**
Miller, *R. F.*, optical constants of crystals of selenium and tellurium between 3000 and 5000 Å., ii, 751.

Miller, *W. L.*, the method of Willard Gibbs in chemical thermodynamics, ii, 399.
concentration and polarisation at the cathode during electrolysis of solutions of copper salts, ii, 798.
Millian, *E.*, action of gelatin on electrolytic cadmium, ii, 680.
Milligan, *A. G.*, trustworthy shaking machine, ii, 150.
Milligan, *C. H.* See *A. S.* **Richardson.**
Millikan, *R. A.*, electron and light-quantum from the experimental point of view, ii, 624.
evidence for the divisibility of the electron, ii, 832.
Millikan, *R. A.*, and *I. S.* **Bowen**, possible reconciliation of Bohr's interpenetration ideas with Sommerfeld's relativistic treatment of electron orbits, ii, 467.
series spectra of three-valency-electron atoms of phosphorus (P III), sulphur (S IV), and chlorine (Cl V), ii, 610.
new light on two-electron jumps, ii, 733.
Millikan, *R. A.* See also *I. S.* **Bowen.**
Mills, *W. H.*, *W. H.* **Palmer**, and (*Miss*) *M. G.* **Tomkinson**, pyridofluorene and some of its derivatives, i, 68.
Milne, *E. A.*, equilibrium of the calcium chromosphere, ii, 628.
Saha's ionisation formula, and the theoretical value of the photo-electric absorption coefficient, ii, 920.
Milobedzki, *T.*, tautomerism of dialkyl phosphites. III., i, 1051.
Milroy, *J. A.*, determination of glucose in blood, i, 1486.
Minakami, *R.*, ionic antagonism, ii, 860.
Mingoia, *Q.* See *B.* **Oddo.**
Mingozzi, *A.* See *G.* **Rastelli.**
Minovici, *S.*, and (*Miss*) *M.* **Iliesco**, determination of lipoids in the blood-serum of nervous cases, i, 452.
Minunni, *G.* [with *G.* **Lazzarini**, and *S.* **D'Urso**], syntheses of heterocyclic nitrogen nuclei. I. Pyrazolecarboxylic acids by condensation of aldehyde-phenylhydrazones with ethyl acetoacetate, i, 1175.
Mirande, *M.*, optical properties of sterol plastids and of phytosterol from bulbs of *Lilium candidum*, i, 618.
phytosterol from bulb scales of the genus *Lilium*, i, 872.
Mircescu, *J.* See *E.* **Angelescu.**
Mirsky, *A. E.* See *M. L.* **Anson.**
Mislowitzer, *E.*, measurement of hydrogen-ion concentration by means of quinhydrone; a new double electrode in beaker form, i, 1483.
measurement of hydrogen-ion concentration of blood; the syringe as electrode, i, 1483.
new potentiometer, i, 1485.
Mislowitzer, *E.*, and *M.* **Vogt**, electrotritration in physiological liquids. I. Determination of chlorides in blood and serum, i, 1485.
Mislowitzer, *E.* See also *P.* **Rona.**
Mita, *J.*, pharmacology of the oxidation products of ether, i, 195.
Mitchell, *A. C. G.*, activation of hydrogen by excited mercury atoms, ii, 1077.
Mitchell, *A. D.*, hydrolytic decomposition of phosphorus trichloride, ii, 316.
Mitchell, *T. C.* See *R. M.* **Caven.**
Mitra, *N. G.* See *S. S.* **Bhatnagar.**
Mitsukuri, *S.*, *T.* **Rokkaku**, and *T.* **Watase**, vapour pressures of hydrogen chloride above aqueous solutions. I., ii, 1050.
Mitter, *P. C.*, and *N.* **Palit**, condensations of amidines with ethoxymethylene derivatives of β-ketonic esters, β-diketones, and cyanoacetic ester. II., i, 1319.
Mittra, *N. M.*, and *N. R.* **Dhar**, induced reactions and diabetes from the point of view of induced oxidation, ii, 576.
Miura, *H.* See *R.* **Hara.**
Miyake, *M.* See *G. A.* **Roush.**
Miyake, *S.*, complex salts of antimony trichloride, ii, 815.
Miyamichi, *E.* See *P.* **Karrer.**
Miyazaki, *K.*, and *J.* **Abelin**, specific dynamic action of foodstuffs. III. Relation between accessory food factors and specific dynamic action of flesh, i, 332.
Mizutani, *M.*, ionisation of weak electrolytes in water-alcohol solutions. II. Relations between chemical constitution and alcohol sensitivity of acids and bases, ii, 867.
Mizutani, *M.* See also *L.* **Michaelis.**
Mockeridge, (*Miss*) *F. A.*, formation of plant growth-promoting substances by micro-organisms, i, 106.
Modern, *F.*, and *W.* **Pauli**, electrolyte-free, water-soluble proteins. IV. Acid–protein compounds. I., ii, 518.
Möller, *K.* See *K. von* **Auwers.**
Moeller, *O.* See *D. B.* **Jones.**
Möllering, *H.* See *Erich* **Müller.**
Moesveld, *A. L. T.* See *E.* **Cohen.**

Mohler, *F. L.*, critical potentials associated with excitation of alkali spark spectra, ii, 615.
soft *X*-ray levels and the Bohr scheme of atomic structure, ii, 1113.
Mohler, *F. L.* See also *P. D.* **Foote**.
Mohr, *J. M.*, pole-effect of barium and neodymium rays in the visible region of the spectrum, ii, 612.
Moir, *J.*, colour and chemical constitution. XIX. Organic fluorescence, ii, 261.
colour and molecular geometry. III. Graphical presentation of the theory, ii, 634.
colour and molecular geometry. IV. Explanation of the colours of cyanine dyes, ii, 1121.
Moir, *J.*, and *J. S.* **Jamieson**, electrolytic determination of moderate amounts of arsenic, ii, 1094.
Moir, *J.*, and *J.* **Lewis**, acocantherine. II., i, 833.
Mokragnatz, *M.* See *G.* **Bertrand**.
Mokruschin, *S. G.*, adsorption of acids by filter-paper, ii, 957.
Mokrzycki, *G.* See *T.* **Peczalski**.
Moldenhauer, *W.*, synthesis of ammonia at high pressures. II., ii, 215.
Molengraaff, *G. A.*, and *A. L.* **Hall**, alkali granite and nepheline syenites, canadite, and foyaite, in the Vredefort mountainland, South Africa, ii, 64.
Moles, *E.*, fundamental atomic weights, ii, 346, 1021.
Moles, *E.*, and *M.* **Crespi**, kinetics of the thermal decomposition of the permanganates, ii, 877.
Moles, *E.*, and *M.* **Marquina**, solubility of mercury halides in mixtures of glycerol and water, ii, 283.
Molinari, *V.*, separation of *o*- from *p*-nitrotoluene and *o*- from *p*-nitrochlorobenzene by rectification in a vacuum, i, 380.
Moll, *W. J. H.*, and *H. C.* **Burger**, vacuum thermo-element, ii, 613.
Molliard, *M.*, effect of the mineral composition of the culture medium on the structure of *Aspergillus niger*, i, 480.
effect of the nature of sugar on the formation of organic acids by *Aspergillus niger* in unbalanced media, i, 480.
Molodyi, *T.*, and *F.* **Pavlov**, determination of surface tension from photographic records of the formation of drops, ii, 1142.
Moltini, *C. B. von.* See *F.* **Klimone**.
Moltschanova, *O. P.* See *B. A.* **Lavrov**.
Monath, *E.* See *M.* **Giua**.
Monceaux, *R.* See *C.* **Richtet**, *jun.*
Mondain-Monval, *P.*, salt solutions, ii 654.
solubility of sucrose, ii, 769.
Mong, *H. yu.* See *A.* **Rosenheim**.
Monroe, *C. F.*, and *A. E.* **Perkins**, mineral metabolism of dairy cows as affected by distilled water and previous feeding, i, 1498.
Monroe, *C. F.* See also *A. E.* **Perkins**.
Montagne, (*Mlle.*) *M.* See *E. E.* **Blaise**.
Montgomery, *E. G.*, determination of cyanates in blood, *i*, 455.
Moog, *L.* See *B.* **Helferich**.
Mook, *H. W.* See *H. J.* **Backer**.
Moor, *F.* See *H.* **Freundlich**.
Moor, *W. O.*, urochromogen, i, 328.
urochromogen and urochrome; the new form of urea, i, 460.
new oxalate from human urine, i, 1490.
Moore, *B. E.* See *W. F.* **Meggers**.
Moore, *C. J.*, liquid hydrogen sulphide as a source of laboratory supply of the gas, ii, 1195.
Moore, *C. W.* See *E. F.* **Armstrong**.
Moore, *F. H.* See *H. H.* **Hodgson**.
Moorhouse, *V. H. K.* See *A. T.* **Cameron**.
Moose, *J. E.*, and *S. W.* **Parr**, redetermination of the heats of oxidation of certain metals, ii, 208.
Moquet, *L.* See *H.* **Bierry**.
Morani, *V.*, presence of Δ^1-menthen-3-one in the essential oil of Sicilian *Mentha pulegium*, i, 146.
essential oil of *Ptychotis verticillata*, Duby, i, 146.
Moraško, *V.*, protein coagulation in drops. VII. Study of the precipitin reaction by means of the drop method, i, 1487.
Morávek, *V.*, preparation of colloidal silver by reduction with chloroform, ii, 775.
Morávek, *V.* See also *H.* **Lundegårdh**.
Morel, *G.* See *R.* **Delaby**.
Morera, *V.* See *P.* **Mazzocco**.
Morey, *G. W.*, and *N. L.* **Bowen**, binary system, sodium metasilicate–silica, ii, 121.
ternary system, sodium metasilicate–calcium metasilicate–silica, ii, 1161.
Morey, *G. W.* See also *R. W. G.* **Wyckoff**.
Morgan, *G. T.*, and *A. R.* **Bowen**, higher fatty acids; eicosoic and stearic acids, i, 114.
Morgan, *G. T.*, *S. R.* **Carter**, and *A. E.* **Duck**, γγ-diethylpentane (tetraethylmethane), i, 877.

organ, *G. T.*, *S. R.* Carter, and *W. F.* Harrison, residual affinity and co-ordination. XXIV. Heats of chelation of dithiolated metallic halides, ii, 1042.
organ, *G. T.*, and *E. A.* Cooper [with *A. W.* Burt], bactericidal action of quinones and allied compounds, i, 207.
organ, *G. T.*, *E. A.* Cooper, and *F. J.* Corby, bactericidal action of tellurium-β-diketones, i, 206.
organ, *G. T.*, and *G. R.* Davies, antimonial analogues of the cacodyl series, i, 1395.
organ, *G. T.*, and *H. D. K.* Drew, interactions of tellurium tetrachloride and acetic anhydride, i, 530.
aromatic derivatives of germanium, i, 1197.
organ, *G. T.*, *H. D. K.* Drew, and *C. R.* Porter, Claisen condensation, i, 363.
organ, *G. T.*, and *W. J.* Hickinbottom, nitration of stereoisomeric aromatic diamines, i, 156.
organ, *G. T.*, and *E.* Holmes, higher methyl ketones, i, 514.
rambutan tallow as source of *n*-eicosoic acid, i, 777.
organ, *G. T.*, and *W. H.* Porritt, arylselenoglycollic acids, i, 1196.
organ, *G. T.*, and *A. D.* Sheasby, acenaphthene series. II. 1-Aminoacenaphthene, i, 1144.
organ, *G. T.*, and *D. G.* Skinner, stereoisomeric azo dyes, i, 1191.
organ, *G. T.*, and *J. D. M.* Smith, residual affinity and co-ordination. XXV. A quadridentate group contributing four associating units to metallic complexes, i, 1457.
the co-ordination theory in its application to the study of mordant dyes, ii, 841.
organ, *G. T.*, and *H. M.* Stanley, acenaphthene series. I. 2-Aminoacenaphthene, i, 133.
organ, *G. T.*, and *C. J. A.* Taylor, *cyclo*telluropentanediones containing aliphatic and aromatic substituents, i, 634.
organ, *G. T.*, and *V. E.* Yarsley, residual affinity and co-ordination. XXIII. Interactions of trimethylstibine and platinic and palladous chlorides, i, 378.
Morgan, *J. D.*, thermal theory of gas ignition by electric sparks, ii, 553.
Morgan, *J. W.* See *W. D.* Harkins.
Morgan, *S. O.* See *H. H.* Lowry.
Morgan, *W. O. P.* See *C. D.* Murray.
Morgen, *A.*, *C.* Windheuser, and *E.* Ohlmer, replacement of protein by urea in rations for milch animals, i, 217.
Morgulis, *S.*, and *O.* Barkus, glycolysis *in vitro*, i, 1344.
Mori, *S.*, parasympathetic stimulants in vitamin extracts, i, 1021.
Mori, *T.* See *U.* Suzuki.
Moriarty, *M. E.* See *G. N.* Hoeffel.
Morimura, *S.*, cetacea. XII. Physicochemical properties of the urine of the rorqual, i, 1348.
Morison, *C. G. T.*, effect of light on settling of suspensions, ii, 774.
Morison, *C. G. T.* See also *G. R.* Clarke.
Moritz, *A. R.*, effect of ultra-violet irradiation on calcium of the blood-serum, i, 995.
Morosov, *N. I.*, influence of excess of reagents on the formation of dispersoid solutions of mercuric sulphide, ii, 197.
Moroz, *A.* See *L.* Marchlewski.
Morris, *J. L.*, and *E. E.* Ecker, destruction of uric acid by bacteria and moulds, i, 478.
Morris, *J. L.* See also *E. E.* Ecker.
Morris, *V. A.* See *D. C.* Henry.
Morris, *V. N.* See *M. G.* Mellon.
Morrison, *D. M.* See *O.* Maass.
Morrison, *F. R.*, chemical examination of the seeds of the "bunya bunya" (*Araucaria bidwilli*, Hooker). I., i, 619.
Morrison, *F. R.* See also *A. R.* Penfold.
Morse, *C. W.* See *F. H.* Rhodes.
Morse, *M.* See *A. S.* Wheeler.
Morse, *S.* See *H.* Fricke.
Mortimer, *B. R.* See *L.* Sattler.
Morvillez, *F.* See *M.* Polonovski.
Mosbacher, *I.* See *A. E.* Hill.
Moser, *L.*, and *K.* Atynski, preparation of selenides from hydrogen selenide and solutions of metallic salts, ii, 583.
Moser, *L.*, *A.* Brukl, and *J.* Vén, separation of iron and aluminium from manganese and magnesium and from phosphoric acid by means of sulphosalicylic acid, ii, 329.
Moser, *L.*, and *R.* Lessing, determination and separation of rarer metals from other metals. V. Separation of zirconium and hafnium from titanium, cerium, and thorium, ii, 718.
Moser, *L.*, and *W.* Maxymowicz, determination of nickel as dioxide, ii, 1206.
Moses, *R. L.* See *M. A.* Ramirez.

Moses, *W.* See *T.* **Sabalitschka.**
Mosettig, *E.* See *E.* **Späth.**
Mosharrafa, *A. M.*, quantum explanation of the Zeeman effect, ii, 830.
Moskovits, *N.*, preparation of acetone and alcohol by the fermentation of carbohydrates with *Bacillus macerans*, i, 1511.
Mosonyi, *J.*, excretion of certain nitrogenous substances in the urine in the course of experimental nephritis, i, 1491.
Mottram, *E. N.* See *A.* **Lapworth.**
Mottram, *J. C.* See *E. C.* **Dodds.**
Mott-Smith, *L. M.* See *J. A.* **Becker.**
Motzoc, *D.* See *E.* **Angelescu.**
Moudgill, *K. L.*, Travancore essential oils. II. Oil from the leaves of *Lantana camara*, i, 565.
Travancore essential oils. III. Oil from the resin of *Canarium strictum*, Roxb. (black dammar), i, 823.
Travancore essential oils. V. Essential oil from *Ageratum conyzoides*, Linn. (appa grass), i, 945.
Travancore essential oils. VI. Oil from *Cymbopogon cæsius*, Stapf. (inchi grass), i, 1293.
Mountain, *E. D.*, potash–oligoclase from Mt. Erebus, Antarctic, and anorthoclase from Mt. Kenya, East Africa, ii, 819.
Moureu, *C.*, destruction of Berthelot's calorimetric bomb; its replacement by a new type of bomb, ii, 427.
Moureu, *C.*, and *C.* **Dufraisse**, autoxidation and anti-oxygenic action. XIII. Deactivation of acraldehyde by quinol; experiments with light; deactivation brought about by quinol does not explain the anti-oxygenic action, i, 362.
so-called poisoning of oxidising catalysts, ii, 413.
Moureu, *C.*, *C.* **Dufraisse**, and *M.* **Badoche**, autoxidation and anti-oxygenic action. XII. Active autoxidisable form of acraldehyde, i, 117.
autoxidation and anti-oxygenic action. XIV. Activation of acraldehyde by light, i, 362.
autoxidation and anti-oxygenic action. XV. Activation of acraldehyde by oxygen and by light and deactivation by quinol, particularly in connexion with the condensation to disacryl, i, 363.
Moureu, *C.*, *C.* **Dufraisse**, and *H.* **Blatt**, diphenylphenylacetylenylcarbinol [triphenylpropargyl alcohol]; ethers. II., i, 136.
Moureu, *C.*, *C.* **Dufraisse**, and *P.* **Lotte**, autoxidation and anti-oxygenic action. XVI. Location of the catalytic property in the oxidisable part of the molecule of the catalyst, ii, 561.
Moureu, *C.*, and *P.* **Landrieu**, calorimetric bomb with platinum lining, ii, 995.
Moureu, *H.* See *C.* **Dufraisse.**
Mourignand, *G.*, *A.* **Leulier**, and *P.* **Michel**, fluctuations of the iron in the blood during the course of experimental scurvy, i, 330.
Moyse, *H. W.* See *H. J.* **Lucas.**
Mrozek, *O.* See *O.* **Mumm.**
Muchamedoff, *A.* See *B.* **Sbarsky.**
Muchin, *G. E.* See *W. F.* **Timoféev.**
Mudd, *S.*, electroendosmosis through mammalian serous membranes. I. Hydrogen-ion reversal point with buffers containing multivalent anions, i, 468.
electroendosmosis through mammalian serous membranes. II. Comparison of the hydrogen-ion reversal points with acetate and with citrate–phosphate buffers, i, 1355.
Mühl, *W.* See *K.* **Brand.**
Muehlberg, *W. F.*, explosion method for peroxide fusions, ii, 899.
Muehlberger, *C. W.*, and *V.* **Lenher**, additive products of selenium dioxide with the halogen acids, ii, 890.
Müller, *Adolf*, absorption of ethylene by ortho-, pyro-, and meta-phosphoric acid, i, 1373.
Müller, *Alex.*, universal *X*-ray spectrograph, ii, 895.
Müller, *Alex.*, and *W. B.* **Saville**, further *X*-ray measurements on long-chain compounds (*n*-hydrocarbons), ii, 367.
Müller, *Alex.* See also *E. von* **Angerer.**
Müller, *Alfred.* See *O.* **Fischer.**
Müller, *Arno*, formation of coumarins from citric acid and phenols, i, 1442.
Müller, *Carl*, very thin, transparent metal films, ii, 1039.
Müller, *Emil.* See also *B.* **Holmberg.**
Müller, *Erich*, system, chromium oxide–chromium hydroxide–chromite-sodium hydroxide, ii, 124.
valency problems, ii, 363.
course of organic reactions, ii, 414.
valency in boron compounds, ii, 841.
simple method for preparing ultrafilters, ii, 1061.
Müller, *Erich* [with *E.* **Reissmann**, and *O.* **Ballin**], system, lead hydroxide–lead oxide–plumbite–sodium hydroxide solution, ii, 125.

Müller, *Erich*, and *H.* Aarflot, potentiometric determinations with mercurous salts, ii, 65.
Müller, *Erich*, and *D.* Junck, potentiometric study of the reaction between chlorine water and iodide ion, ii, 584.
potentiometric study of the reduction of iodate with iodide, ii, 585.
Müller, *Erich*, and *H.* Möllering, potentiometric investigation of the reduction of permanganate by ferrous ion and iodine ion, ii, 305.
Müller, *Erich*, and *F.* Müller, catalytic decomposition by formaldehyde. III., ii, 414.
catalytic decomposition of pyruvic acid, ii, 414.
Müller, *Erich*, and *A.* Schuch, potentiometric study of the reaction between halogens and the cyanogen ion, ii, 825.
Müller, *Ernst* (Heidelberg), and *C.* Gottfried, decomposition of ethyl diazoacetate by copper acetylide, i, 893.
Müller, *Ernst* (Königsberg). See *A.* Sonn.
Müller, *F.*, potentiometric determination of alkaloids with a hydrogen electrode, ii, 607.
Müller, *F.* See also *Erich* Müller.
Müller, *G.* See *B.* Neumann.
Müller, *H.* See *G.* Kornfeld, and *G.* Schroeter.
Müller, *Hans*, and *L.* Kürthy, chemistry and physiology of bismuth. II. Tendency of bismuth to form complex salts, ii, 61.
Müller, *Hans.* See also *L.* Kürthy.
Müller, *Helmut*, guanidine compounds in the extractives of ox-testicles, i, 854.
biological relationship of arginine to agmatine, i, 1496.
galegine, i, 1520.
Müller, *Helmut.* See also *F.* Holtz.
Müller, *Herbert.* See *E.* Weitz.
Mueller, *J. Howard*, tuberculin, i, 616.
Mueller, *J. Howard*, *M.* Wayman, and *H.* Zinsser, chemical composition of residue antigen, i, 1016.
Müller, *John H.*, and *H. R.* Blank, allotropy of germanium dioxide, ii, 145.
Müller, *M.* See *P.* Wenger.
Müller, *P.* See *F.* Fichter.
Müller, *Richard.* See *Hans* Fischer.
Müller, *Robert*, solubility of some inorganic salts in organic solvents, ii, 380.
Müller, *Robert*, *F.* Hölzl, *W.* Knaus, *F.* Planiszig, and *K.* Prett, electrochemistry of non-aqueous solutions. IV. Attempts to deposit certain metals of the earths and alkaline-earths from anhydrous pyridine, ii, 133.
Müller, *Robert*, *R.* Hönig, and *A.* Konetschnigg, electrochemistry of non-aqueous solutions. V. Attempts to deposit certain of the heavy metals from anhydrous pyridine, ii, 134.
Müller, *Robert*, *E.* Pinter, and *K.* Prett, electrochemistry of non-aqueous solutions. VI. Electro-deposition of some metals from anhydrous solutions in amyl alcohol, acetonitrile, aniline, and quinoline, ii, 882.
Müller, *Robert.* See also *R.* Kremann.
Müller-Bardorff, *K.* See *G.* Heller.
Mukerji, *B. K.* See *N. R.* Dhar.
Mukerji, *D. N.* See *S. S.* Bhatnagar.
Mukerji, *K. B.*, and *N. R.* Dhar, decomposition of nitrous acid by light and by catalysts, ii, 691.
Mukherjee, *D. H.* See *S. B.* Schryver.
Mukherjee, *J.*, action of silica on electrolytes, ii, 962.
Mukherjee, *J.* See also *J. C.* Ghosh.
Mukherjee, *J. N.*, interaction between silica and electrolytes in its relation to theories of soil acidity, i, 488.
adsorption of acids by purified silica, ii, 383.
nature of hydrolytic adsorption with reference to the adsorption of electrolytes and of water. I. General and theoretical introduction, ii, 1149.
Mukherjee, *J. N.*, and *B. N.* Ghosh, coagulation of hydrosols by mixtures of electrolytes and ionic antagonism, ii, 394.
Mukherjee, *J. N.*, and *H. L.* Ray, electro-osmotic experiments on intensity of adsorption of a constituent ion by an insoluble salt. I., ii, 385.
Mullaly, *J. M.*, chemical deposits of a regular form, ii, 801.
Mullaly, *J. M.*, and *H.* Jacques, diffusion of mercury and iodine vapours through nitrogen, ii, 27.
Muller, *A.*, structure of stearic and stearolic acids, ii, 748.
Muller, *E. F.* See *E.* Knecht.
Muller, *J. A.*, and (*Mlle.*) *E.* Peytral, sudden pyrogenic decomposition of methyl formate and the principle of minimum molecular deformation, i, 353.

Mulliken, *R. S.*, electronic states of the CN molecule, ii, 18.
isotope effect in band spectra. I., ii, 259.
isotope effect in band spectra. II. Spectrum of boron monoxide, ii, 346.
band of unusual structure probably due to a highly unstable calcium hydride molecule, ii, 469.
isotope effect in the spectrum of silicon nitride, ii, 731.
isotope effect in band spectra. III. Spectrum of copper iodide as excited by active nitrogen, ii, 833.
isotope effect in band spectra. IV. Silicon nitride, ii, 1020.
Mulsow, and **Paine**, production of hydrogen sulphide by members of the colon group of bacteria, i, 1510.
Mumm, *O.* [with *K.* **Behrens**, *A. von* **Fischer-Treuenfeld**, *G.* **Hingst**, *W.* **Lund**, *O.* **Mrozek**, *J.* **Sönksen**, and *O.* **Tonn**], pyridonemethides [methylenedihydropyridines], i, 964.
Mund, *W.*, number of ions produced in a spherical volume by radium emanation (radon), ii, 732.
Mund, *W.*, and *W.* **Koch**, chemical change of some gaseous hydrocarbons by radioactive radiations, i, 625.
polymerisation of acetylene under the action of α-particles, ii, 1173.
Munesada, *T.*, chemical constituents of *Matteuchia orientalis* (*Hk.*), Trev. I., i, 620.
Munro, *L. A.*, and *F. M. G.* **Johnson**, adsorption of vapours by alumina, ii, 191.
Munsell, *H. E.* See *H. C.* **Sherman**.
Munzing, *E.* See *A.* **Eibner**.
Murai, *J.*, synthesis of a homologue of zingerone, 4-hydroxy-3-methoxyphenylethyl *n*-amyl ketone, i, 1157.
synthesis of *m*-hydroxyphenylethyl methyl ketone and β-3-hydroxy-4-methoxyphenylethyl methyl ketone (*iso*zingerone), i, 1157.
Muraour, *H.* See *M.* **Marqueyrol**.
Murch, *W. O.* See *H.* **King**.
Murmann, *E.*, reaction for magnesium and calcium and for rubidium and cæsium, ii, 437.
proving identity of two organic compounds, ii, 719.
Murray, *A. G.*, scrubber for ammonia distillates, ii, 236.
apparatus for the precipitation of barium sulphate, ii, 236.
Murray, *A. G.* See also *S.* **Palkin**.
Murray, *C. D.*, and *A. B.* **Hastings**, maintenance of carbonic acid equilibrium in the body, i, 1342.
Murray, *C. D.*, and *W. O. P.* **Morgan**, oxygen exchange, blood, and the circulation; factors involved in oxygen supply, i, 1481.
Murray, *C. D.* See also *L. J.* **Henderson**.
Murray, *H. A.*, physiological ontogeny. A. Chicken embryos. II. Catabolism; chemical changes in fertile eggs during incubation, i, 1353.
Murray, *H. D.*, hydrolysis of iodine as measured by the iodine electrode, i, 555.
composition of starch iodide, i, 889.
colour test for aniline and toluidine, ii, 163.
portable gas analysis apparatus, ii, 593.
Murray, *M. M.*, determination of iron in small quantities in biological substances, i, 183.
determination of ammonia and urea in blood and urine, i, 710.
Mussehl, *F. E.* See *C. W.* **Ackerson**.
Myers, *C. H.* See *H.* **Gilman**.
Myers, *C. N.*, and *H. B.* **Corbitt**, neurosyphilis. II. Retention and elimination of silver with special reference to silver salvarsan and silver therapy, i, 611.
Myers, *C. N.* See also *L. H.* **Cornwall**, and *J. A.* **Fordyce**.
Myers, *J. E.*, and *W. J.* **Jones**, fractionating column with moving parts, ii, 428.
Myers, *J. E.* See also *E. S.* **Hedges**.
Myrbäck, *K.*, method for the determination of calcium and phosphorus in small quantities of blood, i, 1485.
Myrbäck, *K.*, and *B.* **Everitt**, action of living yeast on lactic acid, i, 105.
Myrbäck, *K.* See also *H. von* **Euler**.

N.

Naamlooze Vennootschap Philips' Gloeilampenfabriken, separation of zirconium and hafnium, ii, 62, 63.
Nachod, *H.* See *R. J.* **Meyer**.
Nachtwey, *P.* See *F.* **Arndt**.
Nacken, *H.* See *K.* **Elbs**.
Naeser, *W.* See *W. A.* **Roth**.
Nagai, *S.* See *Y.* **Tanaka**.
Nagaoka, *H.*, transmutation of mercury into gold, ii, 835.
preliminary note on the transmutation of mercury to gold, ii, 1111.

Nagaoka, *H.*, and *Y.* **Suguira**, distribution of electric field in metal arcs and the Stark effect observed in arcs of silver, copper, magnesium, chromium, nickel, cobalt, iron, and ten other metals, ii, 171.

Nagel, *K.* See *K. A.* **Hofmann.**

Nagornov, *N. N.*, and *L. A.* **Rotinjanc**, surface of state of *cyclo*hexane, ii, 646.

Naidu, *D. S.*, constituents of the marking nut, "*Semecarpus anacardium*," Linn., i, 1224.

Naik, *K. G.*, and *M. D.* **Avasare**, absorption of halogens by mercurous salts. I. Formation and properties of some complex compounds of mercury, ii, 221.

Naik, *K. G.*, and *C. S.* **Patel**, interaction of sulphur monochloride with organic acid amides. II., i, 121.

Naish, *W. A.*, partition of silver between lead and zinc, ii, 506.

Nakahara, *Y.* See *P.* **Rona.**

Nakai, *R.*, mixed dismutation of aldehydes. II., i, 360.

Nakai, *M.* See *K.* **Matsumiya.**

Nakamura, *G.* See *M.* **Kimura.**

Nakamura, *H.*, *X*-ray analysis of electrolytic brass, ii, 745.

Nakamura, *H.* See also *G.* **Bertrand**, and *K.* **Hess.**

Nakamura, *S.*, and *Y.* **Fujioka**, behaviour of some spark lines of carbon in an electric field, ii, 910.

Nakano, *I.* See *R.* **Nakaseko.**

Nakaseko, *R.*, and *I.* **Nakano**, determination of small amounts of lead in animal tissues, ii, 1205.

Nakazono, *T.*, application of liquid amalgams to volumetric analysis. I. Determination of molybdenum, titanium, and iron, ii, 1004.

Name, *R. G. van*, and *F.* **Fenwick**, behaviour of electrodes of platinum and platinum alloys in electrometric analysis. I. Dissimilar electrodes, ii, 594.

behaviour of electrodes of platinum and platinum alloys in electrometric analysis. II. Polarised electrodes, ii, 594.

Nametkin, *S. S.*, order of addition to cyclic double linkings. II., i, 250.

isomeric transformations. II. Isomerisation of rings, i, 1054.

structure of *iso*camphenilone, i, 1079.

mechanism of oxidation of unsaturated compounds by permanganate, i, 1145.

Nametkin, *S. S.* [with *L.* **Abakumovski**, and *A.* **Selivanov**], *iso*bornylane and some of its derivatives, i, 47.

Nametkin, *S. S.*, and *L. J.* **Briusova**, β-methylcamphenilone, i, 1078.

some simple homologues of *cyclo*hexene and their derivatives, i, 1146.

Nametkin, *S. S.*, and *A. G.* **Jarceva**, isomeric transformations. IV. Anomalous hydration of pinene oxide, i, 1081.

Nametkin, *S. S.*, and *A.* **Zabrodin**, secondary α-nitrocamphene, i, 416.

Nanba, *M.*, artificial production of autohæmolysin, i, 1344.

Nanji, *D. R.*, and *F. J.* **Paton**, aluminium amalgam as a reducing agent in the sugar series, i, 117.

Nanji, *D. R.*, and *W. S.* **Shaw**, rôle of silica in plant growth; its assimilation and physiological relation to phosphoric acid, i, 214.

Nanji, *D. R.* See also *A. R.* **Ling.**

Narayan, *A. L.*, and *D.* **Gunnaiya**, infra-red emission and absorption of potassium vapour, ii, 737.

Narayan, *A. L.*, *D.* **Gunnaiya**, and *K. R.* **Rao**, absorption and dispersion of thallium vapour, ii, 5.

absorption of magnesium vapour, ii, 337.

Narayan, *A. L.*, and *K. R.* **Rao**, resonance radiation from thallium vapour, ii, 338.

absorption of light by vapours of lead, tin, bismuth, antimony, and magnesium, ii, 927.

Narayan, *A. L.*, and *G.* **Subrahmanyam**, absorption of electrically luminescent potassium vapour, ii, 737.

Narayanan, *B. T.* See *J. J.* **Sudborough.**

Náray-Szabó, *S. von.* See *E.* **Brummer.**

Narbutt, *J.*, approximate calculation of atomic frequencies of the inert gases, ii, 948.

simple method for the indirect determination of molecular heats of vaporisation, ii, 1140.

Nassau, *M.* See *F.* **Sommer.**

Nath, *D.* See *N. A.* **Yajnik.**

Nathanson, *J. B.*, optical constants of solid cæsium, ii, 187.

Naton, *J.* See *R.* **Dietzel.**

Natta, *G.* See *G. R.* **Levi.**

Nau, *C. A.*, *E. B.* **Brown**, and *J. R.* **Bailey**, methylene-citric anhydride; aniline derivatives of citric and aconitic acids, i, 1379.

Naumann, *W.* See *K.* **Schaum.**

Naves, *R.* See *J. F.* **Durand.**

Navias, *L.*, and *W. P.* **Davey**, differentiation between mullite and sillimanite by their *X*-ray diffraction patterns, ii, 1127.

Naylor, *N. M.* See *H. C.* **Sherman.**
Neale, *S. M.*, elasticity and tensile strength of starch, ii, 783.
Neale, *S. M.* See also *F. D.* **Farrow.**
Neber, *P. W.*, *K.* **Hartung**, and *W.* **Ruopp**, stereoisomeric forms of *o*-nitrobenzyl methyl ketoxime, i, 1072.
Needham, *D. M.* See *J.* **Needham.**
Needham, *J.*, inositol. III. Metabolic behaviour of *i*-inositol in the developing avian egg, i, 192.
Needham, *J.*, and *D. M.* **Needham**, hydrogen-ion concentration and the oxidation–reduction potential of the cell interior; a micro-injection study, i, 1012.
Neergaard, *K. von*, intravenous silver therapy. II. Influence of body electrolytes on the solubility of silver salts, i, 1212.
intravenous silver therapy. III. Solubility of silver salts in blood, i, 1357.
Neeteson, *P. A.* See *M. A. H. van den* **Hout.**
Negelein, *E.*, glycolysis, i, 856.
Negoshi, *K.*, preparation of alcohol by catalytic reduction of acetaldehyde, i, 1375.
Negresco. See **Banu.**
Neill, *J. M.*, oxidation–reduction of hæmoglobin and methæmoglobin. I. Changes induced by *Pneumococci* and by sterile animal tissues, i, 868.
oxidation–reduction of hæmoglobin and methæmoglobin. II. Oxidation and reduction of methæmoglobin by anaërobic bacteria and by sterile plant tissue. III. Formation of methæmoglobin during the oxidation of auto-oxidisable substances. IV. Inhibition of "spontaneous" formation of methæmoglobin, i, 993.
Neill, *J. M.*, and *O. T.* **Avery**, oxidation and reduction by *Pneumococcus*. VI. Oxidation of enzymes in sterile extracts of *Pneumococcus*. VII. Enzyme activity of sterile filtrates of aërobic and anaërobic cultures of *Pneumococcus*, i, 340.
oxidation and reduction by *Pneumococcus*. VIII. Nature of the oxidation–reduction systems in sterile *Pneumococcus* extracts, i, 867.
Neill, *J. M.*, and *A. B.* **Hastings**, influence of tension of molecular oxygen on oxidations of hæmoglobin, i, 709.
Neithammer, *A.*, action of photocatalysers on the bursting of buds and on germination of seeds, i, 1023.
Nelson, *D. H.* See *J. E.* **Greaves.**
Nelson, *E. K.*, non-volatile acids of the blackberry, i, 618.
non-volatile acids of the strawberry, pineapple, raspberry, and Concord grape, i, 762.
Nelson, *E. M.*, and *H.* **Steenbock**, fat-soluble vitamins. XXI. Alleged growth-promoting properties of air irradiated with ultra-violet light, i, 484.
fat-soluble vitamins. XXIV. Non-precipitability by digitonin of the antiophthalmic and antirachitic substances from cod-liver oil, i, 1020.
Nelson, *J. M.*, and *O.* **Bodansky**, mutarotation as a factor in the kinetics of invertase action, i, 1008.
Nelson, *J. M.*, and *B.* **Freeman**, hydrolysis of sucrose by invertase in presence of *α*-methylglucoside. I., i, 739.
Nelson, *J. M.*, and *C. T.* **Sottery**, influence of dextrose and lævulose on rate of hydrolysis of sucrose by invertase from honey, i, 104.
Nelson, *M. T.* See *H.* **Steenbock.**
Nelson, *O. A.*, and *H.* **Wales**, vapour pressures and boiling points of mono- and di-methylanilines and mono- and di-ethylanilines, ii, 494.
Němec, *A.*, hydrogen-ion concentration in seeds, i, 871.
Němec, *A.*, and *M.* **Gracanin**, influence of the soil reaction on absorption of phosphorus and of potassium in presence of various phosphatic manures, i, 1228.
Němec, *A.* See also *K.* **Kvpil.**
Nenadkevitsch, *W.*, occurrence of hydrogen sulphide in limestone and dolomite, ii, 997.
Nenitzescu, *C.*, synthesis of indole, i, 973.
Nenitzescu, *C.* See also *Hans* **Fischer.**
Nešković, *M.*, action of chloral hydrate on the proteins of blood-serum, i, 716.
Netschajeva, *N.* See *A.* **Predvoditelev.**
Nette, *M.* See *G. F.* **Hüttig.**
Neuberg, *C.*, yeast enzymes, i, 336.
Neuberg, *C.*, and *G.* **Gorr**, fermentation of oxalacetic acid, i, 337.
Neuberg, *C.*, and *A.* **Gottschalk**, formation of acetaldehyde in animal organs (acetone liver), i, 199.
anaërobic respiration in plants, i, 213.
fermentation of dihydroxyacetone, i, 337.
significance of acetaldehyde production in frog's muscle, and its manifold relationships to respiration, i, 859.

Neuberg, *C.*, and *M.* **Kobel**, artificial and natural formation of sugar phosphates, i, 476.
phosphorylation of sugar, i, 1508.
Neuberg, *C.*, and *E.* **Simon**, carboligase. VIII. Biochemical acyloin synthesis, i, 737.
sulphatase. V. Animal sulphatase, i, 743.
Neuberg, *C.* See also *A.* **Gottschalk**.
Neubert, *H.*, birefringency and dichroism in dyed gels, ii, 201.
Neuenschwander, *N.* See *P.* **Hodel**.
Neuffer, *L.*, and *A. L.* **Hoffman**, alkyl derivatives of hydroxyurethane and hydroxylamine, i, 891.
Neukirch, *P.* See *E.* **Boden**.
Neumann, *A.*, nature, properties, and preparation of the eosinophile granule substance of the blood. II. Chemical and physical, i, 94.
Neumann, *B.*, and *E.* **Fuchs**, decomposition of sulphur chloride by water, ii, 410.
Neumann, *B.*, and *K.* **Jacob**, equilibrium proportions in the formation of methane from carbon monoxide and hydrogen, and from carbon dioxide and hydrogen, ii, 532.
Neumann, *B.*, and *G.* **Müller**, heat of formation of calcium hypochlorite, ii, 488.
Neumann, *B.*, and *H.* **Richter**, potentials of the alkali metals determined by the measurement of decomposition voltages of molten alkali chlorides, bromides, and iodides, ii, 797.
potentials of metals of the alkaline earths and the rare earths determined by measurement of the decomposition potentials of the molten chlorides, bromides, and iodides, ii, 797.
potential of fluorine from measurements of the decomposition voltages of fused fluorides, ii, 1164.
Neumann, *F.*, stability relations of the modifications of the polymorphous system Al_2SiO_5, ii, 849.
Neuschloss, *S. M.* See *A. H.* **Roffo**.
Newbery, *E.*, overvoltage and transfer resistance, ii, 405.
Newbery, *G.*, action of alkali hydroxide on α-bromo-α-ethylbutyrylcarbamide, i, 375.
determination of arsenic in organic compounds, ii, 901.
Newcomer, *E.* See *P. M.* **Dean**.
Newey, *A. H.* See *J. H.* **Crowe**.
Newham, *H. B.*, *H. G.* **Wiltshire**, and *J. W.* **Scharff**, determination of hæmoglobin, i, 711.
Newitt, *D. M.* See *W. A.* **Bone**, and *D. S.* **Chamberlin**.
Newman, *F. H.*, low-voltage arcs in sodium and potassium vapours, ii, 450.
spectrum of sodium at low voltages, ii, 723.
low-voltage arcs in rubidium and cæsium vapours, ii, 829.
spectrum of potassium at low voltages, ii, 1014.
Newman, *R. K.*, determination of water in mixtures of ether, alcohol, and water, ii, 156.
Nicholas, *S. D.* See *E. A.* **Cooper**.
Nicholls, *F. H.* See *W.* **Wardlaw**.
Nichols, *E. F.*, and *J. D.* **Tear**, joining the infra-red and electric-wave spectra, ii, 917.
Nichols, *E. L.*, neodymium oxide, ii, 259.
visible radiation from niobium oxide, ii, 350.
Nichols, *M. L.*, and *S. R.* **Cooper**, qualitative tests for copper, iron, and cobalt, ii, 715.
Nichols, *M. L.* See also *F. H.* **Rhodes**.
Nicholson, *J. W.*, secondary spectrum of hydrogen, ii, 468.
hydrogen spectrum of constant frequency-difference, ii, 721.
general nature of band spectra, ii, 930.
Nickel, *G.* See *K.* **Brass**.
Nicklin, *G. N.* See *J. A.* **Aeschlimann**.
Nicloux, *M.*, normal presence of carbon monoxide in the blood, i, 321.
determination of carbon monoxide by hæmoglobin absorption, ii, 824.
use of the Cornec–Cottet pipette in the measurement of small volumes in micro analysis, ii, 898.
Nicloux, *M.*, and *J.* **Roche**, oxygen content of methæmoglobin, i, 993.
Nicloux, *M.*, and *A.* **Yovanovitch**, fixation of chloroform by the central nervous system and the peripheral nerves, i, 195.
Nicolas, *E.*, and *G.* **Nicolas**, hexamethylenetetramine as a nutrient for the kidney bean and for white mustard (*Sinapis alba*), i, 623.
effect of urea, thiourea, and allylthiourea on the higher plants, i, 757.
Nicolas, *G.* See *E.* **Nicolas**.
Nicolau, *S.* See *A.* **Fernbach**, and *C.* **Levaditi**.
Nicolaysen, *N. A.*, retention and excretion of nitrogen in hypertrophy of the prostate, i, 857.

Nicolet, *B. H.*, and *J.* **Sacks**, 3-nitrophthalic anhydride as a reagent for alcohols, i, 1277.
Niel, *C. B. van*, and *F. V.* **Hooft**, incorrect application of biological agents in organic chemistry, i, 1237.
Nielsen, *J. R.*, influence of temperature on the photo-electric effect, ii, 172.
Niemann, *G.*, absorption coefficient of mesobilirubinogen and coproporphyrin, i, 1206.
Niemann, *G.* See also *H.* **Fischer**.
Niemann, *W.* See *A.* **Gutbier**.
Niemeyer, *F.* See *K. von* **Auwers**.
Nierenstein, *M.*, constitution of catechin. VII. 4:5:7:3′:4′-Pentahydroxyflavan, i, 279.
Nierenstein, *M.*, *C. W.* **Spiers**, and *A. C.* **Hadley**, gallotannin. XIV. Action of yeast on gallotannin, i, 951.
Nierenstein, *M.*, *C. W.* **Spiers**, and *P. R.* **Hatcher**, gallotannin. XIII. Identity of digallic acid from gallotannin with synthetic *m*-digallic acid, i, 692.
Nierenstein, *M.*, *D. G.* **Wang**, and *J. C.* **Warr**, action of diazomethane on some aromatic acyl chlorides. II. Synthesis of fisetol, i, 34.
Nierenstein, *M.* See also *H. F.* **Dean**, *A. I. M.* **Kahil**, and *H. H.* **Lewis**.
Niethammer, *W.* See *E.* **Heuser**.
Niggli, *P.*, homogeneous equilibria in magmatic melts and their bearing on the processes of igneous rock formation, ii, 784.
Nightingale, *D.* See *R. T.* **Dufford**.
Nikiforovski, *P. M.*, anthocyanins, i, 1224.
Nikitin, *N.*, Thomson circuit in the study of magnetic spectra, ii, 173.
Niklas, *H.*, and *A.* **Hock**, universal indicator for the colorimetric determination of p_H values in soil experiments, i, 348.
application and importance of electrometric titration to the determination of soil reactivity, i, 768.
exchangeable acidity of the soil and the relation between actual and titratable acidity, i, 1525.
comparison of the methods for the estimation of hydrogen-ion concentration in soils, i, 1526.
significance of electrometric titration in the estimation of the lime requirements of soils, i, 1526.
colorimetric determination of hydrogen-ion concentration in soils, ii, 325.
electrometric titration with the use of quinhydrone, ii, 595.
Niklas, *H.*, and *F.* **Vogel**, diphenylamine reaction in problems of plant nutrition, i, 213.
Nikolić, *N.* See *H.* **Křepelka**.
Nilsson, *R.* See *H. von* **Euler**.
Nipper, *W. W.*, spectroscopic evidence of *J*-transformation of *X*-rays, ii, 727.
Nipper, *W. W.* See also *O. K.* **DeFoe**.
Nishi, *S.*, determination of small quantities of carbon dioxide, ii, 1001.
determination of small amounts of carbon dioxide, ii, 1001.
Nishina, *Y.*, *L*-absorption spectra of the elements from Sn(60) to W(74) and their relation to atomic constitution, ii, 457.
Nishina, *Y.* See also *D.* **Coster**.
Nitschke, *A.*, micro-method for the determination of chloride in body fluids, i, 1485.
Nitzescu, *I.*, and *I.* **Cadariu**, glycolysis *in vivo* with normal and depancreatised dogs; action of insulin, i, 1352.
insulin and cholesterol metabolism, i, 1364.
Nitzescu, *I. I.*, and *J.* **Cosma**, oxidising enzymes in the constituents of the seeds of French and soya beans, i, 471.
insulin and the oxydases of muscle, i, 482.
Nitzescu, *I. I.*, *C.* **Popescu-Inotesti**, and *I.* **Cadariu**, cholesterolæmia and cholesterolysis in experimental diabetes, i, 462.
Noack, *E.*, decomposition of sulphur monochloride by water, ii, 989.
Noback, *C. V.* See *R. S.* **Hubbard**.
Noble, *E. C.* See *G. S.* **Eadie**, and *N. A.* **McCormick**.
Nocentini, *D.* See *A.* **Pieroni**.
Noda, *M.* See *H.* **Ota**.
Noddack, *W.*, *I.* **Tacke**, and *O.* **Berg**, two new elements of the manganese group, ii, 939.
Noddack, *W.* See also *J.* **Eggert**.
Nodzu, *R.* See *S.* **Komatsu**.
Nöhren, *M.* See *K.* **Fries**.
Nogaki, *S.*, fate of yeast invertase in the animal organism, i, 745.
Nolan, *L. S.* See *A.* **Chibnall**.
Nolan, *T. J.*, and *H. W.* **Clapham**, preparation of benzylaniline, i, 805.
Noll, *A.*, "chloramine" as a substitute for iodine in chemical analysis, ii, 66.
Nolte, *O.*, neutral salt decomposition by silicic acid, i, 488.
Nomura, *H.*, preparation of zingerone, i, 1157.

Nomura, *H.*, and *S.* **Hotta**, relation between chemical constitution and pungency; synthesis of the reduction products of zingerone and di-β-4-hydroxy-3-methoxyphenylethyl ketone, i, 1156.
synthesis of the homologues of zingerone, i, 1156.
Nonhebel, *G.*, and *H. B.* **Hartley**, activity coefficients and transport numbers of solutions of hydrogen chloride in methyl alcohol, ii, 1061.
Nonhebel, *G.* See also *S. R.* **Pike**.
Norberg-Schulz, *C.* See *F.* **Foerster**.
Norbury, *A. L.*, effects of certain elements on the electrical resistivity of copper, ii, 273.
Nord, *F. F.*, and *G. G.* **Schweitzer**, chaulmoogra and margosa oils and heterogeneous catalysis, i, 734.
Nordefeldt, *E.*, purification and properties of hydroxynitrilese, i, 1506.
Normann, *W.*, electrolytic gas explosions, ii, 996.
Normark, *P.* See *A.* **Palladin**.
Norris, *E. R.* See *A. W.* **Thomas**.
Norris, *F. W.*, and *S. B.* **Schryver**, pectic substances of plants. III. Nature of pectinogen and its relation to pectic acid, i, 1226.
Norris, *J. F.*, and *A. A.* **Ashdown**, reactivity of atoms and groups in organic compounds. I. Relative reactivities of hydroxyl-hydrogen atoms in certain alcohols, i, 626.
Norris, *J. F.*, and *E. O.* **Cummings**, electrolytic preparation of *p*-phenylenediamine, aminosalicylic acid, succinic acid, and hydrocinnamic acid, i, 668.
Norris, *J. F.*, and *R. C.* **Young**, preparation of triphenylmethane and the action of heat on the ethers and esters derived from triphenylcarbinol, i, 20.
Norris, *W. S. G. P.* See *C. F.* **Birch**.
Norrish, *R. G. W.*, rôle of water in the photosynthesis of hydrogen chloride, ii, 1080.
photochemical union of hydrogen and chlorine, ii, 1179.
Norrish, *R. G. W.*, and *E. K.* **Rideal**, photosensitive formation of water from its elements in the presence of chlorine, ii, 572.
North, *E. O.*, and *G. D.* **Beal**, silicododecatungstic acid [determination of alkaloids], ii, 607.
Northrop, *J. H.*, kinetics of the decomposition of hydrogen peroxide by catalase, i, 469.
Northrop, *J. H.*, test for diffusible ions. II. Ionic nature of pepsin, i, 864.
Northrop, *J. H.* See also *H.* **Clark**.
Norton, *A. J.* See *W. G.* **Christiansen**.
Norton, *J. T.*, *X*-ray study of cyanite and andalusite, ii, 1127.
Nothmann, *M.*, distribution of insulin in the organs of normal and depancreatised dogs, i, 1219.
Noüy, *P. L. du*, [uni-molecular films of sodium oleate on water]; determination of the constant *N* of Avogadro, ii, 109.
determination of surface tension by the ring method (torsion balance), ii, 279.
apparatus for the rapid measurement of surface tension at the interface of two liquids; influence of temperature, ii, 647.
determination of molecular dimensions and of Avogadro's number from colloidal solutions, ii, 844.
dimensions of the molecule and molecular weight of crystalline egg-albumin, ii, 939.
highly sensitive physical method for detecting proteins in a solution, ii, 1212.
Nourisson, *A.* See *M.* **Martini**.
Novelli, *A.*, colour reaction for nitrites, ii, 900.
Nowak, *G.* See *H.* **Lüers**.
Noyes, *A. A.*, and *W. P.* **Baxter**, interionic attraction theory of ionised solutes. III. Testing of the theory in alcoholic solvents, ii, 970.
Noyes, *A. A.*, and *W. C.* **Bray**, systematic detection of the rarer chemical elements, ii, 242.
Noyes, *A. A.*, and *H. W.* **Estill**, effect of insulin on the lactic fermentation, i, 107.
Noyes, *H. M.*, and *K. G.* **Falk**, enzyme action. XXIX. Lipolytic actions of rabbit tissues, i, 471.
Noyes, *H. M.* See also *K. G.* **Falk**.
Noyes, *W. A.*, simple differential air thermometer for use at low temperatures, ii, 896.
attempt to prepare nitro-nitrogen trichloride. III. Failure to obtain a compound containing only nitrogen and chlorine from oxides of nitrogen, ii, 988.
preparation of nitric oxide from sodium nitrite, ii, 993.
formation of polar compounds by photochemical reactions, ii, 1081.
Noyes, *W. A.*, and *W. F.* **Tuley**, heat of formation of nitrogen trichloride, ii, 644.

Noyes, *W. A., jun.*, photochemical studies. III. Reaction between nitrogen and hydrogen in presence of mercury vapour: resonance radiation of mercury, ii, 573.
Noziczka, *F.* See *H.* **John**.
Nunan, *T. H.*, and *J. K.* **Marsh**, fluorescence spectra. III. Aromatic amine vapours, ii, 353.
Nunn, *G. R.* See *E. B. R.* **Prideaux**.
Nyberg, *H. D.*, zinc–carbon battery, ii, 42.
Nylén, *P.*, organic compounds of phosphorus, i, 1134.
Nyssens, *P.*, use of phenolphthalein as an indicator for the determination of phosphoric acid by titration of ammonium phosphomolybdate, ii, 1201.

O.

Oberhauser, *F.*, bromometric determination of thiocyanates and cyanides, ii, 828.
Oberhauser, *F.* See also *W.* **Manchot**.
Oberhelman, *H. A.*, and *H. A.* **Dyniewicz**, metabolism study of ethylene anæsthesia, i, 862.
Oberlin, *H.* See *P.* **Pfeiffer**.
Oberlin, *M.* See *J.* **Gadamer**.
Oberwien, *E.* See *H.* **Goldschmidt**.
Obogi, *R.* See *A.* **Kailan**.
Obrist, *J.* See *J.* **Holluta**.
Obrutsheva, *A.* See *G. von* **Hevesy**.
Ochotnikova, *A. J.* See *B. A.* **Lavrov**.
O'Connell, *M. T.* See *R. H.* **Bogue**.
O'Connor, *M. F.* See *W. G.* **Lennox**.
Odaki, *S.* See *U.* **Suzuki**.
Oddo, *B.*, magnesylpyrrole and its use in the synthesis of pyrrole compounds, i, 295.
methylketole-yellow, i, 588.
syntheses by means of magnesylpyrrole. VI. Constitution of the pyrrolenephthalides, i, 978.
Oddo, *B.*, and *Q.* **Mingoia**, syntheses by means of magnesylpyrrole. V. Pyrrolephthalides, i, 978.
Oddo, *G.*, modification of Geissler's bulbs, ii, 431.
nitration and constitution of naphthalene, i, 804.
periodic classification of the elements and the electrical constitution of atoms and of valency, ii, 623.
O'Dwyer, *M. H.*, pectic substance in beech wood, i, 1225.
Oechslin, *C.* See **Les Établissements Poulenc Frères**.
Oehme, *C.* [with *H.* **Paal**], water–salt content of the human organism in relation to the acid–base economy. II. Physiological ionic equilibrium and mineral metabolism, i, 326.
Ölander, *A.* See *H. von* **Euler**.
Oesper, *R. E.*, and *M. P.* **Ballard**, hydroxylamine salts of organic acids, i, 1233.
Oesper, *R. E.*, and *W.* **Broker**, new hydroxyurethanes and chromoisomeric silver salts of their acyl derivatives. III., i, 1407.
Oesper, *R. E.*, *W.* **Broker**, and *W. A.* **Cook**, new chlorocarbonates [chloroformates] derived from aromatic and dihydric alcohols, i, 1408.
Oesper, *R. E.*, and *W. A.* **Cook**, new hydroxyurethanes and chromoisomeric silver salts of their acyl derivatives, i, 523.
Oesterle, *D. A.*, and *G.* **Wander**, "hesperidin" from various plants, i, 1438.
Oesterlin, *H.* See *F.* **Knoop**.
Ogawa, *I.*, fat-hydrolysing enzyme of taka-diastase, i, 103.
Ogawa, *S.*, adrenaline secretion during starvation, i, 1218.
Ogden, *K.*, and *R.* **Adams**, carboxyquinolylphenylarsinic acid and derivatives, i, 706.
Ogden, *W. H.* See *H. J. M.* **Creighton**.
Ohle, *H.*, and *W.* **Bourjau**, compounds of sugars with sulphuric acid. I., i, 634.
Ohlmer, *E.* See *A.* **Morgen**.
Ohri, *D. D.* See *S. S.* **Bhatnagar**.
Ohse, *W.* See *W.* **Steinkopf**.
Oikawa, *S.*, cetacea. XIX. Composition of tendon and sclera; separation of *d*-α-aminobutyric acid from sclera protein, i, 1349.
cetacea. XXII. Cartilage, i, 1349.
Okagawa, *M.*, stereoisomerism and cell-permeability, i, 711.
Okahara, *Y.*, cetacea. XV. Composition of the blood of the fin-back whale, i, 1349.
Okazaki, *K.*, cetacea. XIII. Contents of genital cysts; composition of fluid found in the uterus, i, 1348.
Ôkubo, *J.* See *R.* **Seeliger**.
Okubo, *Y.* See *K.* **Honda**.
Olbrich, *W.* See *O.* **Ruff**.
Oldenberg, *O.*, influence of magnetic and electrical fields on ultraviolet fluorescence of iodine, ii, 88.
fluorescence radiation of nitrogen, ii, 1116.
Oldenberg, *O.* See also *G.* **Cario**.

Oliver, *J.*, and *L.* **Barnard**, effect of valency of cations and anions on negatively and positively charged red blood cells, i, 94.
Oliveri-Mandalà, *E.*, action of hydrazine on cyanotetrazole, i, 78.
imino group, ii, 815.
Olivier, *S. C. J.*, electrolytic reduction of 2:6-dibromobenzoic acid, i, 30.
constitution of the caoutchouc molecule, i, 566.
Olivier, *S. C. J.*, and *G.* **Berger**, is the hydrolysis of esters derived from strong acids accelerated by hydrogen ions? ii, 802.
Oman, *E.*, and *A.* **Gunnelius**, calculation of points in the ethyl alcohol–water distillation curve, ii, 953.
Ongkiehong, *B. L.* See *W. P.* **Jorissen**.
Onnes, *H. K.* See *G.* **Breit**, *E.* **Mathias**, *L.* **Vegard**, *M.* **Wolfke**, and *H. R.* **Woltjer**.
Ono, *A.*, *X*-ray examination of inner structure of strained metals. III. Copper and aluminium under extension, compression, and torsion, ii, 746.
Ono, *K.*, camphor oils. II. Reaction of Japanese acid clay to camphor white oil, i, 941.
camphor oils. V. Sesquiterpenes and sesquiterpene alcohols of Japanese camphor oil, i, 1437.
Onohara, *K.*, chemistry of the blood during activity of the digestive glands, i, 322.
chemistry of the blood during parenteral excitation of the activity of digestive glands, especially of the stomach, i, 712.
Onslow, (*Mrs.*) *M. W.*, and *M. E.* **Robinson**, oxidising enzymes. VIII. Oxidation of certain parahydroxy compounds by plant enzymes and its connexion with "tyrosinase," i, 1010.
Oparin, *A.*, green respiration pigment of *Helianthus annuus*, i, 1517.
retrogressive metamorphosis of proteins in germinating seeds, i, 1518.
Opdycke, *L. H.* See *W. A.* **Patrick**.
Opitz, and **Brehme**, determination of urobilin in human excreta, i, 187.
Oppenheimer, *F.* See *H.* **Freundlich**.
Orcel, *J.*, white chlorite from Madagascar, ii, 821.
Ordelt, *H.* See *F.* **Feigl**.
O'Reilly, *N. G. J.* See *J. J.* **Drumm**.
Orékhov, *A.*, and *M.* **Roger**, semipinacolic deamination of certain amino-alcohols, i, 261.
Orékhov, *A.* See also *M.* **Tiffeneau**.
Orndorff, *W. R.*, and *W. R.* **Barrett**, *iso*phenolphthalein and some of its derivatives, i, 35.
Orndorff, *W. R.*, and *M. S.* **Patel**, *o*-cresoltetrachlorophthalein, some of its derivatives, and *iso-o*-cresoltetrachlorophthalein, i, 672.
Orndorff, *W. R.*, and *C. V.* **Shapiro**, dimethyl and diethyl ethers of phenolsulphonephthalein and of *o*-cresolsulphonephthalein, i, 251.
Orndorff, *W. R.*, and *C.* **Wang**, pyrogallolbenzein and its hydrochloride, i, 277.
Orndorff, *W. R.* See also *D. L.* **Tatern**.
Ornstein, *L. S.*, application of quanta to the electron theory of metals, ii, 733.
intensity of multiple spectral lines, ii, 916.
influence of radiation on chemical reactions, ii, 1077.
Ornstein, *L. S.*, and *H. C.* **Burger**, fine structure of the helium line 5876 Å., ii, 4.
intensities of multiplet-lines, ii, 251.
intensities of components in the Zeeman effect, ii, 340.
Ornstein, *L. S.*, *H. C.* **Burger**, and *W. C. van* **Geel**, intensity of the components in the Zeeman effect, ii, 729.
Orr, *A. P.*, colorimetric determination of ammonia in urine, i, 184.
Orr, *J. B.*, *H. E.* **Magee**, and *J. M.* **Henderson**, effect of ultra-violet light on the mineral metabolism of the lactating animal, i, 1210.
Orr, *T. G.* See *R. L.* **Haden**.
Orth, *O.* See *R.* **Stollé**.
Ortner, *H.* See *R.* **Kremann**.
Orton, *J. H.*, conditions for calcareous metabolism in oysters and other marine animals, i, 1002.
Oryng, *T.*, negative adsorption and oxidising action of suspended charcoal, ii, 656.
Osada, *S.*, conversion of alkaloids of the "aporphine" series into those of the chelidonine series, i, 283.
Osaka, *Y.*, and *K.* **Ando**, equilibria in the system, mercuric chloride, ammonium chloride, potassium chloride, and water at 25°, ii, 123.
Osawa, *A.*, *X*-ray examination of the inner structure of various calcium carbonates, ii, 745.
atomic structure of palladium and platinum black containing adsorbed gases, ii, 747.
Osborn, *D. P.*, apparatus for the determination of blood nitrogen by Folin's method, i, 323.

Osborne, *N. S.*, *H. F.* **Stimson**, and *T. S.* **Sligh**, *jun.*, flow calorimeter for specific heats of gases, ii, 995.
Osborne, *N. S.*, *H. F.* **Stimson**, *T. S.* **Sligh**, and *C. S.* **Cragoe**, specific heat of superheated ammonia vapour, ii, 643.
Oseen, *C. W.*, possible explanation of the Ingersoll non-magnetic nickel film, ii, 734.
—, *T. H.* See *J. F.* **Lehmann**.
Ossetrova, *E. D.* See *A. E.* **Tschitschibabin**.
Osterhout, *W. J. V.*, importance of maintaining certain differences between cell sap and external medium, i, 720.
is living protoplasm permeable to ions? i, 1355.
Osterhout, *W. J. V.*, and *M. J.* **Dorcas**, contrast in the cell sap of valonias and the problem of flotation, i, 868.
Ostermann, *F.*, equilibrium in the liquid system, iron–copper–manganese with varying small proportions of carbon, ii, 1050.
Osterroth, *J.* See *W.* **Lipschitz**.
Ostwald, *U.* See *A.* **Schönberg**.
Ostwald, *Wolfgang*, quantitative filtration as a method for the analysis of dispersoids, ii, 198.
velocity function of the viscosity of disperse systems. I., II., and IV., ii, 291, 392, 663.
theory of Liesegang rings, ii, 530.
Ostwald, *Wolfgang*, *A.* **Kuhn**, and *E.* **Böhme**, relation between swelling of gelatin and hydrogen-ion concentration, ii, 777.
Ostwald, *Wolfgang*, and *Herbert* **Schulze**, S-shaped adsorption curves and their calculation, ii, 657.
Ostwald, *Wolfgang*, and *A.* **Steiner**, foaming power and surface tension, especially of humus sols, ii, 771.
O'Sullivan, *J. B.*, application of the quinhydrone electrode to the measurement of p_H values in solutions containing copper ions and other bivalent ions, ii, 822.
Oswald, *M.*, and *R.* **Pinta**, oxidation of coal and of its naphthalene extracts, i, 793.
Ota, *H.*, and *M.* **Noda**, oxydase-like actions of colloidal silicates, ii, 203.
Otani, *B.*, equilibrium diagram of the binary alloys of antimony and bismuth, ii, 533.
Otani, *Z.*, fate of pyruvic acid in the animal body and in the surviving liver, i, 731.
Ott, *E.*, H. Finger's investigations on the preparation of "cyanurtriazide," i, 599.
transformations of carbon monoxide under the influence of the silent electric discharge, ii, 579.
Ott, *E.*, and *H.* **Finken**, [simple cyano and cyanuric compounds. III. Malononitrile and its halogenation], i, 1251.
Ottens, *B.* See *K. von* **Auwers**.
Ottensooser, *F.* See *F.* **Fischler**.
Otto, *J.* See *L.* **Holborn**.
Oudt, *F. W.*, measurement of intensity ratios of doublets of alkali metals in the principal series, ii, 915.
Overbeck, *W.* See *B.* **Bruckner**.
Owen, *E. A.*, *N.* **Fleming**, and *W. E.* **Fage**, absorption and scattering of γ-rays, ii, 84.
Owen, *E. A.*, and *G. D.* **Preston**, atomic structure of two intermetallic compounds, ii, 93.
Owens, *A. E.* See *W. A.* **Patrick**.
Ozawa, *T.*, wood cellulose. III. Purity of wood cellulose, i, 234.

P.

Paal, *C.*, and *H.* **Boeters**, catalytic action of colloidal metals of the platinum group. XVII. Colloidal cobalt, ii, 1072.
colloidal cobaltic hydroxide, ii, 1090.
Paal, *H.* See *C.* **Oehme**.
Paasch, *E.*, feedings of goats on ammonium acetate, urea, and horn meal as protein substitute, i, 1498.
Pacsu, *E.*, degradation of mercaptals of monosaccharides and a new synthesis of alkyl glucosides, i, 515.
methyl derivatives of *d*-glucose, i, 1242.
Pack, *G. T.* See *F. P.* **Underhill**.
Padelt, *E.* See *M.* **Bodenstein**.
Padoa, *M.* [with *N.* **Vita**], variation of temperature coefficients of photochemical reactions with the frequency, ii, 415.
Padoa, *M.*, and *B.* **Foresti**, new determinations with the micro bomb calorimeter. II., ii, 847.
Paechtner, *J.*, nephelometric investigations on the breakdown of glycogen by salivary diastase, i, 783.
Paffrath, *H.* See *E.* **Abderhalden**, and *E.* **Wertheimer**.
Page, *H. J.*, and *W.* **Williams**, exchange in Rothamsted soils, i, 222.

Page, *L.*, proof of the invariance under the Lorentz transformation of the equation of motion of the electron, ii, 80.
Balmer law as an equation of motion, ii, 468.
Paget, *H.* See *T. A.* **Henry**.
Paget, *M.* See *D.* **Raquet**.
Pagniez, *P.*, *F.* **Coste**, and *I.* **Solomon**, effect of *X*-rays on the acid–base equilibrium of blood, i, 1201.
Paillard, *H.* See *E.* **Briner**.
Paine. See **Mulsow**.
Palacios, *J.*, theory of emission in the Rutherford–Bohr atom, ii, 835.
Palazzo, *F. C.*, and *E.* **Alinari**, essential oil of *Meriandra benghalensis*, Benth., i, 418.
new constituent in oil of juniper, i, 565.
Palit, *C. C.*, and *N. R.* **Dhar**, induced oxidation of carbohydrates, i, 1401.
Palit, *N.* See *P. C.* **Mitter**.
Palkin, *S.*, and *H. M.* **Evans**, preparation of brilliant Congo R ("vital-red") and the suitability of various samples for blood volume work, i, 599.
Palkin, *S.*, *A. G.* **Murray**, and *H. R.* **Watkins**, automatic devices for extracting alkaloidal solutions, ii, 708.
Palkin, *S.*, and *H.* **Wales**, azo dyes from alkaloids of ipecac[uanha] root and their identification by means of the spectroscope, i, 1087.
Palladin, *A.*, excretion of creatinine and creatine by sheep in normal and fasting conditions, i, 327.
biochemistry of experimental scurvy. I., i, 330.
Palladin, *A.*, and *W.* **Bjeljaeva**, aminogenesis in the grey and white substances of the brain during hunger. II. Rabbit's brain, i, 190.
Palladin, *A.*, and *K.* **Kratinova**, biochemistry of experimental scurvy. VI. Influence of a maize diet on the creatinine- and creatine–nitrogen excretion of rabbits and on the weight curves of guinea-pigs, i, 1514.
Palladin, *A.*, and *A.* **Kudrjavzeva**, biochemistry of experimental scurvy. II. Nitrogen metabolism (in particular creatine metabolism) in experimental scurvy, i, 330, 461.
Palladin, *A.*, and *P.* **Normark**, biochemistry of experimental scurvy. III. Blood enzymes in experimental scurvy, i, 461.
Palladin, *A.*, and *E.* **Sawron**, biochemistry of experimental scurvy. IV. Calcium excretion and blood calcium in experimental scurvy, i, 461.
Palladin, *V.*, effect of insufficient feeding with carbohydrates and protein on the excretion of creatine and creatinine, i, 1211.
effect of wounding on the respiration of plants, i, 1221.
effect of light on the growth of isolated etiolated bean leaves, i, 1517.
effect of light on the growth and formation of chlorophyll in isolated etiolated and green leaves, i, 1518.
Palladin, *V.*, and *E.* **Hübbenet**, absorption of ultra-violet light by plants, i, 1223.
Palladin, *V.*, and *V.* **Illjuvijev**, zymase formation in plants, i, 1519.
Palladin, *V.*, and *V.* **Levtschenko**, glycuronic acid in plants, i, 1369.
Palladin, *V.*, and *E.* **Lovtschinovskaja**, decomposition of oxalic acid by plants, i, 1222.
Pallauf, *F.* See *A.* **Eibner**.
Palmaer, *W.*, presentation of the periodic system, ii, 90.
Palmer, *W. G.*, and *F. H.* **Constable**, catalytic activity of copper. V. Comparison of the rates of dehydrogenation of various alcohols, ii, 311.
Palmer, *W. H.* See *W. H.* **Mills**.
Paneth, *F.*, active hydrogen, ii, 57.
Paneth, *F.*, *W.* **Haken**, and *E.* **Rabinovitsch**, preparation and properties of pure tin hydride, ii, 60.
Paneth, *F.*, and *G.* **Joachimoglu**, pharmacological properties of tin hydride and germanium hydride, i, 197.
Paneth, *F.*, and *E.* **Rabinovitsch**, preparation of tin hydride by cathodic reduction, ii, 59.
Paneth, *F.*, and *E.* **Rabinovitsch** [with *W.* **Haken**], the group of volatile hydrides, ii, 760.
Paneth, *F.*, and *E.* **Thilo**, compounds of nickel and copper with diacetyldioxime, i, 1132.
Panichi, *U.*, specific gravities of minerals and crystallised chemical compounds, ii, 64.
specific gravity of solid binary compounds, ii, 493.
Panicker, *P. B.* See *B. S.* **Rao**.
Panisset, *L.*, *J.* **Verge**, and *V.* **Carneiro**, action of distilled water and physiological salt solution on the vitality of bacteria, i, 339.
Panizzon-Favre, *G.*, attempts to synthesise 2-nitro-1:4-naphthaquinone, i, 144.

Pankoke, *K.*, βγ-dihydroxyadipic acid, i, 358.
Pantin, *C. F. A.*, and *L. T.* **Hogben**, colorimetric method for studying the dissociation of oxyhæmocyanin suitable for class work, i, 1481.
Pantin, *C. F. A.*, and *T. H.* **Rogers**, amphoteric substance in the radula of the whelk (*Buccinum undatum*), i, 720.
Paoloni, *C.* See *W. D.* **Treadwell**.
Papaconstantinou, *B.*, protective action of soaps on Zsigmondy's gold sols, ii, 393, 526.
protective action of soaps on arsenious sulphide sols, ii, 393.
Papendieck, *A.*, occurrence of porphyrin in blood-serum, i, 96.
the porphyrin of human fæces. III., i, 98.
Papendieck, *A.*, and *K.* **Bonath**, porphyrins from blood pigment, i, 711.
Parhon, *C. J.*, and *V.* **Marza**, cholesterol content of the testicles and suprarenals, i, 1346.
Parinaud, *E.* See *R.* **Fabre**.
Paris, *G.*, alcoholic zymase and a more exact interpretation of its activity, i, 475.
Pariselle, rotatory power and dispersion in the terpene series, ii, 742.
Pariselle, and **Laude**, co-precipitation of magnesium hydroxide with aluminium hydroxide in ammoniacal solution, ii, 903.
Parisi, *E.* See *R.* **Ciusa**.
Park, *J. R.* See *P. C.* **Austin**.
Parke, *B.* See *O.* **Silberrad**.
Parker, *E. W.* See *H. C.* **Parker**.
Parker, *F. W.*, carbon dioxide content of the soil air as a factor in the absorption of inorganic elements by plants, i, 1223.
absorption of phosphate by Pasteur-Chamberland filters, i, 1372.
Parker, *G. H.*, production of carbon dioxide by nerve, i, 849.
excretion of carbon dioxide by frog nerve, i, 1353.
Parker, *H. C.*, potentiometric hydrogen-ion measurements with non-gas electrodes, ii, 899.
Parker, *H. C.*, and *G. A.* **Dannerth**, calomel half cells for industrial hydrogen-ion measurements, ii, 712.
Parker, *H. C.*, and *E. W.* **Parker**, densities of certain aqueous potassium chloride solutions as determined with a new pycnometer, ii, 288.
Parker, *H. H.* See *H.* **Gilman**.
Parker, *M. A.*, and *H. P.* **Armes**, influence of a magnetic field on certain chemical reactions, ii, 683.
Parker, *W. H.* See *W.* **Wardlaw**.
Parkes, *A. S.*, and *J. C.* **Drummond**, effect of vitamin-*B* deficiency on reproduction, i, 1021.
Parkes, *E. B.* See *I. M.* **Heilbron**.
Parkes, *G. D.* See *F. D.* **Chattaway**.
Parks, *G. S.*, thermal data on organic compounds. I. Heat capacities and free energies of methyl, ethyl, and *n*-butyl alcohols, ii, 491.
Parks, *G. S.*, and *K. K.* **Kelley**, physical chemical properties of mixtures of ethyl and *iso*propyl alcohols, ii, 764.
thermal data on organic compounds. II. Heat capacities of five organic compounds; entropies and free energies of some homologous series of aliphatic compounds, ii, 949.
Parnas, *J. K.*, ammonia content and formation in blood. II., i, 454.
Parnas, *J. K.*, and *J.* **Heller**, ammonia content and formation in blood. I., i, 323.
ammonia in blood, i, 454.
Parnas, *J. K.*, and *M.* **Taubenhaus**, ammonia content and formation in blood. III. Origin of blood ammonia, i, 1484.
Parr, *S. W.* See *J. E.* **Moose**.
Parravano, *N.*, and *G.* **Malquori**, solubility of oxygen in silver, ii, 769, 879.
Parravano, *N.*, and *A.* **Scortecci**, modification of the structure of aluminium alloys containing large proportions of silicon, ii, 281.
Parri, *W.*, differentiation of citric from tartaric acid, ii, 162.
Parry, *J.*, and *F. E.* **Wright**, afwillite, a new hydrous calcium silicate, ii, 429.
Parsons, *A. T.* See *A. G.* **Francis**.
Parsons, *L. B.*, influence of water on certain chemical reactions. I. Effect of various concentrations of water vapour on the reaction between chlorine and potassium iodide or bromide, ii, 880.
influence of water on certain chemical reactions. II. Reaction between hydrogen sulphide and iodine in ethereal solution, ii, 880.
influence of water on certain chemical reactions. III. Reactions between certain metals and iodine, ii, 880.
Parsons, *L. B.*, and *W. S.* **Sturges**, conductivity method as applied to studies of bacterial metabolism, i, 1509.

Parsons, *L. B.*, and *W. S.* **Sturges**, error due to ammonia and ammonium salts in Van Slyke's procedure for amino-nitrogen determination as applied in studies of bacterial metabolism, i, 1509.
Partington, *J. R.*, and *M. F.* **Carroll**, specific heats of carbon monoxide and hydrocyanic acid vapour, ii, 373.
Partington, *J. R.*, and *A. B.* **Howe**, ratio of specific heats of hydrogen, ii, 1041.
Partington, *J. R.*, and *W. G.* **Shilling**, water-gas equilibrium, ii, 395.
Partington, *J. R.*, and *S. K.* **Tweedy**, molecular weight of cholesterol, ii, 273.
Partington, *J. R.* See also *J. W.* **Beeson**, *J. J.* **Doolan**, *K.* **Stratton**, and *I.* **Vogel**.
Pascal, *P.*, complex iron derivatives of triazinetricarboxylic acid, i, 984.
supposed formation of carbon from piperonyl derivatives, i, 1278.
magnetochemistry of polymerides, ii, 371.
definition and preparation of hexametaphosphates, ii, 420.
synthesis of nitric acid by Ostwald's process, ii, 566.
magneto-chemical researches on the formation of open chains and nuclear groupings in organic compounds, ii, 634.
density of bromoform; application to the testing of aluminium, ii, 646.
influence of chemical constitution on the thermal properties of binary mixtures; triazine and benzene derivatives, ii, 953.
magnetochemistry of closed chains, ii, 1123.
Pascal, *P.*, and *E.* **Decarrière**, catalytic oxidation of ammonia, ii, 565.
influence of gaseous impurities on the yield in the catalytic oxidation of ammonia, ii, 565.
Pascual Vila, *J.*, preparation of *iso*-benzylidenedeoxybenzoin, i, 144.
analyses of gases in cystic intestinal pneumatosis, i, 329.
Pascual Vila, *J.*, and *J.* **Cerezo**, benzylbenzoin [benzoylphenylbenzylcarbinol], i, 557.
Passek, *F.*, preparation of di-iodohydroxyquinolines, i, 1170.
Passerini, *M.*, action of potassium cyanide on pernitroso derivatives, i, 1290.
carbylamines. XII. Reactions between phenylcarbylamine and α-naphthol, i, 1298.
Pastak, *I. A.*, constitution of aromatic substances and their chemical and physical properties. I., i, 531.
constitution of aromatic substances and their physical and chemical properties. II. Melting points of benzene derivatives, ii, 759.
Patart, *G.*, synthesis of methyl alcohol by reduction of carbon monoxide, i, 110.
Pate, *W. W.*, influence of the amount and nature of the replaceable base on the heat of wetting of soils and soil colloids, i, 1528.
Patel, *C. S.* See *K. G.* **Naik**.
Patel, *M. S.* See *W. R.* **Orndorff**.
Paterson, *M. J.*, and *S. G. P.* **Plant**, derivatives of δ-*o*-aminobenzoylvaleric acid, i, 1147.
Paterson, *T. R.* See *H. G.* **Rule**.
Paton, *F. J.*, colorimetric determination of sugar in blood, i, 180.
Paton, *F. J.* See also *A. R.* **Ling**, and *D. R.* **Nanji**.
Patrick, *W. A.*, capillary adsorption, ii, 509.
Patrick, *W. A.*, and *N. F.* **Eberman**, adsorption from the standpoint of capillarity, ii, 284.
Patrick, *W. A.*, and *C. E.* **Greider**, heats of adsorption of sulphur dioxide and of water vapour by silica gel at 0°, ii, 870.
Patrick, *W. A.*, *W. L.* **Hyden**, and *E. F.* **Milan**, nature of soap in alcohol, ii, 859.
Patrick, *W. A.*, and *D. C.* **Jones**, adsorption from solution from the standpoint of capillarity. I., ii, 193.
Patrick, *W. A.*, and *J. S.* **Long**, adsorption of butane by silica ii, 382.
Patrick, *W. A.*, and *L. H.* **Opdycke**, adsorption of vapours by silica gel by a dynamic method, ii, 656.
Patrick, *W. A.*, *W. C.* **Preston**, and *A. E.* **Owens**, adsorption phenomena in the vicinity of the critical temperature, ii, 508.
Patrick, *W. A.* See also *R. L.* **Hasche**, *A. S.* **Hunter**, and *M.* **Latshaw**.
Patschke, *E.* See *A.* **Sonn**.
Patta, *A.*, chemical tests of arsenobenzenes, especially the "DM index," i, 1195.
Patterson, *A. M.*, proposed international rules for numbering organic ring systems, i, 824.
Patterson, *J.*, urea determinations on small quantities of blood, i, 1200.
Patterson, *R. A.*, crystal structure of chromium and titanium, ii, 845.

Patterson, *R. A.*, crystal structure of copper–manganese alloys, ii, 1130.
Patterson, *T. S.*, modifications in laboratory apparatus, ii, 151.
Patterson, *T. S.*, and *C.* **Buchanan**, optical superposition. VI. Methyl-*n*-hexylcarbinyl dimethoxysuccinates, i, 115.
Patterson, *T. S.*, and *J. D.* **Fulton**, rotation–dispersion of optically active compounds; dimethoxysuccinates and nicotine, ii, 1120.
Patterson, *T. S.*, *A.* **McMillan**, and *R.* **Somerville**, extraction of the isomeric xylenes from crude "xylol," i, 124.
Patterson, *W. H.*, and *J.* **Duckett**, method of determining the presence or absence of complex salts or ions in dilute aqueous solution, ii, 389.
Patterson, *W. H.* See also *J.* **Duckett**, and *E. E.* **Turner**.
Paul, *B.* See *G.* **Fritz**.
Paul, *T.*, measurement of the second dissociation constants of dibasic acids, with special reference to tartaric acid, ii, 116.
Pauli, *W.*, electrolyte-free, water-soluble proteins. I. Electrodialysis, ii, 319.
Pauli, *W.*, and *M.* **Schön**, electrolyte-free, water-soluble proteins. III. Salt–protein compounds ($ZnCl_2$). I., ii, 198.
Pauli, *W.*, and *E.* **Valkó**, constitution of silicic acid sols. I., ii, 521.
Pauli, *W.* See also *M.* **Adolf**, *E.* **Fried**, *N.* **Kühnl**, and *F.* **Modern**.
Pauli, *W.*, *jun.*, influence of velocity-dependence of electron mass on the Zeeman effect, ii, 251.
relation between the distribution of electrons in the atom into subgroups and the complex structure of spectra, ii, 339.
Pauling, *L.*, crystal structures of ammonium fluoferrate, fluoaluminate, and oxyfluomolybdate, ii, 185.
Pauling, *L.*, and *A.* **Björkeson**, crystal for wave-length measurements of soft *X*-rays, ii, 895.
Pauling, *L.*, and *P. H.* **Emmett**, crystal structure of barite, ii, 485.
Pauling, *L.*, and *S. B.* **Hendricks**, crystal structures of hæmatite and corundum, ii, 368.
Pauling, *L.*, and *R. C.* **Tolman**, entropy of supercooled liquids at the absolute zero, ii, 952.
Pauling, *L.* See also *R. M.* **Bozorth**, and *P.* **Debye**.
Paulson, *P. M.* See *A.* **Mann**.
Pauly, *H.*, dissociation constants of glyoxaline-4:5-dicarboxylic acid, i, 1327.
Pauthenier, *M.*, rotating arc between carbon electrodes, ii, 725.
Pauthenier, *M.* See also *G.* **Bruhat**.
Pavelka, *F.* See *F.* **Feigl**.
Pavlov, *F.* See *T.* **Molodyi**.
Pavlov, *P. N.*, adsorption. IX. Adsorption by soil, ii, 287.
adsorption. VIII. Adsorptive capacity of air-dried manganese dioxide hydrate, ii, 507.
adsorption. XI. Life period of organisms and its dependence on the concentration and volume of the toxic medium and on the concentration of the organisms, ii, 958.
Peacock, *B. L. de G.* See *J. C.* **Peacock**.
Peacock, *D. H.*, velocity of benzylation of certain amines. II., i, 1389.
Peacock, *J. C.*, and *B. L. de G.* **Peacock**, tannin of *Rhus glabra*, i, 1124.
Pearce, *J. N.*, and *A. M.* **Alvarado**, adsorption of vapours by metallic oxides: its bearing on the catalysis of ester formation, ii, 381.
Pearce, *J. N.*, and *R. W.* **Gelbach**, free energy of dilution and the activity of the ions in aqueous solutions of barium chloride, ii, 867.
Peard, *G. H.* See *J. H. S.* **Johnston**.
Pearson, *A. R.*, and *J. S. G.* **Thomas**, gas circulating apparatus, ii, 1194.
Pearson, *L. K.* See *A.* **Lapworth**.
Pease, *R. N.*, and *R. B.* **Purdum**, hydrogenation of benzene in presence of metallic copper, i, 798.
Pease, *R. N.*, and *L.* **Stewart**, catalytic combination of ethylene and hydrogen in the presence of metallic copper. III. Carbon monoxide as a catalyst poison, ii, 691.
Pease, *R. N.*, and *C. C.* **Yung**, equilibrium in the alcohol–ether reaction at 130° and 275°, ii, 37.
Pechhold, *R.* See *R.* **Fürth**.
Pechous, *C. E.* See *E. I.* **McEnery**.
Peczalski, *T.*, and *G.* **Mokrzycki**, chemical compounds of salts in the electric arc, ii, 814.
Peddie, *W.*, colour-vision spectrometer, ii, 1118.
Pedersen, *K. O.* See *E.* **Biilmann**.
Peek, *A. E. J.* See *J.* **Böeseken**.
Pégurier, *G.*, determination of sugar in urines containing santonin, i, 609. Fehling's reagent, ii, 1208.
Peignier, *P.* See *G.* **Vavon**.
Peiser, *E.*, anomalies of salts of nucleic acids, i, 1477.

Pekarskaja, *G.* See *M. A.* **Rakuzin.**
Pélabon, *H.*, direct formation of mercuric oxychlorides, ii, 222.
direct formation of mercuric oxybromides, ii, 697.
action of hydrogen sulphide on mercuric salts, ii, 986.
Pelling, *A. J.*, system, chloride–sulphate–sodium–water, ii, 670.
Pellizzari, *G.*, investigations on guanidine, i, 1047.
Pember, *F. R.*, and *F. T.* **McLean,** economical use of nitrogen, phosphorus, and potassium by barley, oats, and wheat in solution cultures, i, 1121.
Pember, *F. R.* See also *R. L.* **Jones.**
Pemberton, *R.* See *F. A.* **Cajori.**
Pénau, *H.*, and *H.* **Simonnet,** secretin and insulin, i, 482.
Penfold, *A. R.*, essential oils of *Melaleuca erubescens* (Otto), and *M. hypericifolia* (Smith), i, 688.
essential oil of *Boronia safrolifera* (Cheel), i, 688.
Penfold, *A. R.*, and *F. R.* **Morrison,** *Eucalyptus piperita* and its essential oils, with special reference to their piperitone content. I., i, 688.
Penfold, *A. R.*, and *R.* **Grant,** germicidal values of the pure constituents of Australian essential oils, essential oil isolates, and synthetics. II., i, 614.
Penkava, *J.* See *J.* **Stoklasa.**
Pepin, *F.* See *W.* **Jerome.**
Pérard, *A.*, refractive index of air in the visible spectrum between 0° and 100°, ii, 1137.
Pereira, *J. R.*, influence of the hydrogen-ion concentration on the oxygen consumption in sea-water fishes, i, 177.
muscular exercise; lactic acid and the supply and utilisation of oxygen. XII. Technique of determining the resting oxygen intake while breathing oxygen mixtures, i, 1341.
Pereira, *J. R.* See also *R. J.* **Lythgoe.**
Perkin, *A. G.*, and *G.* **Yoda,** reduction products of the hydroxyanthraquinones. VI., i, 1160.
Perkin, *A. G.* See also *O.* **Kubota.**
Perkin, *W. H., jun.*, and *H. S.* **Pink,** $\alpha\gamma$-dialdehydopropane-$\beta\beta$-dicarboxylic acid and $\alpha\gamma$-dialdehydopropane-β-carboxylic acid, i, 359.
Perkin, *W. H., jun.*, and *S. G. P.* **Plant,** action of hydrogen chloride on *cyclo*hexylideneazine and on *cyclo*pentylideneazine, i, 842.
Perkin, *W. H., jun.*, *J. N.* **Rây,** and *R.* **Robinson,** synthesis of oxyberberine. I., i, 695.
Perkin, *W. H., jun.*, *R.* **Robinson,** and *F. W.* **Stoyle,** nitration of 2:3-dimethoxybenzaldehyde, i, 39.
Perkin, *W. H., jun.*, and *W. G.* **Sedgwick,** tetrahydroacridine, octahydroacridine and their derivatives, i, 63.
Perkin, *W. H., jun.*, and *R. B.* **Tapley,** oxidation of acetomesitylene with permanganate, i, 42.
Perkin, *W. H., jun.* See also **British Dyestuffs Corporation, Ltd.,** *J. S.* **Buck,** *G. A.* **Edwards,** *R. D.* **Haworth,** *W. H.* **Linnell,** and *F.* **Lions.**
Perkins, *A. E.*, and *C. F.* **Monroe,** effect of high and low protein content on the digestibility and metabolism of dairy rations, i, 1354.
Perkins, *A. E.* See also *C. F.* **Monroe.**
Perkins, *M. E.* See *W.* **Jones.**
Perkins, *P. P.* See *H.* **Adkins.**
Pernot, (*Mlle.*). See *M.* **Tourneux.**
Perot, *A.*, and *M.* **Collinet,** effect of density on the wave-length of the absorption bands of iodine, ii, 737.
Perpérot, *H.*, action of gaseous ammonia on phosphorus chlorides, ii, 1186.
Perpérot, *H.* See also *H.* **Copaux.**
Perquin, *J. N. J.* See *H. I.* **Waterman.**
Perrakis, *N.*, influence of proximity to the critical solution temperature on the volume, ii, 29.
Trouton's ratio at the absolute zero, ii, 492.
physical properties of binary liquid mixtures in the region of the critical miscibility point, ii, 764.
Perrakis, *N.* See also *L.* **Gay.**
Perraud, *S.* See *F.* **Couturier.**
Perreau, (*Mlle.*) *G.* See *A.* **Boutaric.**
Perrette, (*Mlle.*) *B.*, isotopy of lead, ii, 646.
Perrier, *C.*, determination of the principal refractive indices of doubly refracting substances by means of Federov's plate, ii, 1028.
Perrin, *F.*, theory of polarised fluorescence; influence of viscosity, ii, 353.
Perrin, *F.* See also *P.* **Auger.**
Perrin, *J.*, and (*Mlle.*) **Choucroun,** fluorescence and the general laws of reaction velocity, ii, 55.
Persiel, *H.* See *R.* **Willstätter.**
Perucca, *E.*, electrification by friction between solids and gases, ii, 1028.
Peschard, *M.*, magnetisation of ferro-nickel [alloys] (thermomagnetic properties), ii, 651.
magnetisation of ferro-nickel; saturation and atomic moments, ii, 751.

Peskett, *G. L.*, growth of yeast. I. Influence of volume of culture medium employed, i, 1011.
growth of yeast. II. Allelocatalysis, i, 1012.
Pessôa, *S. B.* See *W. G.* **Smillie**.
Peter, *A. M.* See *G. D.* **Buckner**.
Peters, *F. N., jun.*, *E.* **Griffith**, *D. R.* **Briggs**, and *H. E.* **French**, action of magnesium phenyl bromide on organic acids, i, 543.
Peters, *J. P.*, *A. J.* **Eisenman**, and *H. A.* **Bulger**, plasma proteins in relation to blood hydration. I., i, 1491.
Peters, *R. A.*, modified Claisen vacuum distillation apparatus, ii, 589.
Peters, *R. A.* See *H. W.* **Kinnersley**.
Petersen, *M.* See *J. B.* **Green**.
Petersen, *W. F.*, and *T. P.* **Hughes**, inorganic alterations of the lymph in canine anaphylactic shock, i, 724.
Peterson, *H. A.*, inorganic bone-forming elements of the blood-serum, i, 715.
Peterson, *W. H.*, *E. B.* **Fred**, and *B. P.* **Domogalla**, occurrence of amino-acids and other organic nitrogen compounds in lake water, i, 765.
Peterson, *W. H.*, *E. B.* **Fred**, and *H. R.* **Stiles**, fermentation characteristics of mannitol-forming bacteria, i, 1510.
Peterson, *W. H.* See also *B. P.* **Domogalla**, *E. B.* **Fred**, and *H. R.* **Stiles**.
Petin, *N.* See *E.* **Spitalsky**.
Petit, *M.*, dissociation of auric chloride, ii, 668.
preparation of auric chloride, ii, 1089.
Petit, *P.*, liquefaction of starch paste, ii, 967.
Petit, *P.*, and **Richard**, influence of method of dissolving amylase on saccharification of starch, i, 1504.
Petitcolas, *P.* See *C.* **Courtot**.
Petow, *H.* See *P.* **Rona**.
Petrenko-Kritschenko, *P.*, law of periodicity and the theory of cyclic unsaturated compounds, ii, 1122.
Petrenko-Kritschenko, *P.*, *W.* **Bogatsky**, and *N.* **Lubman**, velocity of ester formation, ii, 556.
Petrenko-Kritschenko, *P.*, and *V.* **Butmi de Katzman**, modification of Hofmann's decomposition reaction of heterocyclic compounds, i, 1094.
Petrenko-Kritschenko, *P.*, *D.* **Talmud**, *B.* **Talmud**, *W.* **Butmi de Katzman**, and *A.* **Gandelman**, chemical activity, ii, 802.
Petrescu, *E.* See *G. G.* **Longinescu**.
Petrikaln, *A.*, chemiluminescence and heteropolar combination, ii, 630.
Petronio, *R.* See *M.* **Giua**.
Petrou, *W.*, a salivary calculus, i, 725.
Petrou, *W.* See also *F.* **Haurowitz**.
Petrovanu, *G.*, effect of hydrogen peroxide on certain groups of bacteria; microbic catalases; autolytic phenomena, i, 1362.
Petry, *R. L.*, critical potentials in secondary electron emission from iron, nickel, and molybdenum, ii, 1017.
Pettersson, *H.*, and *G.* **Kirsch**, disintegration of atoms, ii, 623.
Petzchner, *E.* See *F.* **Hein**.
Peukert, *E.* See *H.* **Biltz**.
Pewsner, *G.* See *O.* **Steppuhn**.
Peytral, (*Mlle.*) *E.*, sudden pyrogenic decomposition of methyl formate at a high temperature, i, 777.
Peytral, (*Mlle.*) *E.* See also *J. A.* **Muller**.
Pfaff. See *A.* **Densch**.
Pfaff, *F.* See *A.* **Skrabal**.
Pfaltz, *M. H.* See *P. A.* **Levene**.
Pfau, *A. S.*, detection of benzyl alcohol as benzyl oxalate, ii, 905.
Pfau, *E.*, ligulin, the colouring matter of privet berries, i, 572.
Pfau, *E.* See also *P. W.* **Danckwortt**.
Pfautsch, *H.*, ternary system, molybdenum–nickel–silicon, ii, 298.
system, molybdenum–nickel–tin, ii, 536.
system, aluminium–molybdenum–nickel, ii, 536.
Pfeffermann, *L.* See *J.* **Eggert**.
Pfeiffer, *H.*, and *F.* **Standenath**, peptidase balance of man and animals. I., i, 1361.
Pfeiffer, *M.* See *L.* **Ruzicka**.
Pfeiffer, *P.*, acid character of ketoximes, i, 677.
compound of veronal and pyramidone, i, 1318.
Pfeiffer, *P.* [with *O.* **Angern**, *P.* **Backes**, *W.* **Fitz**, *E.* **Prahl**, *H.* **Rheinboldt**, and *W.* **Stoll**], halochromism of aromatic amino-ketones, i, 408.
Pfeiffer, *P.* [with *F.* **Goebel**, and *O.* **Angern**], molecular compounds of aromatic amino-ketones, i, 262.
quinhydrones, i, 271.
Pfeiffer, *P.*, and *O.* **Angern**, molecular compounds of the amino-acids and diketopiperazines. I., i, 794.
Pfeiffer, *P.*, *G.* **Armbruster**, *P.* **Backes**, and *H.* **Oberlin**, acid character of ketoximes, i, 270.
Pfeiffer, *P.*, *E.* **Kalckbrenner**, and *H.* **Behr**, border-line between isomerism and polymorphism. IV., i, 547.

Pfeiffer, *P.*, *H.* **Oberlin**, and *E.* **Konermann**, brazilin and hæmatoxylin question. IV. Methoxychromonols and the degradation product of brazilin obtained by Schall and Dralle, i, 1303.
Pfeiffer, *P.*, *E.* **Prahl**, *W.* **Fitz**, and *W.* **Stoll**, attempts to prepare meta condensed ring systems in the aromatic series, i, 680.
Pfeiffer, *P.*, *H.* **Rheinboldt**, and *J.* **Wolf**, halochromic compounds of imines, i, 411.
Pfeil, *L. B.* See *C. A.* **Edwards**.
Pfister, *A.* See *F.* **Ephraim**.
Pfuhl, *W.* See *K. von* **Auwers**.
Pfund, *A. H.*, emission of nitrogen and hydrogen in the infra-red, ii, 11.
halogen isotopes and infra-red reflexion spectra, ii, 255.
Pfyl, *B.*, and *W.* **Samter**, organic phosphorus compounds in milk-serum, i, 1114.
Phelps, *E. P.* See *C. S.* **Hudson**.
Phelps, *I. K.* See *O. S.* **Rask**.
Philip, *J. C.*, and *C. H. D.* **Clark**, molecular condition of phenol in benzene solution, ii, 770.
Philippi, *E.*, and *R.* **Seka** [with *W.* **Bauer**], dinaphthanthracene series. VIII. Substituted derivatives of pyromellitic acid, i, 555.
Philippi, *E.*, and *R.* **Seka** [with *K.* **Funke**], dinaphthanthracene series. VII. Condensation of pyromellitic anhydride with decalin and tetralin; sulphonation of dinaphthanthradiquinone, i, 556.
Philippi, *E.*, and *R.* **Seka** [with *E.* **Hager**, and *M.* **Landau**], certain aliphatic carboxylic acids, i, 511.
Philippi, *E.* See also *K.* **Stosius**.
Philippson, *O.* See *J.* **Tröger**.
Phillips, *H.* See *J.* **Kenyon**.
Phillips, *M.*, methyl*iso*propylanthraquinone, i, 45.
preparation of 2-aminoanthraquinone from phthalic anhydride and chlorobenzene, i, 1076.
Phillips, *T. G.* See *R. C.* **Burrell**.
Phragmén, *G.* See *A.* **Westgren**.
Piatti, *L.* See *G.* **Weissenberger**.
Piaux, *L.*, spontaneous oxidation of 1-methyluric acid and 1:3-dimethyluric acid in alkaline solution, i, 165.
action of catalysts on oxidation of uric acid; copper and cuprous urate, i, 592.
action of free oxygen on uric acid dissolved in aqueous potassium hydroxide; action of catalysts, i, 592.
Piazza, *G.*, variations of the phosphoric acid during glycolysis in blood, i, 1486.
Picard, *F.*, physiological function of tannins; their importance in the ripening of vine-shoots, i, 346.
Picard, *J.* See *F.* **Bourion**.
Picard, *P.* See *M.* **Bridel**.
Piccard, *J.*, co-ordination positions of the oxygen atom, ii, 15.
Piccardi, *G.*, thermal method for the study of gaseous systems, ii, 540.
Piccardi, *G.* See also *L.* **Rolla**.
Pichard, *G.* See *G.* **Rivière**.
Pick, *L.*, determination of reducing sugars, ii, 906.
iodometric determination of reducing sugars, ii, 906.
Pickens, *R. M.* See *H.* **Gilman**.
Pickering, *E. C.* See *F. J.* **Wilson**.
Pickering, *J. W.*, and *R. J.* **Gladstone**, development of blood plasma. I. Genesis of coagulable materials in embryo chicks, i, 1343.
Pickworth, *F. A.*, determination of iodine in thyroid gland, i, 1489.
Picon, effect of vacuum and of heat on the neutral and basic bismuth nitrates; determination of water of constitution and of nitric acid in these salts, ii, 1188.
Picon, *M.* See *P.* **Lebeau**.
Pictet, *A.*, *W.* **Scherrer**, and *L.* **Helfer**, presence of argon in gases produced by alcoholic fermentation of dextrose, i, 865.
presence of argon in living cells, i, 1202.
Pied, *H.*, precipitation of tantalum and niobium by "cupferron" and their separation from iron, ii, 442.
Pien, *J.* See *C.* **Brioux**.
Pienkovski, *S.*, and *A.* **Jablonski**, measurement of the coefficients of the absorption of light by fluorescent substances, ii, 1031.
Pierce, *J. S.*, and *R.* **Adams**, platinum oxide as a catalyst in the reduction of organic compounds. VIII. Reduction of furylalkylcarbinols, i, 824.
Pieroni, *A.* [with *B.* **Haupt**], pyridine derivatives, i, 1316.
Pieroni, *A.*, and *D.* **Nocentini**, iodo derivatives of pyrrole and their behaviour towards nitric acid, i, 1096.
Pierre, *W. H.*, hydrogen-ion concentration of soils as affected by carbon dioxide and by the soil: water ratio, and the nature of soil acidity, i, 1526.
Pike, *S. R.*, and *G.* **Nonhebel**, theory of interionic attraction in strong electrolytes, ii, 1061.

Pilley, *J. E. G.*, attempted electrolytic separation of the isotopes of chlorine and magnesium, ii, 462.
Pilley, *J. E. G.* See also *T. R.* **Merton**.
Pilling, *N. B.*, and *R. E.* **Bedworth**, oxidation of copper–nickel alloys at high temperature, ii, 689.
Pina de Rubies, *S.*, new lines between 3100 and 2200 Å. in the arc spectrum of lanthanum at normal pressure, ii, 612.
arc spectrum of scandium, ii, 829.
Pinck, *L. A.*, determination of cyanamide, ii, 607.
Pinck, *L. A.*, and *M. A.* **Kelly**, solubility of carbamide in water, ii, 955.
Pinckney, *A. J.* See *M. J.* **Blish**.
Pincussen, *L.*, enzymes and light. VI. Influence of iodides on irradiated enzymes, i, 468.
Pincussen, *L.*, and *N.* **Klissiunis**, enzymes and light. VII. Influence of iodides on irradiated enzymes. II., i, 469.
Piness, *G.*, *H.* **Miller**, and *G. A.* **Alles**, extraction of proteins, i, 331.
Pink, *H. S.* See *R. D.* **Haworth**, and *W. H.* **Perkin**, *jun.*
Pinta, *R.* See *M.* **Oswald**.
Pinter, *E.* See *Robert* **Müller**.
Piper, *E.* See *J.* **Meisenheimer**.
Pirani, *M.* See *H.* **Alterthum**.
Pirk, *L.* See *E.* **Fromm**.
Pirsch, *H.* See *A.* **Kuhn**.
Pisarshevski, *L.*, the electron in the chemistry of solutions and in electrochemistry. V. Ionic reactions, the ionisation of metals, and the osmotic theory of the galvanic current. VI. Electrical nature of catalytic phenomena, ii, 210.
Pittarelli, *E.*, an unknown or little-known volatile urinary substance, i, 98.
Pittenger, *W. H.* See *L. H.* **Cretcher**.
Pitts, *C. R.* See *R. D.* **Kleeman**.
Piutti, *A.*, preparation of asparagine by the diffusion method, i, 758.
Piutti, *A.*, and *E.* **Boggio-Lera**, diffusibility of helium through crystalline septa, ii, 500.
rare gases of volcanic exhalations, ii, 1092.
Plăcinteanu, *J. J.*, dependence of the heat of vaporisation and the surface tension of a liquid on the molecular forces, ii, 39.
Plancher, *G.*, *U.* **Colacicchi**, and *O.* **Barbieri**, 2:3:3-trimethyl-β-naphthindolenine and the formula of the indolenines, i, 579.
Plancher, *G.*, and *E.* **Ghigi**, some benzeneazophenylpyrroles, i, 597.
Plancher, *G.*, and *G.* **Rossi**, mercuri-organic compounds of 1-phenylpyrrole, i, 601.
Planck, *M.*, quantising of monatomic gases, ii, 495.
statistical definition of entropy, ii, 951.
Planelles, *J.* See *S. E. de* **Jongh**, and *F.* **Lipmann**.
Planiol, *R.* See *H.* **Abraham**.
Planiszig, *F.* See *Robert* **Müller**.
Plant, *S. G. P.*, and *J. E.* **Facer**, synthesis and reactions of 1-anilino-*cyclo*pentane-1-carboxylic acid, i, 1271.
Plant, *S. G. P.* See also *M. J.* **Paterson**, *W. H.* **Perkin**, *jun.*, and *N. V.* **Sidgwick**.
Plantefol, *L.*, modification of Laulanié's apparatus for the determination of carbon dioxide and oxygen in air, ii, 902.
Plantefol, *L.* See also *A.* **Mayer**.
Plass, *E. D.*, and *C. W.* **Matthew**, placental transmission. III. Amino-acids, non-protein nitrogen, urea, and uric acid in fœtal and maternal whole blood, plasma, and corpuscles, i, 1489.
Plato, *W.* See *A.* **Rosenheim**.
Platon, *J. B.*, oxidation of vitamin-*A* during the preparation of butter from cream, i, 484.
Platt, *B. S.*, and *E. R.* **Dawson**, factors influencing the action of pancreatic lipase, i, 1506.
Plat, *J. H.* See *E.* **Knecht**.
Plaut, *H.* See *M.* **Bodenstein**.
Plechner, *W.* See *L. J.* **Curtman**.
Pleuger, *G.*, solubility in mixed liquids, ii, 283.
Ploetz, *G.* See *K.* **Arndt**.
Plotnikov, *J.*, photochlorination of aliphatic compounds in carbon tetrachloride, ii, 220.
absorption spectra of several ketones, ii, 837.
periodic phenomena in photochemistry, ii, 883.
combination of bromine with unsaturated hydrocarbons under the influence of light, ii, 985.
Plotnikov, *W.*, electrical conductivity of potassium iodide in bromine–iodine solutions, ii, 791.
Plüss, *W.*, catalytic dehydration of phenol–alcohol systems. II. Naphthol–alcohol systems, i, 1410.
Plüss, *W.* See also *E.* **Briner**.
Plyler, *E. K.*, infra-red absorption of ice, ii, 87.

Pochettino, *A.*, optical properties of crystals of certain cyanoplatinates. I., ii, 21.
Podhradsky, *J.* See *J.* **Krizenecky.**
Podjaski, *G. von.* See *H. von* **Wartenberg.**
Podroužek, *W.*, dropping mercury cathode. X. Some organic bases, ii, 677.
Podroužek, *W.* See also *H.* **Křepelka.**
Pohl, *G.* See *W.* **Steinkopf.**
Pohl, *R.* See *B.* **Gudden.**
Pohland, *E.* See *A.* **Stock.**
Pohlmeyer, *W.*, β-ray spectrum of thorium-*B*+*C*, ii, 347.
Pohorecka-Lelesz, *B.*, micro determination of carbamide and ammonium salts by titration with hypobromite, ii, 76.
Poindexter, *F. E.* See *A. L.* **Hughes.**
Poirot, *G.*, detection of copper in distilled water, ii, 242.
Pol, *C. van den.* See *W. P.* **Jorissen.**
Pólányi, *M.*, connexion between osmotic pressure, swelling pressure, and adsorption, ii, 290.
crystal deformation and hardening, ii, 370.
Pólányi, *M.*, and *E.* **Schmid**, strengthening and weakening of tin crystals, ii, 752.
Pólányi, *M.*, and *E.* **Wigner**, formation and decomposition of molecules, ii, 1077.
Pólányi, *M.* See also *W.* **Ewald**, *M.* **Fischenich**, and *G.* **Masing.**
Policard, *A.*, and *A.* **Leulier**, characterisation of hæmatoporphyrin and urobilin in urine by means of Wood's light, i, 1351.
Politzer, *G.*, toxic action of neutral-red, i, 197.
Pollak, *F.*, pernitric acid, ii, 407.
Pollak, *J.*, apparatus for quantitative microanalysis, ii, 431.
Pollak, *J.* See also *R.* **Strebinger.**
Pollard, *A. F. C.*, nephelometry; suggested sensitive test for the stability of explosives, ii, 803.
Pollecoff, *F.*, glycuronic acid as a probable constituent of urochrome, i, 186.
Poller, *K.* See *S.* **Skraup.**
Pollitzer, *F.*, and *E.* **Strebel**, influence of indifferent gases on the saturated vapour concentrations of liquids, ii, 104.
Polonovski, *M.*, and *F.* **Morvillez**, formation of starch from arabinose by plants, i, 1222.
Polonovski, *M.* See also *C.* **Dubois.**
Polonovski, *Max*, and *G.* **Galbrun**, distribution of carbon in cerebrospinal fluid, i, 854.
Polonovski, *Max*, and *Michel* **Polonovski**, alkaloids of the calabar bean. XIII. Tautomeric forms of eserine : nitroso and benzoyl derivatives, i, 151.
oxyeserine and its derivatives, i, 293, 696.
amine-oxides of alkaloids of the tropan group, i, 828.
alkaloids of the calabar bean. XIV. Constitution of eserine and oxyeserine derivatives, i, 959.
Polonovski, *Michel.* See *Max* **Polonovski.**
Polushkin, *E. P.*, determination of the structural composition of alloys by a metallographical planimeter, ii, 189.
Pomeranz, *H.*, constitution of the sulphonation products of the higher unsaturated fatty acids, i, 1380.
Pomeranzeva, *A.* See *N.* **Isgarischev.**
Ponce, *H. P.*, "lecitiburin," a lecithin from the eggs of the shark, i, 97.
Ponder, *E.*, and *W. W.* **Taylor**, changes in conductivity of red cell suspensions during hæmolysis, i, 1202.
Pongratz, *A.* See *A.* **Zinke.**
Ponzio, *G.*, hydroxyglyoximes, i, 8.
dioximes. XXI. and XXIV., i, 139, 1075.
Ponzio, *G.*, and *V.* **Bernardi**, peroxides of dioximes of diacylglyoximes, i, 79.
Ponzio, *G.*, and *G.* **Ruggeri**, dioximes. XXVI., i, 1041.
Poole, *H. J.*, elasticity of gelatin jellies and its bearing on their physical structure and chemical equilibria, ii, 519.
Poore, *H. D.*, citrus fruit pectin, i, 619.
Pope, (*Sir*) *W. J.*, and *T. M.* **Haines**, colloidal kaolin. I. Properties, ii, 1152.
Pope, (*Sir*) *W. J.* See also *F. B.* **Kipping**, and *F. G.* **Mann.**
Popenoe, *C. H.* See *E. H.* **Siegler.**
Popesco, *J. G.*, capillary and photoelectric property of mercury, ii, 952.
Popescu-Inotesti, *C.* See *I. I.* **Nitzescu.**
Popov, *M.*, and *K.* **Seisov**, increased imbibition by colloids through chemical stimulants, i, 606.
Popov, *M.* See also *W.* **Swientoslawski.**
Popov, *S.*, and *J. L.* **Whitman**, standardisation of solutions used in iodometry. II., ii, 1093.
Popovici, *H.*, formation of essential oils, i, 1123.

Popovicki, *A.*, photochemical decomposition of chromium salts in the presence of organic matter, ii, 220.
Popp, *K.*, periodic stratification of magnesium hydroxide, ii, 667.
Popper, *H.* See *N.* **Abelles.**
Porai-Koschitz, *A.*, reduction of nitrosophenols with alkali sulphides, i, 1060.
Porcher, *C.*, complexes containing calcium salts of caseinogen and phosphoric acid, and their coagulation by rennin, i, 846.
action of carbon dioxide on calcium caseinogenate; colloidal calcium carbonate, i, 847.
Porges, *O.* See *D.* **Adlersberg.**
Porlezza, *C.*, and *U.* **Gatti**, action of calcium hydride on certain organic compounds. II. Methyl ethyl ketone, i, 788.
Porritt, *W. H.* See *G. T.* **Morgan.**
Porter, *C. R.* See *G. T.* **Morgan.**
Porter, *C. W.*, and *H. C.* **Ramsperger**, action of ultra-violet light on carbon dioxide and water, ii, 573.
Porter, *M. W.*, optical properties of mixed crystals, ii, 945.
Posnjak, *A.* See *L. A.* **Tschugaev.**
Posnjak, *E.* See *R. B.* **Sosman.**
Posthumus, *K.* See *F. A. H.* **Schreinemakers.**
Postma, *J.* See *H. R.* **Kruyt.**
Postmontier, *R. S.* See *M.* **Kahn.**
Postowsky, *J. J.* See *F.* **Kögl.**
Poulenc Frères. See **Les Établissements Poulenc Frères.**
Poulsson, *E.*, and *G.* **Weidemann**, benzoylallylecgonine and benzoylbenzylecgonine, i, 466.
Povarnin, *G.*, and **Kalje**, reduction of acetic acid and some of its derivatives, i, 1034.
Povarnin, *G.*, and *V.* **Markov**, vapours of the system, acetic acid–water, ii, 851.
physical equilibrium in the system, acetic acid–acetic anhydride, ii, 851.
Powell, *A. R.*, and *W. R.* **Schoeller**, separation of tantalum from niobium, and detection and determination of tantalum in niobium compounds, ii, 1096.
Powell, *D.*, development and distribution of chlorophyll in roots of flowering plants grown in the light, i, 1221.
Powell, *E. B.*, soil colloids as simple suspensions, i, 1032.
Powell, *S. G.*, condensation of *n*-butaldehyde with methyl ethyl ketone, i, 7.
preparation of β-chloropropionic acid, i, 228.
Powell, *S. G.*, and *N. G.* **Johnson**, β-toloxypropionic acids and the corresponding chromanones, i, 278.
Powell, *W. J.*, and *H.* **Whittaker**, chemistry of lignin. II. Comparison of lignins derived from various woods, i, 372.
Power, *A. D.*, resonance radiation from cadmium vapour, ii, 1113.
Power, *F. B.*, and *V. K.* **Chesnut**, alkaline reaction of the cotton plant, i, 758.
odorous constituents of the cotton plant; emanation of ammonia and trimethylamine from the living plant, i, 1026.
Powers, *D. H.* See *L. W.* **Jones.**
Poynton, *F. Y.*, See *G. E.* **Bell.**
Praetorius, *P.* See *A.* **Stock.**
Prahl, *E.* See *P.* **Pfeiffer.**
Prandtl, *W.*, separation of the rare-earths by basic precipitation. VIII. Preparation of pure yttrium oxide, ii, 439.
Prange, *G.* See *C.* **Räth.**
Prasad, *M.*, *D. L.* **Shrivastava**, and *R. S.* **Gupta**, mechanism of the adsorption of sugar by colloidal solutions and precipitates, ii, 957.
Prasad, *M.* See also *S. S.* **Bhatnagar**, *M. B.* **Rane**, and *D. L.* **Shrivastava.**
Prát, *S.*, leaf pigments of *Potamogeton*, i, 487.
Pratolongo, *U.*, alkaline chlorosis of the vine, i, 623.
pedological chemistry. I. Alkalinity of the soil in relation to its lithological constitution, i, 874.
Pratt, (*Miss*) *C. A.*, staling of fungal cultures. II. Alkaline metabolic products and their effect on the growth of fungal spores, i, 106.
Pratt, *D. D.*, and *R.* **Robinson**, synthesis of pyrylium salts of anthocyanidin type. V. Synthesis of cyanidin chloride and of delphinidin chloride, i, 422.
synthesis of pyrylium salts of anthocyanidin type. VI. Polyhydroxyflavylium salts related to chrysin, apigenin, lotoflavin, luteolin, galangin, fisetin, and morin, i, 825.
synthesis of pyrylium salts of anthocyanidin type. VII. Preparation of the anthocyanidins with the aid of 2:4:6-triacetoxybenzaldehyde, i, 826.
Prausnitz, *P. H.*, glass filter apparatus, ii, 996.
Práwdicz-Neminski, *W. W.*, hormonal significance of ammonia; antagonism and synergism of ammonium and magnesium ions in the organism, i, 481.

Predvoditelev, *A.*, theory of diminution of fluorescence, ii, 738.
specific heat of the hydrogen molecule, ii, 1041.
Predvoditelev, *A.*, and *N.* **Netschajeva**, kinetics of photochemical processes in dyes, ii, 575.
Predvoditelev, *A.* See also *G.* **Landsberg**.
Pregl, *F.*, preparation of standard solutions, ii, 998.
Prentiss, *A. M.* See *E. J.* **Cohn**, and *G. P.* **Grabfield**.
Preobraschenski, *N.* See *A.* **Stepanov**.
Presho, *N. E.* See *P. J.* **Hanzlik**.
Preston, *G. D.* See *E. A.* **Owen**.
Preston, *W. C.* See *W. A.* **Patrick**.
Prett, *K.* See *Robert* **Müller**.
Prévost, *C.*, α-phenyl-Δ$^{\alpha\gamma}$-pentadi-inene, i, 878.
Prévost, *C.* See also *R.* **Lespieau**.
Prianischnikov, *D.*, asparagine and urea, i, 213.
physiological character of ammonium nitrate [towards plants], i, 757.
Pribyl, *E.*, determination of small quantities of arsenic in animal organs, i, 1500.
Price, *T. S.*, behaviour of silver iodide in the photo-voltaic cell, ii, 680.
Prichard, *C. R.*, and *C. N.* **Hinshelwood**, interaction of hydrogen and carbon dioxide on the surface of platinum, ii, 564.
Prichard, *C. R.* See also *C. N.* **Hinshelwood**.
Prideaux, *E. B. R.*, and *W. E.* **Crooks**, diffusion potentials and ionic mobilities of benzoates and salicylates and their modification by a membrane of parchment paper, ii, 42.
Prideaux, *E. B. R.*, and *G.* **Green**, molecular weight of selenium dioxide in ethyl alcohol, ii, 96.
Prideaux, *E. B. R.*, and *G. R.* **Nunn**, colorimetric dissociation constants of the mono- and di-nitroquinols, i, 24.
Prideaux, *E. B. R.* See also *J. S.* **Willcox**.
Priess, *O.* See *A.* **Stock**.
Prine, *L. W.* See *F. G.* **Keenen**.
Pringle, *H.*, identity of vitamin-*A*; comparative effects of human and cow's milk, i, 1018.
Pringsheim, *H.*, relationship of the blood-sugar to glycogen, i, 605.
lichen starch, i, 1029.
Pringsheim, *H.*, and *J.* **Bondi**, components of acetone oil, i, 1072.
Pringsheim, *H.*, and *A.* **Genin**, hemicelluloses. VI. Fermentative fission of salep manna, i, 214.
Pringsheim, *H.*, *W.* **Knoll**, and *E.* **Kaston**, constitution of lichenin and cellulose, i, 1385.
Pringsheim, *H.*, and *J.* **Leibowitz**, starch. XIII. α- and β-Amylases, i, 1043.
Pringsheim, *H.*, *J.* **Leibowitz**, and *S. H.* **Silmann**, starch. XIV. Nitric esters of the polyamyloses, i, 1244.
Pringsheim, *P.*, and *A. L.* **Reimann**, fluorescence of benzene vapour by monochromatic excitation, ii, 181.
Prins, *H. J.*, mechanism of substitution reactions in the aromatic nucleus, i, 18, 379.
polar nature of the benzene nucleus, in relation to the theory of induced alternate polarity, i, 894.
mechanism of reduction. IV., ii, 1169.
Priston, *H. E. M.* See *J.* **Kenyon**.
Probert, *M. E.* See *P. H.* **Clifford**, and *R. G.* **Fargher**.
Pročke, *O.* See *J.* **Švéda**.
Proescher, *F.*, and *A. P.* **Krueger**, preparation of polychrome methylene-blue and thiazine-red, i, 597.
Proskouriakoff, *A.*, and *G. W.* **Raiziss**, mercury derivatives of azo dyes, i, 1107.
Prud'homme, *M.*, the three-temperature rule, ii, 99.
molecular heats of vaporisation, ii, 188.
Prüsse, *A.*, synthesis of methylated uric acids by Behrend and Roosen's method, i, 441.
Prunier, *P.* See *F.* **Kehrmann**.
Pryde, *J. E.*, *L.* **Hirst**, and *R. W.* **Humphreys**, constitutional studies in the monocarboxylic acids derived from sugars. III. Isomeric tetramethyl galactonolactones and trimethyl arabonolactones, i, 365.
Przezdziecka-Jedrzejovska, *A.* See *K.* **Jablczyński**.
Pucher, *G. W.* See *G. E.* **Youngburg**.
Pülz, *A.* See *H.* **Haehn**.
Puiggari, *H.*, electric transport in a ferric oxide hydrosol, ii, 129, 792.
Pulevka, *P.*, horn-dissolving action of alkali sulphides, i, 1341.
Pummerer, *R.*, *H.* **Puttfarcken**, and *P.* **Schopflocher**, oxidation of phenols. VIII. Dehydrogenation of *p*-cresol, i, 1262.
Pummerer, *R.*, and *H. M.* **Ulrich**, composition of rubicene, $C_{26}H_{14}$, i, 1259.
Purdum, *R. B.* See *R. N.* **Pease**.
Puri, *A. N.*, effect of methyl and ethyl alcohols on the growth of barley plants, i, 217.
interaction between soil and dilute acids, i, 1372.

Puri, *A. N.*, *E. M.* **Crowther**, and *B. A.* **Keen**, relation between the vapour pressure and water content of soils, i, 492.
Puri, *A. N.*, and *B. A.* **Keen**, dispersion of soil in water under various conditions, i, 768.
Puri, *V. S.* See *A. J.* **Allmand**.
Purvis, *J. E.*, absorption spectra of various aldehydes and ketones and some of their derived compounds, ii, 627.
Pusch, *E.* See *K.* **Fries**.
Pusch, *J.* See *F.* **Arndt**.
Pushin, *N. A.*, influence of pressure on the freezing point of *p*-nitrotoluene, *m*-dinitrobenzene, and guaiacol, ii, 277.
Pushin, *N. A.*, and *J. V.* **Grebenshchikov**, equilibria at high temperatures by the pyrometric method, ii, 38.
Putten, *M. F. van*. See *A. H. W.* **Aten**.
Puttfarcken, *H.* See *R.* **Pummerer**.
Puxeddu, *E.*, chlorination of tetramethylene polymerides, i, 1266.
Pychlau, *H.* See *W.* **Hammer**.
Pyman, *F. L.*, and *E.* **Stanley**, substitution in the benzene nucleus on nitration of 2-phenylglyoxaline and its carboxylic acids, i, 157.
Pyman, *F. L.* See also *V. K.* **Bhagwat**, *R.* **Burtles**, *R.* **Forsyth**, and *W. G.* **Forsyth**.
Pyriki, *C.* See *A.* **Heiduschka**.

Q.

Quagliariello, *G.*, oxygen content of methæmoglobin, i, 89.
Quam, *G. N.*, reactions in liquid hydrogen sulphide, ii, 582.
Quam, *G. N.*, and *J. A.* **Wilkinson**, conductivities in liquid hydrogen sulphide solutions, ii, 542.
Quartaroli, *A.*, autocatalysis, ii, 53.
reciprocal excitation and inactivation of catalysts, ii, 805.
positive and negative catalysts of the dehydration of cupric hydroxide, ii, 806.
Quastel, *J. H.*, possible rôle of pyruvic acid in bacterial growth, i, 1216.
Quastel, *J. H.*, and *M.* **Stephenson**, anaërobic growth of bacteria, i, 1217.
Quastel, *J. H.*, *M.* **Stephenson**, and *M. D.* **Whetham**, reactions of resting bacteria in relation to anaërobic growth, i, 747.
Quastel, *J. H.*, and *M. D.* **Whetham**, dehydrogenations produced by resting bacteria. I. and II., i, 1015, 1217.
Quastel, *J. H.*, and *W. R.* **Wooldridge**, dehydrogenations produced by resting bacteria. III., i, 1217.
Quayle, *O. R.*, and *E. E.* **Reid**, substituted *o*-benzoylbenzoic acids and the corresponding anthraquinones, i, 1289.
Queroix, *M.* See *L.* **Meunier**.
Quick, *A. J.*, effect of sodium carbonate concentration in the determination of sugar by Benedict's method, i, 1115.
Quick, *W. G. E.* See *O. L.* **Brady**.
Quigley, *J. P.*, and *A. D.* **Hirschfelder**, comparison of the action of some secondary and tertiary alcohols with special reference to local anæsthesia, i, 195.
Quill, *L.* See *G. W.* **Sears**.
Quintin, (*Mlle.*) *M.* See *R.* **Audubert**.

R.

Raabe, *H.*, influence of certain factors in the development of the flagellate *Prowazekia* (*Bodo*) *edax*. I. Hydrogen-ion concentration, i, 868.
Rabaté, *H.* See *R.* **Audubert**.
Rabinovitsch, *A. J.*, coagulation of colloids by electrolytes. I. Arsenic trisulphide sols and barium chloride, ii, 778.
Rabinovitsch, *E.* See *F.* **Paneth**.
Rabinovitsch, *I. M.*, sodium, potassium, calcium, and magnesium in blood plasma in renal disease, i, 462.
blood-sugar time curves following ingestion of dihydroxyacetone, i, 1352.
Rabinovitsch, *I. M.* [with *A. B.* **Frith**], iodine. I. Avidity of the thyroid gland for various iodine compounds *in vitro*, i, 1488.
Rabinovitsch, *M.* See *S.* **Jakubsohn**.
Rabl, *C. H. R.* See *H.* **Bernhardt**.
Rachevsky. See **Raschevsky**.
Rackwitz, *E.* See *J.* **Traube**.
Radcliffe, *L. G.*, and *E. H.* **Sharples**, determination of vanillin, piperonal, and coumarin, ii, 1210.
Radet. See **Astruc**.
Radmacher, *W.* See *W.* **Dilthey**.
Radsimovska, *W.*, electrode for the determination of p_H in solid media, i, 338.
Radulescu, *D.*, colour of spirans, i, 1159.
Radulescu, *D.*, and *V.* **Georgescu**, general method for the synthesis of polyspirans, i, 819.

Radulescu, *D.*, and *V.* **Georgescu**, constitution of phthalhydrazide, i, 1185.
derivatives of indandione and di-indone. I. Mechanism of the condensation of indandione with aldehydes, i, 1285.
derivatives of indandione and di-indone. II. Condensation products of aldehydes with di-indone, i, 1286.
Raeck, *M.* See *A.* **Schaarschmidt**.
Räth, *C.*, intramolecular condensation reactions of aminoacetals and amino-aldehydes. III. 2-Amino-3-methylpyridine and 1:2-dihydronaphthyridine, i, 437.
Räth, *C.*, and *E.* **Lehmann**, *cis-trans*-isomerism in the stilbazole series, i, 432.
Räth, *C.*, and *G.* **Prange**, reactions of 5-nitro-2-nitroaminopyridine, i, 978.
Räth, *C.* See also *A.* **Binz**.
Rahlfs, *E.* See *W.* **Biltz**.
Raiford, *L. C.*, and *J. C.* **Colbert**, 3-nitro-4-hydroxydiphenyl and some of its derivatives, i, 808.
Raiford, *L. C.*, and *H. P.* **Lankelma**, effect of the acidity of acyl on the migration from nitrogen to oxygen in *o*-aminophenols, i, 809.
Raikes, *H. R.* See *H. B.* **Hartley**.
Raiziss, *G. W.* See *A.* **Proskouriakoff**.
Rakshit, *J. N.*, alteration of the volume contraction on solution, ii, 288.
molecular contraction in solution, ii, 765.
Rakuzin, *M. A.*, and *G.* **Pekarskaja**, fractionation of egg-yolk by common solvents, i, 607.
Rakuzin, *M. A.*, and *A.* **Rosenfeld**, coagulation of albumins and β-albumins, i, 708.
Raleigh, *J. T.*, and *S. M.* **Marie**, detection of ethyl phthalate in ethyl alcohol, ii, 605.
Ramachandran, *S.*, precipitation of bismuth sulphide from acid medium, ii, 1005.
reaction between bismuth sulphide and hydrochloric acid, ii, 1208.
Ramage, *W. D.*, and *R. C.* **Miller**, salt error of cresol-red, ii, 712.
Raman, *C. V.*, and *S. K.* **Datta**, anomalous dispersion and multiplet lines in spectra, ii, 614.
Raman, *C. V.*, and *L. A.* **Ramdas**, scattering of light by liquid boundaries, and its relation to surface tension. II. and III., ii, 952, 1046.
Ramanathan, *K. R.*, structure of benzene and *cyclo*hexane and their optical anisotropy, i, 1255.
structure of molecules in relation to their optical anisotropy. I., ii, 478.
polarisation of resonance radiation and the duration of excited state, ii, 729.
Ramann, *E.*, chemico-physical influences of quicklime and calcium carbonate on mineral soils, i, 223.
soil acidity and its determination, i, 875.
Ramart, (*Mme.*) *P.*, action of hydrobromic acid on some tertiary alcohols, i, 250.
Ramart, (*Mme.*) *P.*, and (*Mlle.*) **Amagat**, molecular transpositions; preparation and dehydration of some ββ-diarylethyl and diarylalkylethyl alcohols, i, 658.
Ramart, (*Mme.*) *P.* See also *A.* **Haller**.
Rambech, *O.*, aniline hydrogen salts of acids of the oxalic series, i, 885.
Ramdas, *L. A.*, spectrum of potassium excited during its spontaneous combination with chlorine, ii, 334.
Ramdas, *L. A.* See also *C. V.* **Raman**.
Ramirez, *M. A.*, *A. V.* **St. George**, and *R. L.* **Moses**, chemical analysis of blood in asthma, hay fever, etc., i, 999.
Ramon, *G.*, diphtheria anatoxin and anatoxins in general, i, 339.
Ramon, *G.* See also *A.* **Berthelot**.
Ramsbottom, *J. E.* See *D. L.* **Chapman**.
Ramsperger, *H. C.* See *C. W.* **Porter**.
Ranc, *A.*, dissociation of sodium hydrogen carbonate, ii, 414.
Randall, *E. G.*, urinary calculus, i, 1491.
Randall, *H. M.*, and *W. N.* **St. Peter**, infra-red line spectrum of zinc and cadmium, ii, 1101.
Randall, *M.*, and *A. P.* **Vanselow**, activity coefficients of dilute aqueous solutions of hydrogen chloride, thallous chloride, and lead nitrate, ii, 33.
Randoin, *L.*, *J.* **Alquier**, (*Mlle.*) **Asselin**, and (*Mlle.*) **Charles**, nitrogenous materials of corn offal; comparative study of their biological value as factors of existence, growth, and fertility, i, 210.
balanced diets: relative proportions of mineral salts and carbohydrates, i, 1002.
Randoin, *L.*, and *E.* **Lelesz**, variations in blood-sugar and liver glycogen of pigeons fed on normal diet and on diet deficient in vitamin-*B*, i, 751.

Randoin, *L.*, and *A.* **Michaux**, variations of proportion of urea in the blood of a guinea-pig under the influence of a diet lacking in anti-scorbutic factor, i, 751.
Rane, *M. B.*, and *M.* **Prasad**, effect of the addition of some alkaloids on the rate of dissolution of iron in dilute hydrochloric acid, ii, 410.
Ranedo, *J.*, and *A.* **Léon**, hydrogenation of diphenyl-*o*-carboxylic acid, i, 665.
Ranfaldi, *F.*, ethyl ester of *α*-phenyl-*p*-nitrocinnamic acid, i, 399.
Rangier, *M.*, form in which uric acid is excreted, i, 186.
Rangier, *M.* See also *L.* **Chelle**.
Rankin, *J.* See *R. D.* **Haworth**.
Rao, *B. S.*, *P. B.* **Panicker**, and *J. J.* **Sudborough**, essential oil of *Cyperus rotundus*, i, 1164.
Rao, *B. S.*, and *J. J.* **Sudborough**, kachi-grass oil, i, 1164.
Rao, *B. S.*, *J. J.* **Sudborough**, and *H. E.* **Watson**, Indian essential oils, i, 1164.
Rao, *J. C. K.*, opalescence of binary liquid mixtures, ii, 739.
Rao, *K. A. N.* See *M. O.* **Forster**.
Rao, *K. R.*, absorption of the green line of thallium vapour, ii, 455.
fluorescence and channelled absorption of bismuth at high temperatures, ii, 473.
spectra of the metals of the aluminium sub-group, ii, 610.
Rao, *K. R.* See also *A. L.* **Narayan**.
Rao, *M. G. S.*, *C.* **Srikantia**, and *M. S.* **Iyengar**, substitution in resorcinol derivatives. I. Nitration of derivatives of *β*-resorcylaldehyde, i, 675.
Raper, *H. S.*, and *A.* **Wormall**, tyrosinase–tyrosine reaction. II. Theory of deamination, i, 473.
Raper, *H. S.* See also *P. W.* **Clutterbuck**, and *F. C.* **Happold**.
Raquet, *D.*, and *M.* **Paget**, urine analysis, i, 1350.
Raschevsky, *N. von*, vaporisation of electrons, ii, 731.
thermionic effect from the point of view of the phase rule, ii, 920.
kinetic theory of the thermionic effect, ii, 920.
Raschig, *F.*, action of hydrogen sulphites and sulphites on nitro and nitroso compounds, i, 239.
interaction of aniline and calcium hypochlorite, i, 243.
constitution of organic derivatives of sulphurous acid, ii, 245.
action of sodium hypochlorite on *p*-cresoldisulphonic acid, i, 249.
Raschig, *F.*, compounds of gold with nitrogen, ii, 144.
new oxides of nitrogen, ii, 146.
reactions between nitrous and sulphurous acids, ii, 146.
monochloroamine, ii, 146.
composition of nitrogen iodide, ii, 147.
reduction of azoimide, ii, 223.
oxidation of azoimide, ii, 223.
combustion of ammonia to hydrazine and di-imide, ii, 224.
oxidation of hydrazine and its sulphonic acids, ii, 224.
oxidation of hydroxylamine, ii, 224.
hydroxylaminemonosulphonic acid, ii, 225.
hydroxylaminedisulphonic acid, ii, 225.
hydroxylamine*iso*disulphonic acid, ii, 225.
hydroxylaminetrisulphonic acid, ii, 226.
action of sulphite, hydrogen sulphite, and sulphurous acid on hydroxylamine, ii, 226.
potassium "nitrososulphite" [dinitrososulphonate], ii, 226.
preparation and properties of polythionic acids, ii, 229.
constitution of polythionic acids, ii, 230.
potassium chloroiminodisulphonate, ii, 986.
Rasetti, *F.*, duration of the quantic state $2p_2$ of the mercury atom, ii, 340.
Rasetti, *F.* See also *E.* **Fermi**.
Rask, *O. S.*, and *I. K.* **Phelps**, determination of lipoid phosphorus in cereal products, ii, 328.
extraction and determination of lipoids in cereal products, ii, 448.
Rasmussen, *H. B.*, and *S. A.* **Schou**, titration of alkaloids, ii, 247.
Rassweiler, *C. F.*, and *R.* **Adams**, structure of dehydracetic acid, i, 299.
Rastelli, *G.*, behaviour of certain phenylhydrazones dissolved in organic solvents, i, 256.
method of determining molecular weight, ii, 1040.
Rastelli, *G.*, and *A.* **Mingozzi**, constitution of pyrrolealdehyde, i, 1316.
Rathery, *F.* See *H.* **Bierry**, and *A.* **Desgrez**.
Rau, *F.* See *E.* **Berl**, and *H.* **Stobbe**.
Rau, *M. G.*, constituents of some Indian essential oils. XVI. Rate of oxidation of *d*-Δ^3-carene and other terpenes in the presence of catalysts, i, 565.

Rau, *M. G.*, constituents of some Indian essential oils. XVI. Rate of oxidation of *d*-Δ^3-carene and other terpenes in the presence of catalysts, i, 687.
Rau, *M. G.*, and *J. L.* **Simonsen**, constituents of some Indian essential oils. XVII. Abietic acid from the rosin of *Pinus longifolia*, Roxb., i, 687.
Rauch, *A.* See *E.* **Zintl**.
Rauch, *H.* See *F.* **Reindel**.
Rauchalles, *G.* See *H. H.* **Schlubach**.
Rauchenberger, *W.* See *H. H.* **Schlubach**.
Raupenstrauch, *H.* See *A.* **Kailan**.
Rautenfeld, *F. von*, electrical conductivity of rock salt and calcite at high temperatures, ii, 639.
Ravenswaay, (*Mlle.*) *H. J.* See *J.* **Böeseken**.
Rawling, *S. O.*, and *J. W.* **Glassett**, reaction between potassium persulphate and potassium iodide in gelatin sols, ii, 561.
Ray, *B. B.*, irregularity of the *La*-doublet in the *X*-ray spectra, ii, 78.
dependence of the *Kα*-doublet with different chemical compounds, ii, 457.
effect of chemical constitution on the *X*-ray spectrum of sulphur, ii, 914.
Ray, *H. L.* See *J. N.* **Mukherjee**.
Rây, *H. P.* See *P. C.* **Guha**.
Rây, *J. N.*, and *R.* **Robinson**, nitration of *m*-meconine, i, 1153.
Rây, *J. N.* See also *W. H.* **Perkin**, *jun.*
Ray, *K. C. B.* See (*Sir*) *P. C.* **Rây**.
Ray, *N. C. G.* See *A. C.* **Sircar**.
Rây, *P.*, and *P. C.* **Bandopadhyay**, mercury–ammonia compounds, ii, 813.
Rây, *P.*, and *P. B.* **Sarkar**, complex chromium ammonium compounds, ii, 230.
Rây, *P.*, and *P. V.* **Sarkar**, cobalti-ammine chromates and chromato-cobalti-ammines, ii, 815.
Rây, (*Sir*) *P. C.*, oxidation of triethylene tetrasulphide by means of potassium permanganate, i, 352.
varying valency of gold with respect to mercaptanic radicles, ii, 184.
Rây, (*Sir*) *P. C.*, and *K. C. B.* **Ray**, varying valency of platinum with respect to mercaptanic radicals. II., ii, 1121.
Rây, *P. R.*, and *P. N. D.* **Gupta**, double ferrocyanides of hydrazine and metallic elements, i, 377.
Rây, *R. C.*, adsorption of nitrogen peroxide by silica gel, ii, 191.
valency of boron, ii, 267.
action of acids and water on magnesium boride, ii, 417.
Ray, *S. K.* See *P. C.* **Guha**.
Rayleigh, (*Lord*), luminous vapour from the mercury arc and the progressive changes in its spectrum, ii, 738.
Raymond, *A.* See *J. J.* **Abel**.
Raymond, *A. L.*, mechanism of carbohydrate utilisation, i, 1493.
Read, *B. E.*, metabolism studies with chaulmoogra oil. I. Influence of chaulmoogra oil on calcium metabolism. II. Influence of hydnocarpates on urinary nitrogen partition in the dog, i, 194.
chemical constituents of camel's urine, i, 1204.
Read, *J.*, and *A. M.* **McMath**, method of diagnosing potential optical activity. I. Optical activity of chlorobromomethanesulphonic acid, i, 1126.
Read, *J. B.* See *S.* **Sugden**.
Read, *R. R.*, and *F. A.* **Fletcher**, electroreduction of diacetone alcohol, i, 627.
Read, *R. R.*, and *C.* **Lucarini**, large-scale preparation of sodium amalgam in the laboratory, ii, 587.
Rebbeck, *J. W.*, prevention of bumping when boiling liquids, ii, 996.
Reboul, *G.*, study under reduced pressure of the radiations emitted by bodies of high resistance traversed by an electric current, ii, 345.
Réchou, *G.*, *K*-series of heavy elements, ii, 457.
Redlich, *O.*, theory of electrolytic conductivity, ii, 541.
Redonnet, *T. A.*, narcotic effect of derivatives of barbituric acid, i, 862.
Reed, *W. W.*, apparatus for determining carbon dioxide, ii, 714.
Reeve, *L.*, experimental technique of photochemistry. I. The quartz mercury lamp as a photo-chemical light source, ii, 234.
Reeve, *L.* See also *R. G.* **Franklin**.
Reeves, *G.*, preparation of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone, i, 699.
Regno, *W. del*, photo-electric emission of selenium, ii, 81.
transformation of nickel in the neighbourhood of the Curie point, ii, 372.
Rehberg, *P. B.*, microtitration, i, 852.
determination of carbamide in 0·1 c.c. of blood by microtitration, i, 853.
Rehenburg, *P. G. von.* See *R.* **Kremann**.
Rehenburg, *R. G. von.* See *R.* **Kremann**.
Rehorst, *K.* See *F.* **Ehrlich**.
Reich, *H.* See *J. von* **Braun**.
Reich, *R.* See *A.* **Job**.
Reichart, *F.* See *F.* **Fichter**.
Reichel, *G.* See *T.* **Sabalitschka**.

Reichenbächer, *E.*, world-geometrical properties indicated by quantised world-lines of the electron in the hydrogen atom, ii, 624.
orbits in the hydrogen atom as affected by the motion of the nucleus, ii, 734.
Reichinstein, *D.*, "phenomenology" of the Richardson effect, ii, 345.
mechanism of the development of a potential difference at the boundary of two phases, ii, 545.
Reid, *E. E.* See *C. E.* **Garland**, and *O. R.* **Quayle**.
Reid, *F. R.* See *F. E.* **Allison**.
Reifenberg, *A.* See *A.* **Fodor**.
Reihlen, *H.*, *R.* **Illeg**, and *R.* **Wittig**, reactivity of organic substances in complex combination, i, 232.
Reihlen, *H.*, *A.* **Sapper**, and *G. A.* **Kall**, partial valency of the hydroxyl group. IV. Aquo- and pyrido-tri-pyrocatechyl-arsenic and -antimonic acids, i, 912.
Reimann, *A. L.* See *P.* **Pringsheim**.
Reinau, *E.*, is carbon dioxide a climatic factor in plant growth? i, 213.
significance of the carbon dioxide of the soil and of the atmosphere in agriculture, i, 1526.
Reindel, *F.*, and *H.* **Rauch**, new class of indigoid dyes, i, 438.
Reinders, *W.*, action of proteins on gold sols, ii, 1059.
Reinders, *W.*, and *S. I.* **Vles**, reaction velocity of oxygen with solutions of inorganic salts. I. Oxidation of nitrites. II. Catalytic oxidation of arsenites, ii, 308.
reaction velocity of oxygen with solutions of inorganic salts. III. Catalytic oxidation of sulphites, ii, 567.
Reiner, *L.*, oxidation of acetaldehyde. II., ii, 213.
Reinhold, *H.* See *C.* **Tubandt**.
Reinitzer, *F.*, olive resin, i, 146.
Siam benzoin. IV., i, 945.
Reinwein, *H.*, basic constituents in the urine in advanced pulmonary tuberculosis, i, 189.
uroflavine, a new pathological constituent of urine, i, 725.
Reinwein, *H.*, and *H.* **Heinlein**, composition of amniotic fluid [cow], i, 721.
Reinwein, *H.*, and *K. L.* **Kochinki**, putrefaction of agmatine, i, 747.
Reinwein, *H.* See also *D.* **Ackermann**.
Reisenegger, *C.* See *H.* **Wieland**.
Reiss, *P.*, p_H value of the interior of the cell nucleus and its experimental variations, i, 199.
Reisser, *O.*, and *F.* **Hamann**, creatine content of muscles contracted by chemicals; criticism of the theory of Pekelharing and Hoogenhuyze, i, 860.
Reissmann, *E.*, temperature of steam evolved from a [boiling aqueous] solution, ii, 105.
Reissmann, *E.* See also *Erich* **Müller**.
Reissner, *H.*, theory of the electron, ii, 349.
Reiter, *E.* See *A.* **Kirpal**.
Reitmeyer, *H.* See *A.* **Skita**.
Reitstötter, *J.* See *J.* **Eggert**.
Rekschinski, *V.*, preparation of phosphorus trichloride and tribromide from red phosphorus, ii, 994.
Remy, *E.*, decomposition apparatus, ii, 589.
Remy, *H.*, conductivity measurements of very dilute solutions, ii, 299.
Remy, *H.*, and *H.* **Gönningen**, activity of contact substances. II. Catalytic synthesis of water by metals of the iron group and their binary alloys with one another and with the platinum metals, in so far as they are catalytically active at the ordinary temperature, ii, 1176.
Remy, *H.*, and *C.* **Koch**, mists from chemical reactions. III. Examination for electric charge, ii, 107.
Remy, *H.*, and *A.* **Kuhlmann**, determination of the solubilities of sparingly soluble substances. I. Solubility of magnesium oxide in water, ii, 80.
determination of the solubilities of sparingly soluble substances. II. Solubilities of the oxides of beryllium, aluminium, zinc, cadmium, lead, copper, and silver in water, ii, 119.
Remy, *H.*, and *H. J.* **Rothe**, co-ordination chemistry; chloroferrates of substituted ammonium bases, ii, 1088.
Remy, *H.*, and *K.* **Ruhland**, mists from chemical reactions. II. Absorption of chemical mists, ii, 107.
Remy, *H.*, and *B.* **Schaeffer**, activity of contact substances. I. Catalytic synthesis of water by the platinum metals and their alloys, ii, 563.
Renfrew, *A. G.* See *D. A.* **Hahn**, and *T. B.* **Johnson**.
Renshaw, *A.*, insulin, i, 617.
Renshaw, *R. R.* See *I.* **Bencowitz**, and *R.* **Hunt**.
Reti, *L.*, relationships between vegetable aromatic substances and their origin, i, 418.

Reti, *L.*, rapid determination of phenols in essential oils, using small quantities of material, ii, 604.
Retschinsky, *T.*, gold in the mercury lamp, ii, 465.
Retter, *W.* See *F.* **Hein**.
Reuther, *F.* See *P.* **Ludewig**.
Reverdin, *F.*, nitration products of *o'*-nitrotoluene-*p'*-sulpho-*p*-phenetidide, i, 1409.
Revery, *G.* See *H.* **Wieland**.
Reychler, *A.*, photochemical studies. IV. Properties of the silver gelatino-halides, ii, 219.
photochemical studies. V. Actinoscopic reactions, ii, 1180.
Reyerson, *L. H.* See *M.* **Latshaw**.
Reymann, *G. C.*, pathological increase in globulin (in blood); relationship between decomposition of hæmoglobin and increase in globulin, i, 1345.
Reynolds, *F. W.*, effects of gas on the resistance and resistance–temperature coefficient of sputtered platinum films, ii, 108.
Rheinboldt, *H.*, and *H.* **Roleff**, mechanism of Grignard's reaction, i, 6.
reducing action of organo-magnesium halides, i, 542.
Rheinboldt, *H.*, and *O.* **Schmitz-Dumont**, reactions of nitrosyl chloride. I. "Nitrosochlorination" with nitrosyl chloride, i, 1131.
Rheinboldt, *H.* See also *P.* **Pfeiffer**.
Rhodes, *E.*, chemical nature of the membrane of potato cork, i, 1026.
Rhodes, *F. H.*, and *J. T.* **Carty**, corrosion of certain metals by carbon tetrachloride, ii, 1084.
Rhodes, *F. H.*, *M. L.* **Nichols**, and *C. W.* **Morse**, "Höchst test" for the determination of anthracene, ii, 1005.
Ribas, *I.*, surface tension of solutions of the sodium salts of α- and β-diphenylsuccinic acids and of fumaric and maleic acids, ii, 647.
Ribas, *I.* See also *A.* **Madinaveitia**.
Rice, *F. O.*, and *C. F.* **Fryling**, kinetics of the reaction between the halogens and saturated aliphatic ketones in dilute aqueous solution, ii, 556.
Rice, *F. O.*, *C. F.* **Fryling**, and *W. A.* **Wesolowski**, temperature coefficient and mechanism of a chemical reaction, ii, 48.
Rice, *J.*, radiation theory of chemical reaction, ii, 1076.
Rich, *A. R.*, formation of bile pigment from hæmoglobin in tissue cultures, i, 711.
Rich, *A. R.*, and *J. H.* **Bumstead**, identity of hæmatoidin and bilirubin, i, 1475.
alleged power of bacteria to form bile pigment from hæmoglobin, i, 1482.
[non]-formation of bile pigment from hæmoglobin by the action of enzymes, i, 1482.
Rich, *E. M.* See *H. H.* **Lewis**.
Richard. See *P.* **Petit**.
Richard, *C. V.*, triangular benzene molecule, i, 1054.
Richard, *E.*, calorimetric determination of hydrogen-ion concentration, ii, 596.
Richard, *P.* See *H.* **Rivier**.
Richards, *C. E.*, determination of lead, ii, 903.
Richards, *E. M.*, and *T. M.* **Lowry**, rotatory dispersive power of organic compounds. XIV. Simple dispersion in 1-methyl*cyclo*hexylidene-4-acetic acid, ii, 632.
rotatory dispersive power of organic compounds. XVI. β- and π-Sulphonic derivatives of camphor, ii, 934.
Richards, *E. M.* See also *T. M.* **Lowry**.
Richards, *M. B.*, and *W.* **Godden**, Pemberton–Neumann method for the determination of phosphorus, ii, 66.
Richards, *O. W.*, effect of calcium sulphate on the growth and fermentation of yeast, i, 1011.
Richards, *T. W.*, internal pressures produced by chemical affinity, ii, 362.
Richards, *T. W.*, and *H. M.* **Chadwell**, densities and compressibilities of organic liquids and solutions: polymerisation of water, ii, 1049.
Richards, *T. W.*, and *F. T.* **Gucker**, improved differential method for the exact determination of specific heats of aqueous solutions; including results for various salts and organic acids, ii, 848.
Richardson, *A. S.*, *C. A.* **Knuth**, and *C. H.* **Milligan**, heterogeneous catalysis. II. Hydrogenation of marine oils, i, 229.
Richardson, *H. B.*, and *S. Z.* **Levine**, clinical calorimetry. XXXVII. Infection and the ketogenic balance, i, 723.
Richardson, *H. L.*, and *P. W.* **Robertson**, cryoscopic method for adsorption, ii, 383.
Richardson, *O. W.*, structure in the secondary hydrogen spectrum. I., II., and III., ii, 909, 1013.

Richardson, *O. W.*, and *T.* **Tanaka**, regularities in the secondary hydrogen spectrum, ii, 11, 469.
striking and breaking potentials for electron discharges in hydrogen, ii, 13.
Richardson, *O. W.*, and *A. F. A.* **Young**, thermionic work-functions and photoelectric thresholds of the alkali metals, ii, 343.
Richmond, *H. D.*, preparation of Nessler's solution, ii, 327.
Richter, *A.*, influence of alcohol, salts, and temperature on the change point of some indicators and means of avoiding errors in acidimetric titrations, ii, 237.
rôle of auxiliary pigments in the *Cyanophyceæ*, i, 1218.
Richter, *E.* See *H. P.* **Kaufmann**.
Richter, *H.* See *B.* **Neumann**.
Richter, *K.* See *K.* **Ziegler**.
Richter-Quittner, *M.*, sugar content of blood-corpuscles, i, 95.
mineral content of blood plasma, i, 178.
Richtet, *C.*, *jun.*, and *R.* **Monceaux**, effect of cooking on metabolism of meat, i, 859.
Richtmyer, *F. K.*, relative number of *K* and *L* electrons expelled by *X*-rays, ii, 1129.
Richtmyer, *F. K.*, and *R. C.* **Spencer**, structure of the $K\alpha$ lines of molybdenum, ii, 1101.
width of the K_H absorption discontinuity in silver, ii, 1102.
Richtmyer, *F. K.* See also *F. W.* **Warburton**.
Rideal, *E. K.*, reduction potential of dicyan-quinhydrone, ii, 546.
Rideal, *E. K.*, and *E. G.* **Williams**, action of light on the ferrous ferric iodine iodide equilibrium, ii, 416.
Rideal, *E. K.*, and *W. M.* **Wright**, low-temperature oxidation at charcoal surfaces. I. Behaviour of charcoal in the absence of promoters, ii, 806.
Rideal, *E. K.* See also *A. P.* **Cary**, *A. K.* **Goard**, *R. G. W.* **Norrish**, and *R. K.* **Schofield**.
Ridge, *B. P.* See *C.* **Birtwell**.
Ridgway, *L. R.*, and *R.* **Robinson**, new route to the 3-hydroxybenzopyrylium salts, i, 54.
3-chlorobenzopyrylium derivatives, i, 693.
Riding, *R. W.*, and *E. C. C.* **Baly**, occurrence of helium and neon in vacuum tubes, ii, 925.
Riding, *R. W.* See also *J. S.* **Thomas**.
Ridley, *G. N.*, catalytic effects in the oxalate–permanganate reaction, ii, 689.
theories on the constitution of natural silicates, ii, 1130.
Ridout, *C. B.* See *H. G.* **Barbou**.
Ridout, *J. H.* See *C. H.* **Best**.
Ried, *G.* See *A.* **Eibner**.
Riede, *A.*, electrical conductivity and Hall effect for nickel films, ii, 355.
Riedel, *J. D.*, preparation of *apo*cholic acid, i, 406.
preparation of cyclic ketones, i, 407.
preparation of derivatives of 2-phenylquinoline-4-carboxylic acid, i, 1170.
ester of salicylic acid, i, 1423.
barbituric acid derivatives, i, 1453.
Riegel, *E. R.*, and *L.* **Widgoff**, new pattern formed by coloured salts in solid gels, ii, 863.
Rieman, *W.*, and *P. A. van der* **Meulen**, unimolecular soap films in emulsions, ii, 1148.
Riepenkröger, *K.* See *R.* **Anschütz**.
Riesenfeld, *E. H.*, formation of ozone and hydrogen peroxide in the oxyhydrogen flame, ii, 148.
formation and decomposition of polythionates, ii, 229.
formation of ozone in incandescent capillaries, ii, 989.
Riesenfeld, *E. H.*, and *W.* **Haase**, action of ozone on aqueous colloidal solutions of inorganic substances, ii, 988.
Rieser, *A.* See *E.* **Blanck**.
Riety, *L.*, electromotive force of filtration, ii, 796.
Riiber, *C. N.*, mutarotation. IV. Solution volume and refraction constants of α- and β-methylglucoside, i, 8.
Riiber, *C. N.*, and *V.* **Esp** [with *E.* **Berner**], mutarotation. V. Solution volume and refraction constants of lævulose, i, 635.
Riiber, *C. N.*, *T.* **Sörensen**, and *K.* **Thorkelsen**, mutarotation. VI. Solution volumes and refraction constants of some polyhydric alcohols, i, 773.
Rimington, *C.*, effect of ammonium sulphate and other salts on the colorimetric determination of phosphorus, i, 183.
Rinde, *H.* See *T.* **Svedberg**.
Rinderknecht, *R.*, effect of reading errors on the rotatory dispersion constants, ii, 357.
Rinderknecht, *R.* See also *H.* **Rupe**.
Rindfleisch, *H.* See *P.* **Hirsch-Mamroth**.
Ringer, *W. E.*, protein and potassium ions, ii, 662.

Rinkenbach, *W. H.*, and *R. E.* **Hall,** heats of fusion of trinitrotoluene, "tetryl," and picric acid, ii, 207.

Rippel, *A.*, significance of the hydrogen-ion concentration for micro-organisms and their activity in the soil, i, 220.

Rippel, *A.*, and *O.* **Ludwig,** physiological equilibria in plants; dependence of the growth constant of maize on nitrogen nutrition, i, 485.

Risi, *J.* See *A.* **Bistrzycki.**

Riso, *P.* See *P.* **Karrer.**

Ritter, *J. J.* See *M. T.* **Bogert.**

Rivier, *H.*, and *P.* **Richard,** action of some chlorides derived from carbonic acid on dimethylaniline, i, 1416.

Rivière, *D. de la*, and *F.* **Roux,** flocculation of antimeningococcal sera in the presence of alcoholic extracts of meningococci, i, 749.

Rivière, *G.*, and *G.* **Pichard,** substances contained in the leaves of apple trees and in apple skins, i, 845.

Rizzi, *F.*, rotatory powers of fluoro derivatives of benzene and its homologues as a function of the wave-length, ii, 357.

Rjachina, *E.* See *N. D.* **Zelinski.**

Roach, *W. A.*, a laboratory apparatus for the wet grinding of plant tissues out of contact with air, i, 1517.

Roake, *C. E.*, preparation of *o*-tolidine solution for the determination of chlorine [in chlorinated water], ii, 432.

Roberts, *C.*, and *T. B.* **Johnson,** preparation of derivatives of diphenic acid possessing the properties of local anæsthetics, i, 816.

Roberts, *E.*, and *E. E.* **Turner,** relative rates of conversion of phenoxyphenyldichloroarsine and its chloro derivatives into chlorophenoxarsines, i, 1339.

Roberts, *H. M.* See *H.* **McCombie.**

Roberts, *H. S.*, black body for optical pyrometer calibration, ii, 756.

Roberts, *H. S.*, and *T.* **Stadnichenko,** micro-furnace for high magnifications, ii, 707.

Roberts, *J. K.*, thermal expansion of bismuth crystals, ii, 94.

Roberts, *K. G.*, preparation of ethyl acetate and ethyl acetoacetate, i, 114.

Roberts, *R. W.*, magnetic rotatory dispersion of certain paramagnetic solutions, ii, 478.

Robertson, *A. C.*, promoter action in homogeneous catalysis. II. Mechanism of the promotion of copper salts in the catalytic decomposition of hydrogen peroxide by ferric salts, ii, 690.

Robertson, *G. T.* See *E. L.* **Hirst.**

Robertson, *J. B.*, reciprocal salt pair, $Na_2Cr_2O_7 + 2KCl \rightleftharpoons K_2Cr_2O_7 + 2NaCl$, ii, 121.

anode phenomena in the electrolysis of potassium ethyl malonate, ii, 1178.

Robertson, *J. K.*, and *J. T.* **Thwaites,** blackening of a photographic film by *X*-rays, ii, 575.

Robertson, *J. M.*, *C. A.* **Kerr,** and *G. G.* **Henderson,** action of formic acid on certain sesquiterpenes, i, 1293.

Robertson, *P. W.* See *H. L.* **Richardson.**

Robertson, *T. B.*, influence of certain dyes on the multiplication of infusoria (*Enchelys*) with especial reference to the acridine dyes acriflavine and proflavine, i, 1012.

influence of cholesterol and oxycholesterol on the multiplication of infusoria (*Enchelys*), i, 1119.

Robinson, *C.* See *H. R.* **Kruyt.**

Robinson, *F. W.* See *W. T.* **Anderson,** *jun.*

Robinson, *G. C.* See *C. S.* **Burwell.**

Robinson, (*Mrs.*) *G. M.*, and *R.* **Robinson,** synthesis of certain higher aliphatic compounds. I. Synthesis of lactarinic acid and of oleic acid, i, 354.

Robinson, *G. W.*, mechanical composition curves of soils, clays, and other granular substances, i, 224.

Robinson, *G. W.*, and *J. O.* **Jones,** determinations of the degree of humification of soil organic matter, i, 491.

Robinson, *G. W.*, and *R.* **Williams,** base exchange in relation to the problem of soil acidity, i, 222.

Robinson, *G. W.* See also *W.* **McLean.**

Robinson, *H.*, *K*-absorption levels of the light atoms, ii, 614.

Robinson, *H.* See also *O. C. de C.* **Ellis.**

Robinson, *H. R.*, *X*-ray terms and intensities, ii, 728.

Robinson, *M. E.*, and *R. A.* **McCance,** oxidative deamination by a basidiomycete enzyme, i, 745.

Robinson, *M. E.* See also *A. B.* **Callow,** and (*Mrs.*) *M. W.* **Onslow.**

Robinson, *P. L.*, and *H. V. A.* **Briscoe,** atomic weight of bromine; inseparability of the isotopes by fractional crystallisation, ii, 620.

Robinson, *P. L.*, *G. E.* **Stephenson,** and *H. V. A.* **Briscoe,** determination of the melting and transition points of potassium dichromate, ii, 374.

Robinson, *P. L.* See also *H. V. A.* **Briscoe.**

Robinson, *R.*, polarisation of nitrosobenzene, i, 800.
qualitative test for weak [organic] bases, ii, 606.
X-ray crystal analysis as an auxiliary in organic chemical research, ii, 745.
Robinson, *R.*, and *J.* **Shinoda**, synthesis of 2-styrylchromonol derivatives, i, 1301.
Robinson, *R.* See also *James* **Allan**, *J. W.* **Armit**, *W.* **Baker**, *J. M.* **Gulland**, *J.* **Kalff**, *P.* **Lions**, *T.* **Malkin**, *W. H.* **Perkin**, *jun.*, *D. D.* **Pratt**, *J. N.* **Rây**, *L. R.* **Ridgway**, and (*Mrs.*) *G. M.* **Robinson**.
Robinson, *W. O.*, and *R. S.* **Holmes**, soil colloids, i, 624.
Robison, *R.*, and *K. M.* **Soames**, chemical study of defective ossification in rachitic animals, i, 462.
Robison, *R.* See also *M.* **Martland**.
Robison, *S. C.* See *A. M.* **Hjort**.
Robl, *R.*, solubility of nickel in water containing carbon dioxide, ii, 231.
Robson, *W.*, metabolism of tryptophan. I. Synthesis of racemic *Bz*-3-methyltryptophan, i, 297.
Robson, *W.* See also *A. B.* **Hastings**.
Rocard, *Y.*, diffusion of light in fluids, ii, 265.
hypothesis of molecular association, ii, 1045.
Rocasolano, *A. de G.*, ultramicroscopy and coagulation, ii, 523.
Roche, *J.*, respiration of tissues in avitaminosis and inanition, i, 462.
Roche, *J.* See also *M.* **Nicloux**, *E. F.* **Terroine**, and *L.* **Thivolle**.
Rodebush, *W. H.*, *J. W.* **Andrews**, and *J. B.* **Taylor**, temperature–entropy diagrams for nitrogen and oxygen, ii, 492.
Rodebush, *W. H.*, and *A. L.* **Dixon**, entropies of the vapours of zinc and lead, ii, 492.
Rodebush, *W. H.*, and *J. C.* **Michalek**, atomic heat capacities of iron and nickel at low temperatures, ii, 949.
Rodebush, *W. H.*, and *T. de* **Vries**, vapour pressure of sodium, ii, 1142.
Rodebush, *W. H.* See also *F.* **Hovorka**.
Rodillon, detection of urobilin in urine and determination of chlorides in blood, i, 722.
detection of citric acid, ii, 246.
Rodio, *G.*, pigments of the Florideæ, i, 621.
Rodionov, *W.*, and *W.* **Matveev**, products of the action of nitrous acid on *o*- and *p*-phenolsulphonic acids. I., [illegible]
Rodt, *V.*, and *E.* **Kindscher**, separation of small quantities of calcium from large amounts of magnesium, ii, 158.
Röhre, *K.*, distillation of arsenious, antimonious, and stannic chlorides, ii, 157.
Röhrig, *H.*, recrystallisation phenomena [in aluminium], ii, 282.
Roell, *E.* See *A.* **Sieverts**.
Rörig, *W.* See *K.* **Schaum**.
Rössler, *A.* See *M.* **Le Blanc**.
Rössler, *G.* See *G.* **Scheibe**.
Röthler, *H.* See *S.* **Edlbacher**.
Röthlisberger, *A.*, synthesis of 2′-chloroflavone and 2′-chloroflavonol, i, 571.
Rötth, *A. von.* See *J.* **Melly**.
Roffo, *A. H.*, action of *X*-rays on cholesterol, i, 393.
Roffo, *A. H.*, and *L. M.* **Correa**, ultrafilterable calcium in the serum of cancerous subjects, i, 999.
ionic conflict and its relations with the physico-chemical constants of plasma, ii, 293.
Roffo, *A. H.*, and *S. M.* **Neuschloss**, influence of Rb, SeO_3, and SeO_4 ions on the respiration of normal and neoplastic cells, i, 1006.
Roger, *M.* See *A.* **Orékhov**.
Roger, *R.*, synthesis of glycols from atrolactinic acid, i, 659.
Roger, *R.* See also *A.* **McKenzie**.
Rogers, *T. H.* See *C. F. A.* **Pantin**.
Rogozinski, *F.*, and *M.* **Starzevska**, distribution of nitrogen in urine of ruminants, i, 1355.
Roh, *N.* See *B.* **Emmert**.
Rohmann, *C.* See *R.* **Fricke**.
Rohner, *M.* See *F.* **Herrmann**.
Roig, *G. y*, and *K.* **Helmholz**, determination of carbamide in blood, cerebro-spinal fluid, and urine, using permutite, i, 853.
Rokkaku, *T.* See *S.* **Mitsukuri**.
Roleff, *H.* See *H.* **Rheinboldt**.
Rolf, *I. P.* See *P. A.* **Levene**.
Roll, (*Mme.*) *C.* See *G.* **Korschun**.
Rolla, *L.*, and *G.* **Piccardi**, chemical statics of electronic phenomena; mass-action law applied to electronic equilibrium, ii, 1018.
chemical statics of electronic phenomena, ii, 1018, 1105.
Rollefson, *G. K.*, characteristic *X*-rays from lithium, ii, 722.
Rollefson, *G. K.* See also *B. H.* **Carroll**.
Rollet, *A. P.*, dissolution of nickel in sulphuric acid under the influence of an alternating current, ii, 799.
Rollett, *A.*, and *A.* **Schmidt**, β-amyrin from Manila elemi resin. III., i, 945.

Romeo, *G.*, apparently new component of oil of lemon, i, 1293.
determination of formaldehyde, ii, 1009.
Romeo, *G.*, and *E.* **D'Amico**, action of sulphites and hydrogen sulphites on aldehydes and ketones and its application to the quantitative determination of these compounds, i, 1380.
Romer, *W.* See *W.* **Swientoslawski.**
Romieu, *M.*, reaction of dry proteins applicable to histochemistry, i, 607.
Rona, *P.*, *A.* **Fiegel**, and *Y.* **Nakahara**, liver and blood catalase. II., i, 1505.
Rona, *P.*, *F.* **Haurowitz**, and *H.* **Petow**, distribution of ions in blood-serum. II., i, 95.
Rona, *P.*, and *H.* **Kleinmann**, nephelometric investigations on enzymic hydrolysis of proteins. II. Influence of ions on peptic digestion, i, 103.
nephelometric investigations on enzymic hydrolysis of proteins. III. Determination of peptic and tryptic digestion of casein, i, 473.
nephelometric investigations on enzymic hydrolysis of proteins. IV. Kinetics of peptic hydrolysis of serum-albumin, i, 1507.
Rona, *P.*, and *A.* **Lasnitzki**, determination of lipase in body fluids and in tissues, i, 471.
Rona, *P.*, *E.* **Mislowitzer**, and *S.* **Seidenberg**, autolysis. IV., i, 335.
Rona, *P.*, *H.* **Petow**, and *E.* **Wittkower**, distribution of ions in the blood. III., i, 94.
Rona, *P.*, and *P. E.* **Speidel**, hydrolysis of leucine ester by pancreatic enzymes, i, 103.
Rooney, *T. E.*, determination of oxygen in pure iron, ii, 327.
Rosbaud, *P.*, and *E.* **Schmid**, increase in strength of single crystals by alloying and cold-drawing, ii, 488.
Rose, *A. R.*, micro determination of nitrogen, ii, 900.
Rose, *A. R.*, *G. J.* **Shiple**, and *C. P.* **Sherwin**, oxidation of cystine and cysteine in the animal organism, i, 190.
Rose, *D. C.* See *P.* **Lowe.**
Rose, (*Sir*) *T. K.*, density of rhodium, ii, 278.
Rose, *W. C.*, and *K. G.* **Cook**, relation of histidine and arginine to creatine and purine metabolism, i, 1003.
Rose, *W. C.*, and *P. S.* **Dimmett**, nephropathic action of the dicarboxylic acids and their derivatives. IV. Mucic acid, i, 733.
Rose, *W. C.*, *C. J.* **Weber**, *R. C.* **Corley**, and *R. W.* **Jackson**, nephropathic action of the dicarboxylic acids and their derivatives. III. Acids with six to nine carbons, i, 733.
Rosen, *I.* See *J. A.* **Fordyce.**
Rosén, *W.* See *B.* **Holmberg.**
Rosenbach, *A.* See *A.* **Schönberg.**
Rosenbaum, *S.*, behaviour of amino-acids in the blood; significance of the liver in protein metabolism, i, 464.
Rosenberg, *A.* See *H.* **Bechhold**, and *A.* **Fodor.**
Rosenblum, *S.*, determination of the ratio of the velocities of the two groups of α-particles emitted from the active deposit of thorium, ii, 463.
Rosenbohm, *A.* See *R.* **Bierich.**
Rosenfeld, *A.* See *M. A.* **Rakuzin.**
Rosenfeld, *H.* See *E.* **Speyer.**
Rosenfeld, *L.*, combination of auxoureases with the enzyme, i, 336.
behaviour of urease towards alcohol, i, 336.
phytochemical reduction of $\alpha\alpha\beta$-trichlorobutaldehyde to $\alpha\alpha\beta$-trichlorobutanol, i, 615.
sulphatase. VI. Occurrence and behaviour of sulphatase in human organs, i, 743.
Rosenfeld, *L.* See also *Martin* **Jacoby.**
Rosenheim, *A.*, internally complex borates, i, 31.
Rosenheim, *A.*, and *I.* **Baruttschisky**, bismuth salts of pyrocatechol, i, 808.
Rosenheim, *A.*, and *F.* **Lehmann**, internally complex beryllates, ii, 220.
Rosenheim, *A.*, and *W.* **Plato**, optically active tripyrocatechylarsenic acids, i, 1412.
Rosenheim, *A.*, and *H. yii* **Mong**, salts and complex compounds of quadrivalent vanadium, i, 1411.
Rosenheim, *M. C.* See *H. W.* **Dudley.**
Rosenheim, *O.*, isolation of spermine phosphate from semen and testis, i, 180.
Rosenheim, *O.*, and *J. C.* **Drummond**, delicate colour reaction for the presence of vitamin-*A*, i, 1515.
Rosenheim, *O.* See also *J. C.* **Drummond**, and *H. W.* **Dudley.**
Rosenmund, *K. W.*, and *A.* **Joithe**, aluminium oxide as a condensing agent and the rôle of carriers in catalysis, i, 1403.
Rosenmund, *K. W.*, and *G.* **Jordan**, mechanism of the catalytic reduction of oximes and nitriles and a new method for the preparation of secondary amines, i, 245.
catalytic reduction of aromatic aldehydes, i, 257.

Rosenov, *L. P.*, action of bile on the digestion of proteins by pancreatic juice, i, 1507.
Rosenthal, *A.* See *H.* **Freundlich.**
Rosenthal, *S. M.*, liberation of adsorbed substances from proteins; a function of the bile salts. I., i, 1203.
Rosenthal, *S. M.*, and *E. C.* **White**, hepatic function. VI. Pharmacological behaviour of phthalein dyes; value of phthalein compounds in estimation of hepatic function, i, 101.
Rosenthaler, *L.*, distribution of linamarase enzymes of *Phaseolus lunatus*, i, 1008.
influence of nitrogenous substances on dextrose determinations, ii, 1006.
Rosin, *J.* See *W. D.* **Collins.**
Rosinsky, *W.* See *A.* **Sonn.**
Ross, *J. F.* See *G. F.* **Smith.**
Ross, *P. A.*, and *D. L.* **Webster**, Compton effect with no box around the tube, ii, 269.
Compton effect: its relation to Duane's box effect, ii, 270.
Ross, *P. A.* See also *D. L.* **Webster.**
Ross, *S. G.* See *J. L.* **Gamble.**
Ross, *V.*, potassium chlorate: its influence on the blood-oxygen-binding capacity (hæmoglobin concentration), its rate of excretion, and quantities found in the blood after feeding, i, 732.
Ross, *W. H.*, and *R. M.* **Jones**, solubility and freezing-point curves of hydrated and anhydrous orthophosphoric acid, ii, 971.
Rossbach, *E.* See *H. P.* **Kaufmann.**
Rosseland, *S.*, spectral theory and the origin of the "nebulium" lines, ii, 3.
Rosset, *H.* [derivative of] phosphorus chloronitride, i, 600.
Rossi, *G.*, and *M.* **Andreanelli**, electrical conductivity and coagulating power of acids and bases, ii, 394.
Rossi, *G.*, and *A.* **Basini**, theory of dyeing, ii, 286.
Rossi, *G.*, and *C.* **Bocchi**, colloidal mercuri-organic compounds, i, 601.
Rossi, *G.*, and *B.* **Cecchetti**, action of carbon disulphide on benzidine, i, 701.
Rossi, *G.* See also *G.* **Plancher.**
Rossner, *E.* See *E.* **Abderhalden.**
Rost, *C. O.*, and *E. A.* **Fieger**, effect of drying on the acidity of soil samples, i, 348.
Rostock, *P.*, determination of pepsin in gastric juice, i, 1009.
Roth, *F.* See *L.* **Claisen.**
Roth, *W. A.*, test of the efficiency of a stirring contrivance, ii, 150.
buffer method in high-temperature calorimetry, ii, 949.
Roth, *W. A.*, and *R.* **Lassé**, heats of combustion of decahydronaphthalenes and β-decalones, ii, 275.
combustion micro-bomb and micro-calorimeter. II., ii, 591.
Roth, *W. A.*, and *W.* **Naeser**, white and black diamonds and their relation to [other forms of] carbon, ii, 1140.
Rothe, *H. J.* See *H.* **Remy.**
Rother, *J.* See *T.* **Brugsch.**
Rothler, *H.* See *K.* **Felix.**
Rothmann, *H.* See *K.* **Dresel.**
Rothmund, *V.*, combination of water in the zeolites, ii, 710.
Rothmund, *V.* [with *F.* **Eisenkolb** and *E.* **Steinherz**], influence of anions on the "passivability" of metals, ii, 131.
Rothstein, *E.*, *A.* **Stevenson**, and *J. F.* **Thorpe**, ring-chain tautomerism. XIV. Structure of Balbiano's acid, i, 884.
Rothstein, *K.*, trimethylenedithioglycollic [trimethylenedithiolacetic] acid, i, 231.
Rothwell, *C. S.*, direct precipitation of calcium in cow's milk, i, 1350.
Rotinjanc, *L. A.* See *N. N.* **Nagornov.**
Rougé, *E.* See *J. T.* **Durand.**
Roughton, *F. J. W.* See *H.* **Hartridge.**
Roush, *G. A.*, and *M.* **Miyake**, equilibrium of the system, cryolite–alumina, ii, 974.
Rouse, *G. F.*, and *G. W.* **Giddings**, ionisation of mercury vapour by ultra-violet light, ii, 919.
Rousseau, *E.*, separation of nickel and iron in presence of chromium by electrolysis, ii, 441.
Roussel. See *F.* **Bordas.**
Roux, *E.* See *D. de la* **Rivière.**
Rouyer, *E.*, association of polyhydric phenols, i, 911.
Row, *K. K.* See *B. B.* **Dey.**
Rowe, *A. W.*, and *J.* **Chandler**, metabolism of galactose. II. Blood-sugar curves, i, 1354.
Rowe, *A. W.*, and *B. S.* **Wiener**, relative reducing powers of some common sugars, i, 885.
Rowe, *F. M.*, and *V. J.* **Tarbett**, hydrogenation in the naphthalene series; properties of derived azo dyes, i, 317.
Rowe, *H. N.* See *S.* **Dushman.**
Roy, *L.*, hydrogen-ion concentration of some injection liquids; influence of sterilisation, i, 1084.

Roy, *S. C.*, modification of the laws of emission of ions from hot metals by the quantum theory, ii, 731.
application of quanta in the theory of chemical reactivity, ii, 1167.
Royds, *T.*, apparent tripling of certain lines in arc spectra, ii, 249.
spectroheliograms with different parts of the H_α line, ii, 450.
Royer, *L.*, orientation of ammonium iodide by muscovite mica, ii, 270.
regular growth of crystals of different species, ii, 749.
Royer, *L.* See also *G.* **Foex**.
Royer, *M.*, orientation of ammonium iodide crystals on the surface of muscovite, ii, 110.
rotatory power of cholesteric substances, ii, 184.
Roylance, *J.* See *R.* **Burtles**.
Ruark, *A. E.*, multiple electron transitions and primed spectral terms, ii, 1016.
Ruark, *A. E.*, and *G.* **Breit**, proposed test of the space quantisation of atoms in a magnetic field, ii, 477.
Ruark, *A. E.*, and *R. L.* **Chenault**, stages in the excitation of the spectra of cadmium, ii, 725.
fine structures of spectrum lines, ii, 1103.
Rubenstein, *L.*, substitution in derivatives of quinol ethers, i, 1278.
substitution in vicinal trisubstituted benzene derivatives. III., i, 1428.
Rubino, *P.* See *J. A.* **Collazo**.
Rudberg, *E.* See *H. von* **Euler**.
Rudberg, *K.* See *H. von* **Euler**.
Rudd, *G. V.*, separation of proteoses derived from egg-albumin, i, 320.
proteoses, peptones, and polypeptides, i, 321.
Rudolfs, *W.*, influence of water and salt solution on absorption and germination of seeds, i, 1120.
selective absorption of ions by seeds, i, 1367.
effect of seeds on hydrogen-ion concentration equilibrium in solution, i, 1368.
Rudy, *R.* See *A. G.* **Worthing**.
Ruell, *D. A.* See *W. N.* **Haworth**.
Ruer, *R.*, Le Chatelier principle and its application to the crystallisation processes in binary systems, ii, 125.
Ruer, *R.*, and *K.* **Bode**, copper oxide and the atomic weight of copper, ii, 620.
Ruff, *O.*, oxides, metals, and carbides at high temperatures, ii, 579.
Ruff, *O.*, and *W.* **Busch**, electrolytic production of magnesium (from fused mixtures containing the oxide), ii, 569.
Ruff, *O.*, and *B.* **Hirsch**, fractional precipitation. I. Dependence on solubility products, dissociation constants, constitution of the precipitate, etc., ii, 992.
Ruff, *O.*, and *E.* **Hohlfeld**, active charcoal. III. Spacial and stoicheiometric relations of adsorption (chemical complex formation), ii, 192.
Ruff, *O.*, *G.* **Schmidt**, and *W.* **Olbrich**, amorphous carbon and graphite, ii, 1125.
Ruff, *O.*, and *F.* **Thomas**, reduction of inorganic halides. IV. Tantalum pentachloride, ii, 1187.
reduction of inorganic halides. V. Derivatives of tantalum trichloride, ii, 1187.
Ruff, *O.*, and *E.* **Vidic**, ruthenium pentafluoride; separation of platinum and ruthenium, ii, 443.
valency of ruthenium; ruthenium tetroxide and ruthenium halides, ii, 480.
Ruggeri, *G.*, dibenzoylglyoxime peroxide, i, 79.
Ruggeri, *G.* See also *G.* **Ponzio**.
Ruggli, *P.*, and *E.* **Brunner**, *o*-nitroaldehydes of the anthraquinone series, i, 561.
Ruggli, *P.*, and *A.* **Fischli**, dyeing processes. IV. Influence of particle size on the process of dyeing, ii, 194.
Ruhland, *K.* See *H.* **Remy**.
Rule, *H. G.*, and *T. R.* **Paterson**, influence of substituents on chemical and physical properties: the velocity of reaction between substituted benzoic anhydrides and an aliphatic alcohol, i, 29.
Rule, *H. G.*, and *J.* **Smith**, optical activity and the polarity of substituent groups. II. Menthyl esters of substituted acetic acids, ii, 1120.
Rump, *W.*, Döppler effect in the reflexion of resonance fluorescence, ii, 473.
resonance fluorescence of the line 1849 Å. of mercury vapour, ii, 473.
Rump, *W.* See also *E.* **Warburg**.
Runge, *C.*, Paschen–Back effect, ii, 341.
Runge, *H.* See *G.* **Ettisch**.
Ruopp, *W.* See *P. W.* **Neber**.
Ruoss, *H.*, clinical detection of dextrose in urine with alkaline copper–glycerol solution, i, 185.
reducing power of organic compounds in alkaline solution and the determination of sugar by analysis in stages and with separation of colloidal cuprous oxide, ii, 244.

Rupe, *H.*, and *F.* **Gisiger**, catalytic reduction of cyano compounds, i, 1095.
Rupe, *H.*, and *G. A.* **Guggenbühl**, conversion of isatin into a tetrahydroquinazoline derivative, i, 1100.
Rupe, *H.*, and *E.* **Hodel**, catalytic reduction of β-methylbutyronitrile and of α-cyanocamphor, i, 275.
Rupe, *H.*, and *E.* **Kopp**, influence of constitution on the rotatory power of optically active substances. XVIII. Anomalous rotation-dispersion of ketones, i, 274.
Rupe, *H.*, and *R.* **Rinderknecht**, influence of constitution on the rotatory power of optically active substances. XVIII. Influence of acetylenic linkings, i, 533.
derivatives of citronellol and their optical rotations, i, 658.
Rupe, *H.*, and *E.* **Tschopp**, β-camphorylpropionic acid and the inner anhydride of γ-borneolpropyl alcohol, i, 1079.
Rupe, *H.*, and *F.* **Vonaesch**, influence of constitution on the rotatory power of optically active substances. XIX. Influence of acetylenic linkings, i, 499.
Rupp, *E.*, luminescence of phosphors under magnetic and electric fields, ii, 13.
Hahn's iron titration method and Rosenmund's modification thereof, ii, 71.
excitation of phosphorescence by high-frequency radiation, ii, 262.
Rupp, *E.* [with *W.* **Wegner** and *P.* **Maihs**], titration of mercury with potassium cyanide and Jellinek's titration of weakly dissociated salts, ii, 716.
Rupp, *E.*, and *G.* **Siebler**, bromate determination of hydrogen peroxide, peroxides, and per-salts, ii, 432.
Rupp, *E.*, *G.* **Siebler**, and *W.* **Brachmann**, determination of antimony in stibnite and in antimony pentasulphide, ii, 244.
Ruppert, *F. von.* See *A.* **Kircher**.
Ruschhaupt, *F.* See *R.* **Fricke**.
Russel, *J. C.*, *E. G.* **Jones**, and *G. M.* **Bahrt**, temperature and moisture factors in nitrate production, i, 1031.
Russell, *A.* [with *H. F.* **Harwood**], native arsenic in Cornwall, ii, 429.
Russell, *A. S.*, passivity of iron and other metals, ii, 406.
transformation of mercury into gold, ii, 924.
Russell, *A. S.*, and *D. C.* **Evans**, determination of metals dissolved in mercury; rapid method of purifying mercury, ii, 1205.
Russell, *A. S.* See also *W. P.* **Widdowson**.
Russell, *H. N.*, intensities of lines in multiplets, ii, 614.
intensities of lines in multiplets. I. Theory, ii, 725.
intensities of lines in multiplets. II. Observed data, ii, 725.
Russell, *H. N.*, and *F. A.* **Saunders**, regularities in the spectra of the alkaline earths, ii, 911.
Russell, *R. P.* See *W. G.* **Whitman**.
Russell, *W. W.*, and *H. S.* **Taylor**, promoter action of thoria on nickel catalysts, ii, 1071.
Ruszczynski, *P.*, precipitation curves of serum proteins, i, 322.
Ruszczynski, *P.* See also *M.* **Bálint**.
Ruszkowski, *M.*, use of iodic acid and potassium hydrogen carbonate for the preparation of standard solutions, ii, 156.
Rutgers, *A. J.* See *A.* **Smits**, and *J. P.* **Wibaut**.
Rutherford, (*Sir*) *E.*, disintegration of atomic nuclei, ii, 348.
Rutherford, (*Sir*) *E.*, and *J.* **Chadwick**, artificial disintegration of elements, ii, 83.
scattering of α-particles by atomic nuclei and the law of force, ii, 1109.
Ruzicka, *L.*, conversion of camphor into fenchone, i, 274.
Ruzicka, *L.*, and *E.* **Capato**, higher terpene compounds. XXIV. Ring formation in sesquiterpenes; complete synthesis of bisabolene and of a hexahydrocadaline, i, 943.
Ruzicka, *L.*, *J.* **Meyer**, and *M.* **Pfeiffer**, higher terpene compounds. XXVI. Degradation of abietic acid by potassium permanganate and ozone, i, 1419.
Ruzicka, *L.*, and *M.* **Pfeiffer**, higher terpene compounds. XXV. Anhydride formation and nitric acid oxidation of abietic acid, i, 1419.
Ruzicka, *L.*, *C. F.* **Seidel**, and *F.* **Liebl**, syntheses in the quinine series. IV. Aliphatic quinatoxins, monocyclic quinaketones, and carbinols, i, 289.
Ruzicka, *L.* See also *H.* **Staudinger**.
Ryan, *H.*, and *P. J.* **Cahill**, condensation of aldehydes with methyl ethyl ketone, i, 558.
Ryan, *H.*, and *J. J.* **Lennon**, condensation of aldehydes with methyl ethyl ketone, i, 1282.
Ryan, *H.*, and *M. J.* **Shannon**, condensation of aldehydes with butylacetoacetic ester [ethyl α-acetylhexoate], i, 558.
Ryan, *H.* See also *J. J.* **Drumm**.

Ryder, *E. A.* See *W. E.* **Garner.**
Ryschkewitsch, *E.*, melting point and vaporisation of graphite, ii, 276, 374.
Ryskaltchouk, *A.* See *S.* **Kostytschev.**
Rzymkovski, *J.*, determination of benzoquinone by means of thiosulphate, ii, 907.

S.

Sabalitschka, *T.*, and *W.* **Erdmann**, iodometric determination of methylene-blue, ii, 908.
Sabalitschka, *T.*, and *C.* **Jungermann**, behaviour of the alkaloids of alkaloid-containing seeds during germination, i, 1223.
simple determination of the alkaloid-content of nux vomica and of *Strychnos* preparations, ii, 608.
Sabalitschka, *T.*, and *G.* **Kubisch**, urea oxalates and their determination as secondary oxalate in fertilisers, i, 347.
Sabalitschka, *T.*, and *W.* **Moses**, behaviour of calcium fluoride in strong acids, ii, 417.
Sabalitschka, *T.*, and *G.* **Reichel**, alkalimetric determination of aluminium salts and free acids in the presence of one another, ii, 602.
Sabalitschka, *T.*, and *C.* **Schultze**, malt amylase. I. Determination of the dextrin-forming and saccharifying action of amylase. II. Influence of different experimental conditions on the action of amylase. III. Influence of adsorbents on the dextrin-forming and saccharifying action of amylase. IV. Influence of caffeine and aldehydes on the dextrin-forming and saccharifying action of amylase, i, 1358.
Sabbatani, *L.*, pharmacological investigations on iron. VI. Colloidal ferrous sulphide prepared in presence of sugar, i, 196.
Saccardi, *P.*, simplification in the detection of certain cations, ii, 158.
Saccharin-Fabrik, Aktien-Gesellschaft vorm. Fahlberg, List, & Co., preparation of mercury derivatives of phenols substituted in the nucleus, i, 1197.
Sacchetto, *I.*, lipin and fat metabolism of the liver cells of fasting animals and animals poisoned with phosphorus. III. Course of the fat-infiltration into surviving liver tissue *in vitro*, i, 1357.
Sachs, *G.*, hardening of metals, ii, 870.
Sachs, *G.*, and *L.* **Balassa**, coloured compounds of mercury sulphide and mercaptide, i, 1034.
Sachs, *G.*, and *H.* **Blessl**, mercury compounds of *o*-thiolbenzoic acid, i, 1274.
Sachs, *G.* See also *F.* **Saeftel.**
Sachs, *H.*, and *A.* **Klopstock**, serological differentiation of lecithin and cholesterol, i, 1486.
Sackett, *G. E.*, modification of Bloor's method for determination of cholesterol in blood, i, 995.
Sacklovski, *A.*, *X*-ray investigation of the structure of alloys, ii, 939.
Sacklovski, *A.* See also *F.* **Kruger.**
Sacks, *J.* See *B. H.* **Nicolet.**
Sad, *S.* See *R.* **Lesser.**
Sadikov, *W. S.*, products of the catalytic hydrolysis of goose feathers (investigation of the syrup soluble in amyl alcohol), i, 175.
nitrogen distribution in individual fractions of catalytically hydrolysed collagen, i, 176.
Sadikov, *W. S.*, and *A. K.* **Michailov**, micro determination of molecular weights by the method of K. Rast, ii, 32.
Saeftel, *F.*, and *G.* **Sachs**, mechanical properties and structure of some alloys with a restricted range of mixed crystals; silver-rich binary solid solutions containing magnesium, aluminium, tin, zinc, cadmium, and manganese, ii, 1051.
Saeger, *A.*, growth of duckweeds in mineral nutrient solutions with and without organic extracts, i, 755.
Saerens, *E.*, compressibility, internal pressure, and chemical affinity, ii, 91.
Safar, *I.* See *F.* **Kehrmann.**
Saftien, *K.*, acridine syntheses from 4:5-benzocoumarandione and aniline, i, 1318.
Saftien, *K.* See also *K.* **Fries.**
Sagastume, *C. A.*, and *C. E.* **Spegazzini**, biochemical method for the determination of vitamins, i, 209.
Saha, *M.*, spectrum of singly ionised silicon, ii, 1100.
phase rule and its application to problems of luminescence and ionisation of gases, ii, 1161.
Saha, *M.*, and *R. K.* **Swe**, influence of radiation on ionisation equilibrium, ii, 254.
Sahashi, *Y.*, occurrence of dihydroxyquinolinecarboxylic acid (the β-acid of Suzuki) in rice husks, i, 1520.
Sahli, *H.*, determination of the free acid of gastric juice, i, 458.
Sahlin, *B.*, effect of some potassium salts on succinodehydrogenase, i, 743.
Šahović, *K.*, blood coagulation in cold-blooded animals, i, 716.

Saillard, *E.*, Clerget's method (inversion coefficient of sucrose), i, 1133.
catalysis and the inversion of sucrose by acetic acid, ii, 307.
Saint, *S. J.*, relation between the p_H value, the lime requirement, and the thiocyanate colour of soils, i, 220.
St. George, *A. V.* See *M. A.* **Ramirez.**
St. Peter, *W. N.* See *H. M.* **Randall.**
Saitô, *M.* See *Y.* **Utida.**
Sakoschanasky, *A.*, fluorescent derivative of β-naphthol, i, 1061.
Sakurai, *K.*, re-formation of methæmoglobin. I. Experiments *in vitro*, i, 1199.
Salabartan, *J.* See *E.* **Aubel.**
Salant, *E. O.*, heat capacity of solid aliphatic crystals, ii, 1042.
Salauze, *J.*, electrolysis of alkali acetates in methyl-alcoholic solution, i, 504.
Saldau, *P.*, equilibrium in the system, gold–zinc, ii, 205.
Saldau, *P. J.*, measurement of electrical conductivity at high temperatures and its significance for explaining the nature of solid solutions, ii, 872.
Salgue, *R.* See *C.* **Levaditi.**
Salis, *G. von*, first spark spectra of zinc and cadmium, ii, 334.
Sallick, *M. A.* See *F. P.* **Underhill.**
Salmon, *W. D.*, vitamin-*B* in the excreta of rats on a diet low in this factor, i, 1516.
Saloman, *T.* See *H.* **Gault.**
Saltmarsh, *M. O.*, spectra of doubly and trebly ionised phosphorus, ii, 724.
Salvesen, *H. A.*, blood calcium under normal and pathological conditions, i, 713.
Salzmann, *G.* See *K.* **Hess.**
Samdahl, *B.*, condensation of menthone with *p*-tolualdehyde, i, 414.
Samec, hydrolysis of natural and synthetic amylophosphates by enzymes, i, 1504.
chemical properties of colloidal starch derivatives, ii, 1153.
Samet, *J.* See *I.* **Greenwald.**
Sammet, *K.* See *O.* **Lemmermann.**
Samoilov, *J. V.*, dehydration of kaolinite, ii, 698.
Samsoen, *M.*, expansion of glasses; boric anhydride, ii, 1051.
Samter, *W.* See *B.* **Pfyl.**
Samuel, *R.*, ionisation of potassium vapour by light, ii, 459.
Samyslov, *A.* See *A.* **Bach.**
Sanarelli, *G.*, "intestinal" anthrax, i, 477.
Sandberg, *M.*, and *E.* **Brand**, papain lipase, i, 1009.
Sandberg, *V.* See *H. von* **Euler.**
Sandeman, *I.*, secondary spectrum of hydrogen at higher pressures, ii, 909.
Sander, *K.* See *E.* **Waser.**
Sander, *L.*, "indine," *iso*indigotin, "hydrindine" and the inner anhydride of αβ-bis-*o*-aminophenylmalic acid [hydroxydihydro*iso*indigotin], i, 977.
indigoid dyes, i, 982.
Sander, *P.* See *H.* **Leuchs.**
Sandera, *K.*, influence of colloidal solutions on the electrocapillarity of mercury, ii, 659.
Sandera, *K.* See also *M.* **Cikrtová.**
Sanderson, *E. S.* See *P. E.* **Howe.**
Sando, *C. E.*, anthocyanin formation in *Helianthus annuus*, i, 1026.
Sandonnini, *C.*, certain physico-chemical properties of mixtures of water and acetone, ii, 765.
Sandoz, *M.* See *F.* **Kehrmann.**
Sands, *C. E.*, isolation and identification of quercetin in apple peels, i, 216.
Sandstrom, *W. M.* See *R. A.* **Gortner.**
Sané, *S. M.*, and *S. S.* **Joshi**, behaviour of nitrophenols with *p*-toluenesulphonyl chloride, i, 134.
Sani, *G.*, and *V.* **Grilli**, conservation and transformation of nitrogen in stable manure, i, 218.
Sanigar, *E. R.*, dropping mercury cathode. VIII. Electrolysis of some complex cyanides, ii, 676.
Sano, *S.*, effect of diffusion on time rate of chemical change, ii, 681.
time rates of vaporisation and chemical changes on surface of contact of two fluids, ii, 681.
Santi, *U.* See *D.* **Ganassini.**
Santomauro, *P.*, phytochemical reduction of methyl α-chloroethyl ketone, i, 203.
Sanyal, *R. P.*, and *N. R.* **Dhar**, induction periods in chemical reactions, ii, 136.
Sanyal, *R. P.* See also *N. R.* **Dhar.**
Sapper, *A.* See *H.* **Reihlen.**
Saprikin, *S.* See *I. L.* **Kondakov.**
Sarkar, *N. N.* See *R. N.* **Sen.**
Sarkar, *P. B.* See *P.* **Rây.**
Sarkar, *P. V.* See *P.* **Rây.**
Sas, *F. E. R.*, determination of morphine by conductometric titration with silicotungstic acid, ii, 1011.
Sasahara, *T.*, *X*-ray analysis of solid solutions of potassium chloride and potassium bromide, ii, 745.
Sasaki, *N.*, dissociation of polyatomic salts. I. and II., ii, 399, 512.
volumetric determination of iodides, ii, 433.

Sasaki, *R.*, metabolism of mineral salts in the animal body. I. Effect of alkali metals on the growth of animals, i, 331.

Sasaki, *R.* See also *S.* **Sawamura.**

Saslavsky, *I. I.*, dependence of coefficient of expansion of liquids on temperature and chemical structure, ii, 26.

contraction regularities in the formation of solid chemical compounds, ii, 933.

Sass, *L. von.* See *K. von* **Auwers.**

Satanovski, *S.*, organic phosphorus and calcium of the blood plasma during the development of callus in fracture, i, 1208.

Sattler, *L.*, improved Fischer vacuum fractionator, ii, 708.

Sattler, *L.*, and *B. R.* **Mortimer**, distilling flask for corrosive liquids, ii, 589.

Sauer, *E.*, and *E.* **Kinkel**, determination of the elasticity of gelatin gels, ii, 519.

Sauerwald, *F.*, and *G.* **Jackwirth**, nature of the martensitic structure [of steel], ii, 22.

Sauerwald, *F.*, and *E.* **Jaenichen**, force of adhesion between metal surfaces. IV. Synthetic metal structures, ii, 387.

Sauerwald, *F.*, and **Knehans**, relation between the hardness of metals and temperature, ii, 279.

Saunders, *F. A.* See *H. N.* **Russell**, and *T.* **Lyman.**

Saunders, *S. W.* See *W. E.* **Garner.**

Savaritzki, *N.* See *M.* **Vrevski.**

Saville, *W. B.*, and *G.* **Shearer**, *X*-ray investigation of saturated aliphatic ketones, ii, 366.

Saville, *W. B.* See also *Alex* **Müller.**

Savino, *E.*, effect of insulin on the phosphorus of the blood, i, 482.

Savron, *E.* See *A.* **Palladin.**

Sawamura, *S.*, and *R.* **Sasaki**, water-soluble proteins of *Fagopyrum esculentum*, Moench, i, 346.

Sawyer, *R. A.*, and *E. J.* **Martin**, vacuum spark spectrum of zinc in the region 2100–4000 A., ii, 1100.

Saxon, *R.*, electrolysis of equimolar mixtures, ii, 984.

electrolytic separation of alkali and alkaline-earth metals, ii, 984.

...ee, *L. A.*, and *H. V. A.* **Briscoe**, method of measuring the dielectric constants of liquids, ii, 263.

Sbarsky, *B.*, and *D.* **Michlin**, isolation of the perhydridase (Schardinger's enzyme) of milk, i, 472.

Sbarsky, *B.*, and *A.* **Muchamedoff**, adsorption of protein degradation products by the formed elements of the blood *in vivo* and *in vitro*. IV. Adsorption of certain amino-acids by the red blood-corpuscles, i, 451.

Sborgi, *U.*, double decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftharpoons Na_2B_4O_7+(NH_4)_2SO_4$, in aqueous solution. VIII., ii, 207.

electronic theory of the anodic behaviour of metals, especially those exhibiting passivity phenomena. I. and II., ii, 550.

Sborgi, *U.*, and *E.* **Bovalini**, double decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftharpoons Na_2B_4O_7+(NH_4)_2SO_4$, in aqueous solution. V., ii, 206.

Sborgi, *U.*, *E.* **Bovalini**, and *M.* **Medici**, double decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftharpoons Na_2B_4O_7+(NH_4)_2SO_4$, in aqueous solution. VI., ii, 207.

Sborgi, *U.*, and *E.* **Burichetti**, double decomposition, $(NH_4)_2B_4O_7+Na_2SO_4 \rightleftharpoons Na_2B_4O_7+(NH_4)_2SO_4$, in aqueous solution. VII., ii, 207.

Scagliarini, *G.*, additive compounds of stannic iodide and organic bases, i, 890.

complex derivatives of quinquevalent molybdenum, ii, 891.

Scagliarini, *G.*, and *A.* **Airoldi**, tervalent vanadium, i, 920.

Scagliarini, *G.*, and *G.* **Tartarini**, oxidation of complex sulphites of tervalent cobalt, ii, 1193.

Scarborough, *H. A.* See *W. I.* **Jones**, and *H.* **McCombie.**

Scarpa, *O.*, experiments on the conductivity and ionisation of electrolytes, ii, 128.

apparatus for physical chemistry laboratories, ii, 150.

Scarth, *G. W.*, elasticity of gelatin in relation to p_H and swelling, ii, 862.

Scatchard, *G.*, influence of gelatin on transport numbers, ii, 41.

activities of strong electrolytes. I. The activity of hydrochloric acid derived from the electromotive force of hydrogen–silver chloride cells, ii, 397.

activities of strong electrolytes. II. A revision of the activity coefficients of potassium, sodium, and lithium chlorides, and potassium hydroxide, ii, 397.

activities of strong electrolytes. III. The use of the flowing junction to study the liquid junction potential between dilute hydrochloric acid and saturated potassium chloride solutions; and the revision of some single electrode potentials, ii, 398.

Scatchard, *G.*, activities of strong electrolytes. IV. Application of the Debye–Hückel equation to alcoholic solutions, ii, 971.
Schaarschmidt, *A.*, new process of nitration with the aid of nitrogen oxides from the air or ammonia. I., i, 123. nitrogen peroxide, ii, 227.
Schaarschmidt, *A.*, *H.* **Balzerkiewicz**, and *J.* **Gante**, new process of nitration with the aid of nitrogen oxides from air or ammonia. II., i, 532.
Schaarschmidt, *A.*, *L.* **Hermann**, and *B.* **Szemzö**, [behaviour of] aldehydes and ethylene oxide in the Friedel–Crafts synthesis, i, 1278.
Schaarschmidt, *A.*, and *H.* **Hofmeier**, internal oxidation reactions with additive compounds of nitrogen tetroxide and olefines, i, 877.
Schaarschmidt, *A.*, *C.* **Mayer-Bugström**, and *J.* **Sevon**, new condensation products from anthracene and phenanthrene, i, 241.
Schaarschmidt, *A.*, and *M.* **Raeck**, condensation reactions with nitrosyl chloride, i, 380.
Schacherl, *R.* See *F.* **Feigl**.
Schade, *H.*, water fixation in colloids, from the medical point of view, ii, 36.
Schade, *W.* See *D.* **Vorländer**.
Schäfer, *A.*, absorptive power of lipoid mixtures, ii, 1149.
Schaefer, *A.* See *W.* **Dilthey**.
Schaefer, *R.*, and *F.* **Schmidt**, quinhydrone electrode for clinical p_H determinations, i, 611.
Schäfer, *W.* See *B.* **Helferich**.
Schaeffer, *B.* See *H.* **Remy**.
Schäffner, *A.* See *E.* **Waldschmidt-Leitz**.
Schalek, *E.* See *H.* **Freundlich**.
Schaller, *W. T.*, sincosite, a new vanadium mineral, ii, 152.
Schantl, *E.*, Goppelsroeder's reaction for aluminium and its application in microchemistry, ii, 440.
Schaposchnikov, *K.*, and *V. S.* **Fedorov**, mechanics of electrons and light quanta, ii, 1105.
Scharff, *J. W.* See *H. B.* **Newham**.
Scharlov, *L.* See *M.* **Vrevski**.
Schaulin, *A.* See *H.* **Kämmerer**.
Schaum, *K.* [with *W.* **Naumann**, *K.* **Unger**, and *H.* **Hoffarth**], changes in state of aggregation and polymorphism. V., ii, 1132.
Schaum, *K.*, and *A.* **Feller**, activation of chlorine by electric discharge, ii, 90.
Schaum, *K.*, and *P.* **Friederich**, alleged influence of light on electrophoresis, ii 220.
Schaum, *K.*, and *M.* **Funck**, photometric and spectrophotometric studies. IV. The influence of temperature on the absorption spectra of borax and phosphate beads, ii, 178.
Schaum, *K.*, and *W.* **Körig**, changes in state of aggregation and polymorphism. II. Microscopical study of transition processes, ii, 95.
Schaum, *K.*, and *W.* **Schleussner**, photochemical potential changes, ii, 985.
Schechtmann, *J.*, variation in the surface tension of solutions as a function of the concentration, ii, 1148.
Schedler, *J. A.* See *F.* **Kehrmann**.
Scheff, *G.*, red pigment obtained by treatment of normal human urine with *p*-dimethylaminobenzaldehyde, i, 855.
Scheffer, *F.*, interactions of quicklime in the soil, i, 624.
Scheffer, *F.* See also *E.* **Blanck**.
Scheffer, *F. E. C.*, and (*Miss*) *H. J. de* **Wijs**, ammonia solutions, ii, 783.
Scheffler, *K.*, Winkler's bromine method of determining the iodine value of fats, ii, 1008.
Scheibe, *G.* [with *G.* **Rössler**, and *F.* **Backenköhler**], mutability of the absorption spectra of non-polar compounds and halochromism of unsaturated ketones. II., ii, 352.
Scheibler, *H.*, isomerisation of *O*-acyl into *C*-acyl compounds under the catalytic influence of noble metals. I., i, 918.
Scheibler, *H.*, and *H.* **Friese**, mechanism of the Claisen cinnamic ester synthesis, i, 1417.
Scheibler, *H.*, *E.* **Marbenkel**, and *D.* **Bassanoff**, metallic compounds of the enolic forms of carbonyl compounds and their application to syntheses. IV. Reaction between ester-enolates and alkyl or acyl halides, i, 918.
Scheibler, *H.*, and *Otto* **Schmidt**, metallic compounds of the enolic forms of carbonyl compounds and their application to syntheses. III. Action of carbon monoxide on ketone- and ester-enolates, i, 917.
Scheibler, *H.*, *F.* **Sotschek**, and *H.* **Friese**, [tetrahydrofurfuraldehyde], i, 1298.
Scheiderer, *S.* See *F. L.* **Hahn**.
Scheil, *E.*, secondary crystallisation of steel, ii, 122.
Scheinost, *E.* See *B. M.* **Margosches**.
Scheljakin, *O.* See *W.* **Arzichovski**.
Scheller, *E.* See *F.* **Konrich**.
Schelte, *F.*, adsorption, ii, 286.

Schenck, *M.*, bile-acids. XII. A calculus from the rennet-sac of a goat. XIII. Presence of deoxycholic (choleic) acid in the hydrolysed bile of the goat, i, 854.
bile-acids. XIV. Occurrence of deoxycholic (choleic) acid in the hydrolysed bile of the sheep, i, 1488.
Schenck, *M.*, and *F. von* **Graevenitz**, preparation of tetramethylguanidines, i, 377.
Schenck, *R.*, chemical equilibrium between lead sulphide and its roasting products. III., ii, 1160.
Schenck, *R.*, and *W.* **Borkenstein**, chemical equilibria between lead sulphide and its roasting products. II., ii, 419.
Schenck, *R.*, and *A.* **Imker**, vapour pressure of germanium hydride, ii, 279.
Schepmann, *W.* See *A* **Lehne**.
Schepp, *R.* See *C. G.* **Schwalbe**.
Scherer, *P. C.* See *R. F.* **Chambers**.
Scherer, *W.* See *H.* **Wieland**.
Scheringa, *K.*, deliquescence of salts, ii, 296.
sensitive reaction for copper and bromine, ii, 326.
Scherpenberg, *A. L. van.* See *M. A. H. van den* **Hout**.
Scherrer, *W.* See *A.* **Pictet**.
Schertz, *F. M.*, determination of xanthophyll by means of the spectrophotometer and the colorimeter, i, 871.
physical and chemical properties of carotin and preparation of the pure pigment, i, 1024.
properties and preparation of pure xanthophyll, i, 1024.
Scheuing, *G.*, benzilic acid transformation, i, 44.
Scheuing, *G.*, and *A.* **Hensle**, potassium stilbenediol, i, 27.
Scheunert, *A.*, and *A. J.* **Candelin**, vitamins. V. Storage of vitamin-*A* by young white rats after administration of horseflesh to the mother during pregnancy, i, 1515.
Scheunert, *A.*, and *C.* **Hermersdörfer**, vitamins. IV. Content of vitamins-*A* and -*B* in horseflesh, i, 617.
Schidlöf, *A.*, quantum hypothesis and gas theory, ii, 843.
Schiebold, *E.*, hardening phenomena in metals as revealed by *X*-rays, ii, 186.
Schierkolk, *K.*, infra-red absorption spectrum of ammonia, ii, 180.
Schill, *E.*, and *J.* **Kunze**, influence of intravenous administration of urea on the non-protein nitrogen of the blood, i, 712.
Schilt, *W.* See *F.* **Hefti**.
Schimizu, *K.*, excretion of carbon in the urine on a normal and on a deficient dietary, i, 185.
Schimmel & Co., essential oils, i, 417.
Schlatter, *C.* See *T.* **Batuecas**.
Schlee, *H.*, and *W.* **Thiessenhusen**, silver-ion concentration in solutions of colloidal and complex silver preparations with special reference to their medicinal use. II., i, 197.
physico-chemical examination of medicinal silver preparations, ii, 114.
Schleicher, *A.*, pseudo-complexes, ii, 22.
Schleicher, *A.*, and *W.* **Schmitz**, intermediate compound of high molecular weight in the decomposition of $[Pt\,en_2]I_2$ by acids, ii, 704.
Schleicher, *A.*, and *L.* **Toussaint**, electrometric titration of hypochlorous acid, ii, 433.
electro-analytical precipitation of antimony, ii, 1004.
Schleicher, *A.*, and *W.* **Wesly**, electrometric titration of chlorous acid and its determination in presence of hypochlorus acid, ii, 433.
Schlemmer, *F.* See *R.* **Dietzel**.
Schlesinger, *E. F.* See *G.* **Haas**.
Schlesinger, *N.*, spatial relationships around the copper atom, i, 1249.
Schliessmann, *O.* See *G. F.* **Hüttig**.
Schleussner, *W.* See *K.* **Schaum**.
Schlœsing, *A. T.*, efficiency of catalysts [in oxidation of ammonia], ii, 566.
determination of nitrous vapours, ii, 599.
Schlöttig, *O.* See *E.* **Krause**.
Schlubach, *H. H.*, and *K.* **Maurer**, syntheses of polysaccharides. I. Synthesis of an *iso*trehalose, i, 888.
Schlubach, *H. H.*, and *G.* **Rauchalles**, fission of γ-methylfructoside by invertase; configuration of sucrose, i, 1243.
Schlubach, *H. H.*, and *W.* **Rauchenberger**, syntheses of polysaccharides. II. The galactosidoglucose of E. Fischer and E. F. Armstrong, i, 888.
Schlubach, *H. H.* See also *R.* **Kuhn**.
Schlumbohm, *H.* See *F.* **Krollpfeiffer**.
Schlundt, *H.*, and *A. F. O.* **Germann**, dielectric constant of liquid phosgene [carbonyl chloride], ii, 355.
Schmalfuss, *H.*, and *K.* **Kalle**, condensation of formaldehyde. I. Condensation with magnesium oxide, i, 116.
apparatus for concentrating specially sensitive solutions, ii, 320.

Schmalfuss, *H.*, and *H.* **Werner**, formation of pigments. III. Fermentative micro-detection of 1-α-amino-3:4-dihydroxyphenylpropionic acid in the presence of tyrosine; connexion between constitution and chromogenic properties, i, 1361.
extraction apparatus for solid substances at a raised temperature, ii, 234.
sensitive, qualitative method for the detection of oxygen with pyrogallol and potassium hydroxide, ii, 238.
apparatus for evaporating under diminished pressure liquids that "bump," ii, 590.
simple apparatus for extracting liquids with a specifically heavier solvent, ii, 897.
qualitative test for oxygen, ii, 1198.
Schmalfuss, *H.*, and *M.* **Wetzel**, Grignard's reaction in presence of water, i, 395.
Schmedes, *K.*, action of formaldehyde on alkylated methyluracils, i, 435.
Schmid, *E.*, increase of tensile strength and recovery of zinc crystals, ii, 752.
Schmid, *F.* See also *M.* **Polanyi**, and *P.* **Rosbaud**.
Schmid, *L.*, methylation of polysaccharides, i, 1386.
Schmid, *L.*, and *B.* **Bangler**, products of the condensation of 2-aminopyridine with fatty-aromatic ketones. I., i, 1459.
Schmid, *L.*, and *B.* **Recker**, alkali compounds of carbohydrates, i, 1386.
cryoscopic determinations of molecular weight in liquid ammonia, i, 1386.
Schmidt, *A.* See *A.* **Rollett**.
Schmidt, *C. F.* See *K. K.* **Chen**.
Schmidt, *C. L. A.* See *D. M.* **Greenberg**.
Schmidt, *D.*, polysaccharide produced by *Aspergillus niger*, i, 868.
Schmidt, *Erich* (Göttingen), absorption spectrum of oxygen in the extreme ultra-violet, ii, 336.
Schmidt, *Erich* (Münschen), and *A.* **Ascherl**, synthesis of α-hydroxyketones. I., i, 364.
Schmidt, *Erich*, and *W.* **Bartholomé** [with *E.* **Asmas**], bromotrinitromethane. III., i, 136.
Schmidt, *Erich*, *W.* **Haag**, and *L.* **Sperling**, incrustive substances of plants. VI., i 1370.
Schmidt, *Erich*, and *G.* **Malyoth**, incrustive substances of plants. V., i, 213.
Schmidt, *F.* See *R.* **Schaefer**.
Schmidt, *G.* See *O.* **Ruff**.
Schmidt, *G. C.*, atomic rays, ii, 251.
Schmidt, *H.*, ripening of photographic emulsions from the point of view of ionic deformation, ii, 810.
Schmidt, *H. W.* See *D. T.* **Ewing**.
Schmidt, *K.*, compressibility of some organic liquids, ii, 497.
Schmidt, *Otto* (Berlin). See *H.* **Scheibler**.
Schmidt, *Otto* (Karlsruhe). See *K.* **Freudenberg**.
Schmidt, *O. T.* See *R.* **Willstätter**.
Schmidt, *Richard*, mechanism of the reaction in the reduction of titanium tetrachloride with hydrogen and the behaviour of the reduction products in a vacuum, ii, 315.
Schmidt, *Rudolf*. See *H.* **Meerwein**.
Schmidt, *T.* See *Arthur* **Simon**.
Schmidt, *W.* See *H.* **Vollmer**.
Schmidt, *W.* (Marburg). See *K. von* **Auwers**.
Schmidt, *Werner*, carbon dioxide as a stimulant and a nutrient, i, 758.
Schmidtmann, *M.*, determination of hydrogen-ion concentration in tissues and in cells, i, 99.
Schmieder, *F.*, economy coefficients of phosphorescent substances, ii, 931.
Schmitt, *F.* See *H.* **Franzen**.
Schmitt-Krahmer, *C.*, determination of phosphoric acid in metabolic investigations, i, 613.
Schmitz, *B.*, preparation of the magnesium ammonium phosphate precipitate for the determination of phosphoric acid or of magnesia, ii, 67.
Schmitz, *E.*, calcium content of the growing embryo, i, 456.
Schmitz, *E.*, and *F.* **Chrometzka**, formation of lactic and phosphoric acids in the [salivary] gland, i, 859.
Schmitz, *W.* See *A.* **Schleicher**.
Schmitz-Dumont, *O.* See *H.* **Rheinboldt**.
Schmoss, *I. W.*, action of phosphorus on salts containing oxygen [nickel nitrate], ii, 889.
Schneider, *A.*, paramœcial method for determining the phenol coefficient of disinfectants, i, 1006.
Schneider, *A.* See also *C.* **Dhéré**.
Schneider, *K.* See *R.* **Willstätter**.
Schneider, *W.*, heat of transformation of martensite, ii, 95.

Schneider, *Walter*. See *H.* **Wieland.**
Schnell, *B.* See *K.* **Ziegler.**
Schnider, *O.* See *P.* **Karrer.**
Schniderschitsch, *N.* See *F. X.* **Erben.**
Schnücke, *R.*, phosphorus metabolism of certain moulds, particularly *Aspergillus niger*, i, 204.
Schob. See **Schümann.**
Schoder, *F.* See *W.* **Küster.**
Schöbl, *O.*, semiselective antiseptic effect of the vapours of vegetable oils, essential oils, their constituents, and similar compounds, i, 1006.
Schoeler, *A.* See *J.* **Gadamer.**
Schöller, *R.* See *A.* **Klemenc.**
Schoeller, *W. R.* See *A. R.* **Powell.**
Schön, *M.* See *W.* **Pauli.**
Schoen, *R.* See *C.* **Levaditi.**
Schönberg, *A.* [benzilic acid transformation], i, 254.
Schönberg, *A.* [with *R.* **Abelsdorff**, *B.* **Antonoff**, and *H.* **Kirchrath**], valency. II. Decomposition of organic substances, i, 557.
Schönberg, *A.* [with *H.* **Krüll**], preparation of dixanthylen from xanthion, i, 149.
Schönberg, *A.* [with *A.* **Rosenbach**, *H.* **Krüll**, and *U.* **Ostwald**], organic compounds of sulphur. III. Thioketones, i, 1300.
Schoenemann, *K.* See *D.* **Vorländer.**
Schönfeld, *R.* See *A.* **Fodor.**
Schoenmaker, *P.* See *A.* **Smits.**
Schoenówna, *J.* See *K.* **Dziewoński.**
Schoep, *A.*, dumontite, a new radioactive mineral, ii, 64.
crystal structure, chemical analysis, and dehydration of becquerelite and schoepite, ii, 235.
sklodowskite, a new uranium mineral and its relation to uranotile, ii, 235.
chemical composition of fourmarierite, ii, 236.
buttgenbachite, a new mineral, ii, 1196.
Schöpf, *C.* See *H.* **Wieland.**
Schoepfle, *C. S.*, preparation of triarylmethyl acetates, i, 811.
Schöppach, *A.* See *W.* **Elle.**.
Schörnig, *L.* See *J. von* **Braun.**
Schofield, *F. H.*, thermal and electrical conductivities of some pure metals, ii, 273.
Schofield, *R. K.*, and *E. K.* **Rideal**, kinetic theory of surface films. I. Surfaces of solutions, ii, 960.
Schollenberger, *C. J.*, calomel electrodes, ii, 711.
Schollenberger, *C. J.* See also *J. W.* **Ames.**
Scholz, *E.* See *F.* **Arndt.**
Schonland, *B. F. J.*, absorption of cathode rays in aluminium, ii, 459.
Schoorl, *N.*, structure of benzene, i, 894.
dehydrating power of salts, ii, 400.
determination of invert-sugar in presence of sucrose and development of invert-sugar in sucrose solutions, ii, 445.
determination of invert-sugar in presence of sucrose, ii, 828.
Schopflocher, *P.* See *R.* **Pummerer.**
Schorger, *A. W.*, seed hairs of the milkweed, i, 872.
Schorigin, *P.*, transformations of benzyl ethers. II., i, 1404.
Schott, *W.* See *E.* **Heuser.**
Schottky, *W.* [theory of the diffusion of positive and negative ions to the walls of a discharge tube], ii, 79.
Schou, *S. A.* See *H. B.* **Rasmussen.**
Schramme, *A.* See *A.* **Windaus.**
Schreckental, *G.* See *R.* **Seka.**
Schreinemakers, *F. A. H.*, in-, uni-, and multi-variant equilibria. XXVII. and XXVIII., ii, 124, 402.
equilibria in systems in which the phases are separated by a semi-permeable membrane. I.—X., ii, 399, 538, 869, 975, 1062, 1063.
in-, uni-, and multi-variant equilibria. XXIX. Influence of one or more new substances on an equilibrium in which a phase reaction may occur, ii, 975.
Schreinemakers, *F. A. H.*, *G.* **Berkhoff**, and *K.* **Posthumus**, system, cupric nitrate–ammonium nitrate–water, ii, 123.
Schreiner, *E.*, determination of the molecular thermal conductivity and the molecular heat of diatomic gases at low temperatures, ii, 97.
thermodynamics of quinhydrone electrodes; chemical constants of hydrogen, ii, 978.
Schriever, *H.* See *E.* **Wöhlisch.**
Schrödinger, *E.*, hydrogen-like spectra from the point of view of the polarisability of the atom-core, ii, 722.
statistical definition of entropy of an ideal gas, ii, 951.
Schroedter, *E.* See *D.* **Vorländer.**
Schroer, *E.*, benzene ring problem, i, 379.
Schroeter, *G.* [with *A.* **Gluschke**, *E. van* **Hulle**, and *S.* **Götzky**], hydrogenation of anthracene, i, 127.

Schroeter, *G.* [with *E. van* **Hulle**, and *H.* **Müller**], hydrogenation of phenanthrene, i, 130.
Schroeter, *G.* [with *E. van* **Hulle**, *A.* **Gluschke**, *G.* **Stier**, and *H.* **Müller**], chemistry of syntheses and degradations by means of aluminium chloride, i, 125.
Schroeter, *G.* [with *F.* **Zadek**, and *J.* **Hoffmann**], transformations of 5-tetralone [1-keto-1:2:3:4-tetrahydronaphthalene], i, 677.
Schroth, *A.* See *A.* **Klemenc**.
Schrutka, *W.* See *L.* **Kofler**.
Schryver, *S. B.*, *H. W.* **Buston**, and *D. H.* **Mukherjee**, isolation of a product of hydrolysis of the proteins hitherto undescribed, i, 794.
Schryver, *S. B.* See also *H. L.* **Kingston**, *J.* **Knaggs**, and *F. W.* **Norris**.
Schtschodro, *N.*, changes in the conductivity of coloured films on bleaching, ii, 1134.
Schtschukarev, *S.*, periodic classification of the elements from the point of view of the study of isotopes, ii, 462.
Schtschukina, *M.* See *A.* **Stepanov**.
Schuch, *A.* See *Erich* **Müller**.
Schükarev, *A.*, magneto-chemical phenomena, ii, 47, 264.
Schüler, *H.*, fine structures in the first lithium spark spectrum, ii, 339.
Schüler, *H.*, and *K. L.* **Wolf**, dispersion constants and critical electron velocities of molecular hydrogen, ii, 1118.
Schümann, and **Schob**, determination of small quantities of magnesium in copper–zinc alloys, ii, 902.
Schüssler, *H.* See *S.* **Goldschmidt**.
Schueter, *H.* See *M.* **Trautz**.
Schütz, *E.* See *E.* **Wöhlisch**.
Schütz, *L.* See *L.* **Taub**.
Schütz, *W.*, calcspar lenses for intense polarised light, ii, 706.
Schütz, *W.* See also *W.* **Gerlach**.
Schuhecker, *K.*, blood-sugar of the goat, i, 715.
Schulek, *E.*, Prussian-blue reaction, ii, 71.
determination of sulphide, polysulphide, and thiosulphate sulphur in solutions of alkali and alkaline-earth sulphides, ii, 327.
detection and determination of chloride, bromide, and thiocyanate in the presence of cyanide, ii, 432.
determination of formaldehyde, ii, 606.
detection and determination of chloride, bromide, and thiocyanate in the presence of cyanide, ii, 712.
Schulek, *E.*, determination of iodide, ii, 712.
determination of hypoiodite and iodate, hypobromite and bromate, and bromate and sodate in the presence of each other, ii, 1197.
Schuler, *H.*, and *K. L.* **Wolf**, continuous hydrogen spectrum, ii, 829.
Schuler, *K.* See *G.* **Weissenberger**.
Schulhof, *K.* See *L.* **Hektoen**.
Schulmann, *R.* See *M.* **Loeper**.
Schultz, *G.*, and *K. L.* **Ganguly**, chemical action of light on the polynitrotoluenes, i, 647.
Schultz, *G.* See also *R.* **Anschütz**.
Schultze, *C.* See *T.* **Sabalitschka**.
Schultze, *G.* See *K.* **Hess**.
Schultze, *H.* See *F.* **Krollpfeiffer**.
Schultze, *K.*, capillarity, evaporation, and efflorescence, ii, 287.
capillarity and wetting, ii, 856.
Schulz, *H.* See *G.* **Jander**.
Schulz, *L.* See *F.* **Eisenlohr**.
Schulz, *O. F.* See *F.* **Sommer**.
Schulz, *R. G.*, distribution of surface-active substances between water and organic solvents, ii, 956.
Schulz, *W.* See *R. J.* **Meyer**.
Schulze, *F.* See *H.* **Gilman**.
Schulze, *F. A.*, ratio of specific heats for liquids, ii, 491.
Schulze, *Heinrich*, and *Gottfried* **Berger**, aconite alkaloids; new alkaloid from *Aconitum napellus*, i, 282.
Schulze, *Herbert.* See *Wolfgang* **Ostwald**.
Schulze, *R.* See *F.* **Mayer**.
Schumacher, *J.*, chemistry of the action of salvarsan *in vitro* and *in vivo*, i, 733.
action of ter- and quinque-valent arsenic preparations, i, 733.
Schumann, *R.*, free energy and heat content of tellurium dioxide and of amorphous and metallic tellurium; reduction potential of tellurium, ii, 670.
Schumm, *O.*, formation of porphyrin from blood pigment. II., i, 88.
transformation of pigments in putrefying flesh, i, 341, 721.
porphyrins, i, 846.
natural hæmatin-like pigments and their related porphyrins, i, 854.
conversion products of the pigments of flesh and blood. IV. Production of porphyrins in flesh. V. Hæmochromogens and hæmatins derived from putrefied flesh and blood, and the related porphyrins, i, 1347.
Schuster, *F.*, theory of state of matter. I. Internal pressure, vapour pressure, and critical data, ii, 951.

Schuster, *F.*, theory of state of matter. II. Internal pressure, co-volume, and association, ii, 1142.
Schuster, *F.* See also *G.* **Weissenberger.**
Schwab, *E.* See *E.* **Abderhalden.**
Schwab, *G. M.*, ozone, ii, 149.
Schwab, *G. M.*, and *G.* **Hanke**, solubility of chlorine in carbon tetrachloride, ii, 190.
Schwab, *G. M.*, and *S.* **Loeb**, formation of nitric oxide by purely electrical means, ii, 150.
Schwaibold, *J.* See *F.* **Kieferle.**
Schwalbe, *C. G.*, determination of α-cellulose, ii, 720, 1209.
Schwalbe, *C. G.*, and *G. A.* **Feldtmann**, occurrence of *d*-glycuronic acid in vegetable fibres, i, 1238.
Schwalbe, *C. G.*, and *R.* **Schepp**, hydrolysis of solutions of magnesium chloride, i, 1045.
Schwalbe, *C. G.*, and *G.* **Teschner**, adsorption and swelling of cellulose fibres, i, 889.
Schwalbe, *H.*, determination of lignin, i, 643.
Schwarte, *G.* See *A.* **Windaus.**
Schwartz, *A.* See *L.* **Fournier.**
Schwarz, *F.*, metachromatic staining of plant cell-walls with substantive dyes. I. and II., i, 755.
Schwarz, *R.*, and *T.* **Hoefer**, mechanism of silane formation. II., ii, 418.
Schwarz, *R.*, and *E.* **Menner**, silicic acids. II., ii, 222.
Schwarz, *R.*, and *R.* **Walcker**, origin of natural aluminium hydrosilicates, ii, 887.
Schwarz, *R.*, and *H.* **Weiss**, photochemistry of complex compounds. I., ii, 576.
Schwarz, *R.* See also *F.* **Arndt.**
Schwarzkopf, *E.* See *A.* **Windaus.**
Schweikert, *G.* See *L.* **Grunmach.**
Schweitzer, *G. G.* See *F. F.* **Nord.**
Schweizer, *J.* See *W. H.* **Arisz.**
Schweizer, *K.* See *T. von* **Fellenberg.**
Scortecci, *A.* See *N.* **Parravano.**
Scott, *A.* See *J. W.* **Mellor.**
Scott, *A. F.*, relationship between atomic numbers and the properties of ions in the crystal lattice, ii, 369.
Scott, *D. A.*, action of trypsin on insulin, i, 870.
Scott, *D. A.*, and *C. H.* **Best**, preparation of insulin, i, 617.
sugar of the blood, i, 1343.
Scott, *J. W.* See *J. B.* **Collip.**
Scott, *N. D.*, and *T.* **Svedberg**, measurements of the mobility of egg-albumin at different acidities, ii, 204.
Scott, *W. O.* See *W. E.* **Lawson.**
Scott, *W. W.*, determination of lead in minute quantity, ii, 903.
inexpensive method for determining lead, ii, 903.
Scott-Blair, *G. W.*, periodic precipitation in dilute gelatin gels, ii, 519.
Scottish Dyes, Ltd. See *E. G.* **Beckett.**
Scremin, *L.*, chemical condition of circulating lead, i, 465.
Sčukarev, *S.* See *P.* **Lukirsky.**
Sehrbundt, *K.* See *R.* **Kunz.**
Sears, *F. W.* See *F. G.* **Keyes.**
Sears, *G. W.*, and *L.* **Quill**, fusion of rare-metal ores. I. Pyrosulphate fusion of titanium ores, ii, 580.
Sedgwick, *W. G.* See *W. H.* **Perkin**, *jun.*
Sedström, *E.*, gold–copper alloys, ii, 104.
Sedström, *E.* See also *S.* **Holgersson.**
Seekles, *L.*, refractivity of *o*-phthalaldehydic acid, i, 31.
Seekles, *L.* See also *B.* **Sjollema.**
Seelen, *D. von*, electrical conductivity of rock salt crystal, ii, 185.
Seeliger, *R.*, cooling of hot bodies in gases and liquids, ii, 492.
Seeliger, *R.*, and *W.* **Lindow**, spectrophotometric studies of the glow discharge, ii, 739.
Seeliger, *R.*, and *J.* **Ôkubo**, [intensity and distribution of] light emission from the striated discharge, ii, 79.
Segitz, *F. A.* See *F.* **Hein.**
Seguin, *L.* See *M.* **Francois.**
Seibert, *F. B.*, and *E. R.* **Long**, interfering effect of glycerol on the biuret reaction, i, 1110.
Seide, *O.*, action of sodamide on 3-methylpyridine, i, 72.
attempted preparation of 1:8-naphthyridine derivatives, i, 72.
constitution of "α-quinoquinolone," i, 159.
constitution of the 4-phenyl-1:8-naphthyrid-2-one of Pàlazzo and Tamburini; tautomerism of 2-aminopyridine, i, 487.
2-amino-3-methylpyridine, i, 1328.
Seidel, *C. F.* See *L.* **Ruzicka.**
Seiden, *R.*, influence of different external factors on the ash-content of plants, i, 1518.
Seidenberg, *S.* See *P.* **Rona.**
Seifert, *F.*, preparation of 1-alkyl*cyclo*hexan-3-ones, i, 407.
Seifert, *W.* See *A.* **Lottermoser.**
Seifriz, *W.*, emulsions. I. Hydrocarbon oil emulsions. II. Effect of electrolytes on petroleum oil emulsions, ii, 663.

Seifriz, *W.*, emulsions. III. Double reversal by the same electrolyte. IV. Multiple systems. V. Stabilisation membrane, ii, 779.
emulsions. VI. Effect of acidity on type and reversibility. VII. Effect of phase ratio and handling on type. VIII. Comparison of vegetable oils with petroleum oils, ii, 864.
Seisov, *K.* See *M.* **Popov**.
Seith, *W.*, effect of capillary-active substances on the surface tension of salt solutions; its relation to ionic hydration, ii, 961.
Seitz, *F.* See *E.* **Waldschmidt-Leitz**, and *R.* **Willstätter**.
Seitz, *W.*, asymmetric emission of electrons by *X*-rays. I. and II., ii, 168, 1034.
Seka, *R.*, heterocyclic ring systems. I. and II., i, 57, 1298.
substituted indole derivatives. II., i, 67.
8-aminoquinoline and its derivatives, i, 587.
Seka, *R.*, and *G.* **Schreckental**, pyridanthrone synthesis, i, 1316.
Seka, *R.* See also *E.* **Philippi**, and *E.* **Späth**.
Selim, *M.* See *D.* **Holde**.
Sélincourt, *M. de*, effect of temperature on the anomalous reflexion of silver, ii, 275.
Selivanov, *A.* See *S. S.* **Nametkin**.
Seljakov, *N.*, röntgenographic measurement of absolute dimensions of a single crystal in bodies of fine crystalline structure, ii, 270.
Seljakov, *N.*, and *A.* **Krasnikov**, new $K\beta_1$ doublet of the elements manganese and chromium, ii, 914.
Seljakov, *N.*, *L.* **Strutinski**, and *A.* **Krasnikov**, structure of glass, ii, 849.
Selke, *W.* See *D.* **Vorländer**.
Sellner, *E.* See *H.* **Lüers**.
Semencov, *A.* See *E.* **Grischkevitsch-Trochimovski**.
Semenov, *N.*, evaluation of the magnetic moment of atoms, ii, 618.
Sementschenko, *W.*, theory of binary electrolytes, ii, 117.
Semeria, *G. B.*, configuration of Δ^{α}-oleic acid, i, 5.
Semmens, *E. S.* See *E. C. C.* **Baly**.
Semon, *W. L.*, and *V. R.* **Damerell**, preparation of dimethylglyoxime, i, 1039.
Sen, *H. K.*, biochemical transformation of *as*-dichloroacetone into optically active $\alpha\gamma$-dichloropropan-β-ol, i, 203.
reduction of $\alpha\alpha$-dichloroacetone by yeast, i, 337.
Sen, *H. K.*, and *C.* **Barat**, reduction of *s*-dichloroacetone by yeast, i, 1241.
Sen, *J. N.*, and *T. P.* **Ghose**, vasicine; an alkaloid present in *Adhatoda vasica*, Nees, i, 958.
Sen, *K. C.*, stability of colloidal solutions. III. Coagulation of copper ferrocyanide sol, ii, 664.
theory of peptisation and protective effect of colloids and non-electrolytes, ii, 666.
Sen, *K. C.*, and *M. R.* **Mehrotra**, stability of colloidal solutions. II. Stability of colloidal solutions of chromium hydroxide and copper ferrocyanide in presence of stabilising ions and coagulation of the colloids by mixtures of electrolytes, ii, 665.
Sen, *N.* See *M. von* **Laue**.
Sen, *R. N.*, and *N. N.* **Sarkar**, condensation of primary alcohols with resorcinol and other hydroxy aromatic compounds, i, 812.
Sen, *R. N.*, *N. N.* **Sinha**, and *N. N.* **Sarkar**, condensations of chloroform, carbon tetrachloride, and iodoform with resorcinol and similar other hydroxy aromatic compounds, i, 916.
Sen, *R. N.*, and *S. S. G.* **Sircar**, condensation of resorcinol and other hydroxy aromatic compounds with some acids, esters, lactones, and lactams, i, 554.
Senderens, *J. B.*, preparation of ethers, i, 113.
preparation of *cyclo*hexenols by catalytic dehydration of *cyclo*hexanediols, i, 537.
Sendroy, *J.*, *jun.* See *A. B.* **Hastings**.
Senftleben, *H.*, action of radiation on gas mixtures, ii, 883.
Seng, *M. I.* See *D. W.* **MacKenzie**.
Senter, *G.*, and *A. M.* **Ward**, Walden inversion. VIII. Influence of the solvent on the sign of the product in the conversion of β-hydroxy-β-phenylpropionic acids into β-bromo-β-phenylpropionic acids, i, 31.
Walden inversion. IX. Influence of the solvent on the sign of the product in the conversion of β-bromo-β-phenylpropionic acids into β-hydroxy-β-phenylpropionamides, i, 1128.
Serebrijski, *J.* See *H.* **Vollmer**.
Serono, *C.*, *E.* **Trocello**, and *A.* **Cruto**, physiological action of insulin, i, 208.
Sessions, *W. V.* See *C. A.* **Kraus**.
Seth, *T. N.*, activation of pancreatic juice by enterokinase, i, 202.

Seth, *T. N.*, and *J. M.* **Luck**, relation between the metabolism and the specific dynamic action of amino-acids, i, 1002.
Seth, *T. N.* See also *J. M.* **Luck**.
Seuffert, *R. W.*, *T.* **Ito**, and *T.* **Yokoyama**, nitrogen, sulphur, and "formol" nitrogen on feeding amino-acids, i, 730.
Seuffert, *R. W.*, and *E.* **Marks**, influence of amino-acids on the decomposition of proteins, i, 730.
Sève, *P.*, optical properties of calamine, ii, 18.
Sever, *W.* See *D. H.* **Bangham**.
Sevon, *J.* See *A.* **Schaarschmidt**.
Sevringhaus, *E. L.*, and *M. E.* **Smith**, pancreatic response to carbohydrate ingestion, i, 727.
Sexl, *T.*, influence of occluded gas on the electrical resistance of a wire, ii, 642.
electric charges carried by individual microscopic particles, ii, 832.
Seyer, *W. F.*, and *A. F.* **Gill**, mutual solubility of sulphur dioxide and *n*-hexane, ii, 504.
Seyer, *W. F.*, and *J. L.* **Hugget**, mutual solubilities of cetene (hexadecene) and liquid sulphur dioxide, ii, 504.
Seyewetz, *A.* See *A.* **Lumière**.
Shadduck, *H. A.* See *D. T.* **Ewing**.
Shaffer, *I. W.*, effect of hydrogen-ion concentration on the precipitation of colloidal benzoin and gold solutions by cerebrospinal fluid, i, 326.
Shaffer, *S.* See *H. F.* **Lewis**.
Shannon, *E. V.*, and *E. S.* **Larsen**, merrillite and chlorapatite in stony meteorites, ii, 321.
Shannon, *M. J.* See *H.* **Ryan**.
Shapiro, *C. V.* See *W. R.* **Orndorff**.
Shark, *T. M.* See *T. A.* **Henry**.
Sharma, *R. K.*, spontaneous combustion of ethylene during the preparation of ethylene dichloride, i, 109.
Sharp, *J. F.* See *E. J.* **Bowen**.
Sharp, *P. F.*, wheat and flour studies. III. Amino-nitrogen content of the immature wheat kernel and the effect of freezing, i, 622.
Sharp, *T. M.* See **Wellcome Foundation, Ltd.**
Sharp & Dohme, Inc., and *A. R. L.* **Dohme**, preparation of alkylresorcinols and aralkylresorcinols, i, 541.
preparation of alkylresorcinols, i, 809.
Sharpe, *J. S.*, determination of guanidines in urine as picrates, i, 722.
Sharples, *E. H.* See *L. G.* **Radcliffe**.
Shaver, *W. W.*, extreme ultra-violet spectra of the alkali metals, ii, 451.
Shaver, *W. W.*, electrodeless discharge in the vapours of phosphorus and sulphur, ii, 471.
Shaver, *W. W.* See also *J. C.* **McLennan**.
Shaw, *B. D.*, 2:6-distyrylpyridine and its derivatives, i, 68.
fission of the pyridine nucleus during reduction. II. Preparation of glutardialdoxime, i, 299.
Shaw, *P. E.* See *H. W.* **Gilbert**.
Shaw, *T. P. G.*, heat of formation of acetaldol, ii, 644.
Shaw, *W. M.* See *W. H.* **MacIntyre**.
Shaw, *W. S.*, application of the "formol titration" to the Kjeldahl method of nitrogen determination, ii, 66.
Shaw, *W. S.* See also *D. R.* **Nanji**.
Shaxby, *J. H.*, *X*-ray analysis of mother-of-pearl, ii, 93.
Shearer, *G.*, *X*-ray investigation of the crystalline nature of china clays, etc., ii, 698.
distribution of intensity in the *X*-ray spectra of certain long-chain organic compounds, ii, 938.
Shearer, *G.* See also *W. B.* **Saville**.
Sheasby, *A. D.* See *G. T.* **Morgan**.
Sheely, *C.* See *A. E.* **Wood**.
Shelley, *H. J.* See *G. M.* **Goodwin**.
Shelton, *E. M.*, and *T. B.* **Johnson**, proteins. VII. Preparation of the protein "sericin" from silk, i, 602.
Shenstone, *A. G.*, low-voltage arc spectra of copper, ii, 77.
arc spectra of silver and copper, ii, 453.
analysis of the arc spectrum of copper, ii, 1014.
Sheppard, *A. B.* See *E. E.* **Turner**.
Sheppard, *S. E.*, photographic gelatin, ii, 966.
plasticity in relation to gelatin, ii, 1058.
apparently anomalous protection against oxidation, ii, 1084.
Sheppard, *S. E.*, and *E. K.* **Carver**, plasticity in relation to cellulose and cellulose derivatives, ii, 1058.
Sher, *B.* See *M. S.* **Kharasch**.
Sherman, *H. C.*, and *L. C.* **Boynton**, quantitative experiments on the occurrence and distribution of vitamin-*A* in the body, and the influence of the food, i, 1018.
Sherman, *H. C.*, *M. E.* **Caldwell**, and *N. M.* **Naylor**, influence of tryptophan and other amino-acids on the stability and enzymic activity of pancreatic amylase, i, 1007.
Sherman, *H. C.*, and *F. L.* **MacLeod**, calcium content of the body in relation to age, growth, and food, i, 1001.

Sherman, *H. C.*, and *F. L.* **MacLeod**, relation of vitamin-*A* to growth, reproduction, and longevity, i, 1019.
Sherman, *H. C.*, and *A. T.* **Merrill**, cystine in the nutrition of the growing rat, i, 730.
Sherman, *H. C.*, and *H. E.* **Munsell**, determination of vitamin-*A*, i, 1018.
Sherman, *H. C.*, and *L. B.* **Storms**, bodily store of vitamin-*A* as influenced by age and other conditions, i, 1019.
Sherman, *L. P.* See *J. W. E.* **Glattfield**.
Sherman, *M. S.* See *E. W.* **Guernsey**.
Sherrill, *M. L.*, reaction of bromonitromethane with aromatic compounds in the presence of aluminium chloride, i, 237.
Sherwin, *C. P.* See *L. R.* **Cerecedo**, and *A. R.* **Rose**.
Sherwood, *T. K.*, solubilities of sulphur dioxide and ammonia in water, ii, 852.
Shibata, *K.*, depolymerisation of proteins and re-synthesis of protein-like substances from the fission products, i, 1109.
Shidei, *J.*, composition of a precipitated aluminium hydroxide, ii, 1185.
Shikata, *M.*, electrolysis of nitrobenzene with the mercury dropping cathode. I. Reduction potential of nitrobenzene. II. Influence of the cathodic potential on the adsorption of nitrobenzene, ii, 304.
Shikata, *M.* See also *J.* **Heyrovský**, and *Z.* **Kontníková**.
Shilling, *W. G.* See *J. R.* **Partington**.
Shimo, *K.*, synthesis of *p*-hydroxyphenylglycine, i, 1423.
Shimomura, *A.*, action of acid anhydrides on benzidine, i, 981.
Shimura, *K.*, deposition, separation, and reabsorption of hæmoglobin in the organism and their relation to the deposition of iron pigment, i, 1342.
Shinoda, *G.*, metabolism in avitaminosis, i, 610.
Shinoda, *G.* See also *T.* **Brugsch**.
Shinoda, *J.* See *R.* **Robinson**.
Shinoda, *O.* See *S.* **Kato**.
Shiple, *G. J.* See *A. R.* **Rose**.
Shipley, *J. W.*, *I. R.* **McHaffie**, and *N. D.* **Clare**, corrosion of iron in absence of oxygen, ii, 688.
Shipley, *P. G.* See *E. V.* **McCollum**.
Shiver, *H. E.* See *G.* **Edgar**.
Shmook, *A.*, formation of the pyrrole ring by the action of ammonia on carbohydrates, i, 577.
Shoesmith, *J. B.*, and *J.* **Haldane**, condensation of diphenylformamidine with phenols. II. General nature of the reaction, i, 39.
Shoesmith, *J. B.*, and *R. H.* **Slater**, polarity effects in the isomeric ω-bromoxylenes and isomeric iodotoluenes, i, 16.
reduction of anethole nitrosochloride by stannous chloride and hydrochloric acid, i, 908.
Shohan, *J. B.* See *W. G.* **Christiansen**.
Short, *K.*, and *W. F.* **Short**, polymerisation of formaldehyde in presence of inorganic substances, i, 232.
Short, *W. F.*, condensation of phenylethylamine with *s*-dichlorodimethyl ether, i, 387.
Short, *W. F.* See also *K.* **Short**.
Shorter, *S. A.*, thermodynamics of water absorption by textile materials, ii, 789.
Shorter, *S. A.*, and *W. J.* **Hall**, hygroscopic capacity of wool in different forms and its dependence on atmospheric humidity and other factors, ii, 782.
Shriner, *R. L.* See *J. W.* **Kern**.
Shrivastava, *D. L.*, *R. S.* **Gupta**, *M.* **Prasad**, and *S. S.* **Bhatnagar**, chemical theory of the protective action of sugars. II., ii, 293.
Shrivastava, *D. L.* See also *S. S.* **Bhatnagar**, and *M.* **Prasad**.
Shrum, *G. M.* See *J. C.* **McLennan**.
Shukla, *P. P.* See *M. O.* **Forster**.
Shukov, *I.*, and *S. A.* **Stschoukarev**, distribution of hydrogen ions between gelatin and water, ii, 386.
Shumaker, *J. B.* See *H.* **Gilman**.
Shutt, *F. T.*, influence of grain growing on the nitrogen and organic matter content of the western prairie soils of Canada, i, 768.
Shutt, *W. J.* See *T. A.* **Heppenstall**.
Sickel, *H.* See *E.* **Abderhalden**.
Sidener, *C. F.* See *A. E.* **Stoppel**.
Sideris, *C. P.*, effect of hydrogen-ion concentration on the extracellular pectinase of *Fusarium cromyophthoron*, i, 1117.
rôle of hydrogen-ion concentration on the development of pigment in *Fusaria*, i, 1363.
Sidgwick, *N. V.*, structure of the enolic forms of β-keto-esters and β-diketones, i, 630.
behaviour of the simple halides with water, ii, 102.
Sidgwick, *N. V.*, and *E. K.* **Ewbank**, measurement of vapour pressures of aqueous salt solutions by depression of the freezing point of nitrobenzene, ii, 38.
hydration of salts and their effect on the vapour pressure of water, ii, 38.

Sidgwick, *N. V.*, and *S. G. P.* **Plant**, co-ordinated compounds of the alkali metals, i, 298.
Siebe, *P.*, action of iron on copper at high temperatures, ii, 317.
Siebel, *G.* See *G.* **Tammann.**
Sieber, *R.*, action of dilute acids on wood cellulose, i, 519.
Siebler, *G.* See *E.* **Rupp.**
Siedentopf, *H.*, form of ultramicrons, ii, 637.
Siedich, *A. S.*, bacterial decomposition of starch, i, 1510.
Siedschlag, *E.*, ternary system, chromium–nickel–molybdenum, ii, 298.
Sieg, *H.* See *A.* **Sonn.**
Siegbahn, *M.*, spectroscopic evidence of *J*-transformation of *X*-rays, ii, 727.
Siegbahn, *M.* See also *E.* **Bäcklin**, and *E.* **Hjalmar.**
Siegler, *E. H.*, and *C. H.* **Popenoe**, some insecticidal properties of the fatty acid series, i, 489.
Sieglitz, *A.*, and *H.* **Koch**, dibenzohomopyran, i, 278.
Sierakovski, *S.*, mechanism of alterations in the hydrogen-ion concentration of bacterial cultures, i, 204.
Sierakovski, *S.*, and *R.* **Zajdel**, rôle of carbon dioxide in bacterial cultures, i, 338.
Sieverts, *A.*, transformation velocity of ammonium nitrate, ii, 558.
Sieverts, *A.*, and *E.* **Roell**, absorption of hydrogen by cerium, lanthanum "mischmetall," and cerium-magnesium alloys, ii, 854.
Sigmund, *W.*, influence of the end-products of metabolism on plants. IV. Influence of nitrogen-free end-products of plant metabolism (resins, colouring matters) on the germination of seeds, i, 344.
Silbermann, *H.* See *F.* **Zetzsche.**
Silberrad, *C. A.* See *O.* **Silberrad.**
Silberrad, *O.*, photochemical action of iodine on moist *p*-chlorotoluene, i, 16.
Silberrad, *O.*, and *C. A.* **Silberrad**, selenium as chloride carrier, ii, 1191.
Silberrad, *O.*, *C. A.* **Silberrad**, and *B.* **Parke**, sulphuryl chloride. III. Influence of catalysts on the chlorination of toluene, i, 1137.
Silfversvärd, *B.* See *E.* **Kylin.**
Silmann, *S. H.* See *H.* **Pringsheim.**
Silverman, *A.* See *G. D.* **Kammer.**
Simek, *A.*, and (*Miss*) *H.* **Kadlcova**, electrokinetic phenomenon; electrocapillarity of fused tellurium dioxide, ii, 678.
Simington, *R. M.* See *H.* **Adkins.**
Simmonds, *N.* See *E. V.* **McCollum.**
Simms, *H. S.* See *P. A.* **Levene.**
Simon, *Alexander*, action of bismuth on the red blood-corpuscle, i, 1500.
Simon, *Arthur*, and *T.* **Schmidt**, hydrated ferric oxide and iron oxides, ii, 534.
Simon, *A. W.* See *A. H.* **Compton.**
Simon, *E.* See *C.* **Neuberg.**
Simon, *F.*, electrical conductivity of metals, ii, 94.
chemical constants of monatomic gases, ii, 98.
Simon, *L. J.*, structure of monobasic unsaturated acids and their behaviour on oxidation with sulphuric–chromic acid, i, 505.
relation between structure and the sulphochromic oxidation, i, 511.
chromic acid oxidation and molecular structure; tariric and stearolic acid derivatives, i, 778.
neutralisation of chloric acid by alkalis studied by viscosity measurements, ii, 288.
conditions for applying the argento-sulphochromic method in determining carbon, ii, 436.
viscosimetric neutralisation of monobasic acids by alkalis; comparison of alkali chlorates and bromates with nitrates, ii, 512.
Simon, *L. J.*, and *A. J. A.* **Guillaumin**, derivatives of tetra-acetylmucic acid, i, 116.
Simon, *L. J.*, and *V.* **Hasenfratz**, *l*-arabonolactone and some of its derivatives, i, 511.
Simon, *R. H.* See *J. W.* **Ames.**
Simon, *W.* See *H.* **Stobbe.**
Simonis, *H.* See *A.* **Löwenbein.**
Simonnet, *H.* See *H.* **Pénau.**
Simons, *L.*, *X*-ray emission of electrons from metal films, with special reference to the region of the absorption limit, ii, 81.
Simonsen, *J. L.*, constituents of some Indian essential oils. XIV. Essential oil from the seeds of *Zanthoxylum ovalifolium*, i, 565.
constituents of some Indian essential oils. XV. Essential oil from the seeds of *Juniperus communis*, i, 565.
constituents of some Indian essential oils. XIII. Essential oil from a new species of *Andropogon* occurring in the Etawah District, U.P., i, 1164.
Simonsen, *J. L.* See also *L. A. P.* **Anderson**, *C. S.* **Gibson**, and *M. G.* **Rau.**
Simpson, *C.* See *L.* **Higginbotham.**

Simpson, *G. E.*, urinary excretion of tartrates following administration to animals, i, 1211.
Simpson, *T. P.* See *H. J.* **Lucas.**
Sims, *H. des B.*, preparation and purification of bios. I., i, 1017.
Singer, *R.* See *K.* **Hess.**
Singh, *B. K.*, phototropism in solution. II. Optical activity as an aid to the study of phototropy, ii, 195.
Singh, *M.*, and *R.* **Singh**, carboxycamphoranilic acids, i, 1276.
Singh, *R.* See *M.* **Singh.**
Sinha, *N. N.* See *R. N.* **Sen.**
Sinozaki, *H.* See *R.* **Hara.**
Sircar, *A. C.*, and *P. C.* **Dutt**, dyes derived from phenanthraquinone. V. Phenanthraphenazinazines, i, 593.
Sircar, *A. C.*, and *B. K. S.* **Gupta**, dyes derived from phenanthraquinone. VI. Phenanthraquinone-phenyl azomethines and phenanthraphenazine azo dyes, i, 983.
Sircar, *A. C.*, and *N. C. G.* **Ray**, reaction between aromatic aldehydes and phenanthraquinone in presence of ammonia, i, 980.
Sircar, *S. S. G.* See *R. N.* **Sen.**
Sirk, *H.*, calculation of molecular diameters from heat of vaporisation and surface tension data, ii, 184.
molecular diameters, ii, 364.
Sisco, *F. T.*, and *M. R.* **Whitmore**, properties and structure of some alloys of aluminium and chromium, ii, 1051.
Sisson, *W. E.* See *H. J.* **Stander.**
Sitsen, *M. H. P.*, colorimetric determination of acetone in urine, i, 855.
Sittenberger-Kraft, *A.* See *E.* **Freund.**
Sittig, *L.* See *E.* **Friederich.**
Sjöberg, *K.*, Pringsheim's "amylase complement," i, 1504.
Sjöberg, *K.*, and *E.* **Eriksson**, amylase, i, 736.
Sjollema, *B.*, and *L.* **Seekles**, condensation of dihydroxyacetone and of methylglyoxal with thiocarbamide, i, 1175.
Skanavy-Grigorjeva, *M.* See *L. A.* **Tschugaev.**
Skene, *M.*, and *G. L.* **Stuart**, acidity produced in salt solutions by sphagnum, i, 765.
Skinner, *D. G.* See *G. T.* **Morgan.**
Skinner, *G. S.* See *V.* **Voorhees.**
Skinner, *H. W. B.*, relative absorbing powers of the *L*-levels for radiation of varying wave-length, ii, 5.
Skinner, *H. W. B.* See also *P.* **Kapitza.**
Skinner, *J. J.* See *F. E.* **Allison.**
Skita, *A.* [with *K.* **Warnat**, and *H.* **Reitmeyer**], nuclear hydrogenation of aromatic and heterocyclic compounds with colloidal platinum as catalyst, i, 140.
Skobeltzyn, *D.*, recoil effect in scattering of γ-rays, ii, 257.
effective wave-length of γ-rays, ii, 835.
Skrabal, *A.*, and *M.* **Baltadschieva**, rate of hydrolysis of ethyl orthocarbonate, ii, 139.
Skrabal, *A.*, and *A.* **Matievic**, dynamics of the malonic ester equilibrium, ii, 36.
Skrabal, *A.*, *F.* **Pfaff**, and *H.* **Airoldi**, hydrolysis of esters of ketonic acids, ii, 139.
Skraup, *S.*, and *K.* **Poller**, benzene substitution. I. Indirect substitution, i, 143.
Slansky, *P.*, catalysis of linseed oil oxidation. I., i, 114.
catalysis of linseed oil oxidation. II. Theory of the mechanism of catalysis, i, 115.
Slater, *J. C.*, quantum theory of optical phenomena, ii, 478.
methods for determining transition probabilities from line absorption ii, 734.
nature of radiation, ii, 926.
Slater, *J. C.* See also *G. R.* **Harrison.**
Slater, *R. H.* See *J. B.* **Shoesmith.**
Slater, *W. K.*, metabolic processes in *Ascaris lumbricoides*, i, 1208.
Slattery, *M. K.*, crystal structure of tellurium and selenium and of strontium and barium selenides, ii, 369.
Slawiński, *K.*, structure of dicyclic terpenes, i, 48.
Sligh, *T. S.*, automatic control of low temperatures, ii, 756.
Sligh, *T. S.* See also *N. S.* **Osborne.**
Sligh, *T. S., jun.* See *N. S.* **Osborne.**
Sloan, *A. W.* See *J. B.* **Conant.**
Sloan, *C. H.* See *J.* **Kendall.**
Slobodska-Zaykovska, *N.*, use of the milk-agar of Freudenreich in the investigation of lactic acid bacteria, i, 1510.
Slooten, *J. van.* See *P.* **Karrer.**
Slosse, *A.* See *P.* **Mendeléev.**
Slotta, *K. H.*, oxidation of uric acid glycols, i, 1189.
Slotta, *K. H.*, and *L.* **Lorenz**, carbimides. I. Preparation of aliphatic carbimides, i, 1047.
Sluyters, *A.* See *E.* **Laqueur.**
Sly, *C.* See *C. S.* **Hamilton.**
Slyke, *D. D. Van.* See *A.* **Hiller.**
Small, *J. O.*, viscosity of cotton cellulose, ii, 499.
Small, *L. F.* See *J. B.* **Conant.**

Smechel. See *D.* **Keller.**
Smedley, *S. P.* See *J. F.* **King.**
Smedt, *J. de,* diffraction of *X*-rays by polymerised liquids, i, 6.
Smedt, *J. de,* and *W. M.* **Keesom,** structure of solid nitrous oxide and carbon dioxide, ii, 484.
Smekal, *A.,* quantum theory of radioactive process. II., ii, 347.
" meta-stationary " atomic and molecular states, ii, 1022.
Smiles, *S.* See *C. M.* **Bere,** *D. T.* **Gibson,** *C. J.* **Miller,** and *R. F.* **Twist.**
Smillie, *W. G.,* and *S. B.* **Pessôa,** anthelmintic properties of the constituents of the oil of *Chenopodium,* i, 194.
Smirnov, *A. J.,* rôle of the mineral constituents in plants. II. Influence of neutral salts on peroxydase, i, 486.
Smirnov, *A. P.* See *P.* **Karrer.**
Smirnov, *V. A.* See *N. D.* **Zelinski.**
Smith, *A. H.,* a protein of the orange, i, 619.
Smith, *A. W.,* latent heat determinations, ii, 756.
Smith, *C. C.* See (*Miss*) *M. J.* **Field.**
Smith, *C. P.,* and *C. T.* **Zahn,** dielectric constants of ethane, ethylene, acetylene, and butylene, and the symmetry of unsaturated bonds, ii, 1118.
Smith, *D. F.,* rate of thermal decomposition of sulphuryl chloride; a first-order homogeneous gas reaction, ii, 876.
Smith, *D. F.* See also *G. N.* **Lewis,** and *R. F.* **Mehl.**
Smith, *E. R.,* moving boundaries and the phase rule, ii, 399.
Smith, *E. R.,* and *D. A.* **MacInnes,** transport numbers by the moving-boundary method. IV. Transport numbers of some chloride solutions, ii, 542.
Smith, *F. E.* See *A. T.* **Larson,** and *C. S.* **Marvel.**
Smith, *G. F.,* separation and determination of the alkali metals, using perchloric acid. I. Solubilities of the perchlorates of the alkali metals in mixed organic solvents, ii, 436.
Smith, *G. F.,* and *J. F.* **Ross,** separation and determination of the alkali metals, using perchloric acid. II. Precise determination of the insoluble alkali metal perchlorates, ii, 437.
separation and determination of the alkali metals, using perchloric acid. III. *n*-Butyl alcohol and ethyl acetate as mixed solvents in the separation and determination of potassium, sodium, and lithium, ii, 601.
Smith, *H. F.,* combustion of carbon. III., ii, 1085.
Smith, *H. F.,* and *W. C.* **Ebaugh,** combustion of carbon. I., ii, 888.
Smith, *H. G.,* fine structure of band spectra of sodium, potassium, and sodium–potassium vapours, ii, 86.
spiral springs of quartz, ii, 818.
Smith, *H. H.* See *E. M.* **Hume.**
Smith, *I. A.* See *A.* **McKenzie.**
Smith, *J.* See *H. G.* **Rule.**
Smith, *J. C.,* micro-determination of methoxyl, ii, 905.
Smith, *J. D. M.,* tridentate groups in complexes of tetrahedral and octahedral symmetry, ii, 841.
distribution of electrons in atoms, ii, 1023.
Smith, *J. D. M.* See also *G. T.* **Morgan.**
Smith, *J. E.,* spark photography as a means of measuring rate of explosion, ii, 804.
Smith, *J. H.,* molecular symmetry in crystal structure, ii, 271.
Smith, *L. E.* See *H.* **Gilman.**
Smith, *L. F.* See *G. A. R.* **Kon.**
Smith, *L. I.,* action of certain reagents on ozone, ii, 890.
laboratory ozoniser yielding high concentrations of ozone, ii, 896.
Smith, *L. L.* See *L. A.* **Congdon.**
Smith, *M. E.* See *E. L.* **Sevringhaus.**
Smith, *M. I.,* and *W. T.* **McClosky,** bio-assay of pituitary extracts; action of the standard infundibular powder on the secretion of urine, i, 207.
dialysis of the physiologically active constituents of the infundibulum, i, 207.
Smith, *R. C.,* physical state of catalysts, ii, 1072.
Smith, *R. G.,* decay of the xylem of the apple caused by *Polystictus versicolor,* Fr., i, 1226.
Smith, *R. G.* See also *A.* **Hunter.**
Smith, *S.,* electrically exploded wires, ii, 1017.
Smith, *S.* See also *R. J.* **Lang.**
Smith, *T. O.* See *H. R.* **Kraybill.**
Smits, *A.,* influence of intensive drying on internal change. II., ii, 116.
electromotive behaviour of aluminium. I., ii, 130.
composition of simple substances as revealed by intensive drying, ii, 268.
influence of intensive drying on inner equilibrium, ii, 532.
electromotive behaviour of magnesium, ii, 544.
electrical overvoltage, ii, 547.

Smits, *A.*, and *H.* **Gerding**, electromotive behaviour of aluminium. II., ii, 794.
Smits, *A.*, *H.* **Gerding**, and (*Miss*) *R.* **Kroon**, potentials of metals against pure water, ii, 795.
Smits, *A.*, and *A. J.* **Rutgers**, complexity of the solid state. II. Behaviour of phosphorus pentoxide. I., ii, 268.
Smits, *A.*, and *P.* **Schoenmaker**, complexity of the solid state. I. Behaviour of pure sulphur trioxide. I., ii, 267.
Smits, *A.*, and *G.* **Wallach**, pyrophoric phenomenon in iron, ii, 276.
Smolczyk, *E.* See *F.* **Auerbach.**
Smolenski, *K.*, acetic acid as a hydrolysis product of pectin, i, 216.
Smolik, *L.*, displacement of aluminium by potassium ions in different soils, i, 1032.
hydrogen peroxide catalase of marsh soils, i, 1524.
Smorodincev, *I. A.*, and (*Mlle.*) *A. N.* **Adova**, influence of some quinine preparations on the fermentation processes of the organism. III. Effect of some compounds of quinine and urea on α-proteases, i, 335.
standards for the colorimetric determination of trypsin, i, 473.
limits of precipitability of gelatin by tannin. I., i, 847.
Smrz, *J.*, dropping mercury cathode. IX. Tin, ii, 677.
Smyth, *C. P.*, refraction and electron constraint in ions and molecules, ii, 843, 1019.
electric moments of the molecules of monocarboxylic acids and their esters, ii, 846.
Smyth, *H. D.*, primary and secondary products of ionisation in hydrogen, ii, 459.
Smythe, *W. R.* See *J. A.* **Becker.**
Snapper, *J.*, *A.* **Grünbaum**, and *S.* **Sturkop**, oxidation of benzyl alcohol and benzyl esters in the human organism, i, 467.
Snedker, *S. J. C.*, mechanism of the formation of thiocarbanilide, i, 385.
Snellgrove, *D. R.* See *J.* **Kenyon.**
Snow, *H. R.* See *M.* **Gomberg.**
Snyder, *E. F.* See *W. C.* **Holmes.**
Soames, *K. M.*, growth-promoting and anti-rachitic value of cod-liver oil when injected intraperitoneally, i, 210.
Soames, *K. M.* See also *R.* **Robison.**
Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, *A. R.* **Wahl**, and *R.* **Lantz**, new derivatives of naphthaquinone, i, 413.
Société Chimique des Usines du Rhône, preparation of *r*-*o*-dihydroxyphenylethanolmethylamine hydrochloride, i, 136.
Society of Chemical Industry in Basle, preparation of intermediate products [triazines], i, 441.
preparation of aryl 4-hydroxynaphthyl ketones, i, 558.
preparation of asymmetrically acylated derivatives of ethylenediamine and their *N*- and *C*-substituted compounds, i, 1133.
preparation of anthracene-2-thioglycol-3-carboxylic acid, i, 1150.
alkyl esters of α-dialkylaminomethyl-α-alkylacetoacetic acid, i, 1249.
anthraquinone- and anthracene-oxythionaphthens, i, 1312.
Sobotka, *H.*, dried yeast, i, 865.
Sobotka, *H.* See also *P. A.* **Levene.**
Soden, *H. von*, essential oils obtained by extracting fresh flowers with volatile solvents (essential flower-extract oils). II., i, 1123.
Soderman, *M. A.*, and *T. B.* **Johnson**, utilisation of *p*-toluidine in the synthesis of aromatic esters of the novocaine type, i, 814.
Söderbäck, *E.*, action of free thiocyanogen on unsaturated compounds, i, 899.
Sönksen, *J.* See *O.* **Mumm.**
Soep, *L.*, surface tension crystal *v.* saturated solution; the concentration cell: finely divided salt | supersaturated solution ‖ saturated solution | large crystals, ii, 1046.
Sörensen, *M.*, determination of small quantities of phosphorus in proteins, ii, 900.
Sörensen, *M.*, and *S. P. L.* **Sörensen**, proteins. VII. Coagulation of proteins by heating, ii, 518.
Sörensen, *S. P. L.*, solubility of proteins, i, 602.
proteins. VIII. Solubility of the serum-globulins, i, 1110.
Sörensen, *S. P. L.* See also *M.* **Sörensen.**
Sörensen, *T.* See *C. N.* **Riiber.**
Sokhey, *S. S.* See *C. H.* **Fiske.**
Solaja, *B.*, gravimetric determination of aluminium and its separation from manganese by the use of "infusible white precipitate," ii, 602.
Solari, *A. A.*, chemical composition of normal and luetic sera, i, 858.
Solé, *A.* See *A.* **Fröhlich.**
Sollman, *T.* See *R. L.* **Howard.**
Solnijeva, *A. E.* See *A. A.* **Kalushski.**
Solomon, *I.* See *P.* **Pagniez.**

Somazzi, *S.*, rapid determination of the acid value of oils, ii, 828.
Somerville, *R.* See *T. S.* **Patterson.**
Someya, *K.*, selective determination of vanadium in presence of iron and chromium. I. Determination of vanadium in presence of iron, ii, 161.
use of liquid amalgams in volumetric analysis. II. Determination of tungsten, etc., by means of lead and bismuth amalgams, ii, 904.
use of liquid amalgams in volumetric analysis. III. Determination of phosphorus by means of lead amalgam, ii, 1200.
Sommelet, *M.*, diphenylmethane series; benzhydryltrimethylammonium bromide, i, 247.
synthesis of homologues of benzyl chloride, i, 803.
Sommer, *F.*, *O. F.* **Schulz**, and *M.* **Nassau**, amidopersulphuric acid [hydroxylamine*iso*monosulphonic acid], ii, 939.
Sommer, *L. A.*, spark spectrum of cæsium, ii, 4.
Sommer, *L. A.* See also *K.* **Bechert.**
Sommerfeld, *A.*, theory of the periodic system, ii, 177.
quantum theory and the Bohr atom, ii, 835.
Sommerfeld, *A.*, and *H.* **Hönl**, intensity of multiplet lines, ii, 468.
Sommermeyer, *E.* See *F.* **Krollpfeiffer.**
Sonn, *A.* [with *Ernst* **Müller**, *W.* **Bülow**, and *W.* **Meyer**], syntheses with 3:4:5-trimethoxybenzaldehyde, i, 932.
Sonn, *A.*, and *W.* **Bülow**, tautomerism of derivatives of phloroglucinol; monomethyl derivatives of phloroacetophenone, i, 1267.
Sonn, *A.*, *E.* **Hotes**, and *H.* **Sieg**, synthetic experiments in the glyoxaline group, i, 157.
Sonn, *A.*, and *W.* **Meyer**, conversion of trimethylgallic acid into trimethylgallaldehyde [3:4:5-trimethoxybenzaldehyde], i, 931.
Sonn, *A.*, and *E.* **Patschke**, preparation of *Bz*-hydroxycoumarone compounds, i, 282.
substitution in the benzene nucleus; varying influence of certain alkoxy groups on the synthesis of aldehydes by means of hydrocyanic acid, i, 1279.
Sonn, *A.*, and *W.* **Rosinsky**, configuration of the malic acids, i, 1237.
Sonnenschein, *L.* See *R.* **Weiss.**
Soper, *F. G.*, hydrolysis of acylchloroamines in water, i, 381.
Soper, *F. G.*, ionisation constant of hypochlorous acid, ii, 37.
Sorensen, *A. J.*, magnetic properties of thin films of ferromagnetic metals produced by the evaporation method, ii, 82.
Sorg, *K.*, lipoids in the testes of cattle, i, 457.
Sorrels, *J. H.* See *W. M.* **Walker.**
Sosman, *R. B.*, and *E.* **Posnjak**, artificial and natural ferromagnetic ferric oxide, ii, 944.
Sossiedov, *L.* See *A. V.* **Blagovestchenski.**
Sotschek, *F.* See *H.* **Scheibler.**
Sottery, *C. T.* See *L. P.* **Hammett**, and *J. M.* **Nelson.**
Soule, *B. A.*, detection and determination of nickel by means of α-furildioxime, ii, 603.
Southgate, *H. W.*, effect of fermentation on the water-soluble vitamin content of [beer] wort, i, 209.
effect of alcohol, under varying conditions of diet, on man and animals, with some observations on the fate of alcohol in the body, i, 1503.
effect of high temperatures on the accessory food factor content of cod-liver oil, i, 1515.
Spacu, *G.*, detection of copper, ii, 1003.
separation of copper and mercury, ii, 1004.
separation of iron from mercury, ii, 1206.
Spängler, *T.* See *T. H.* **Faust.**
Späth, *E.*, synthesis of ψ-ephedrine, i, 291.
Späth, *E.*, and *E.* **Bernhauer**, laudanidine, i, 294.
Späth, *E.*, and *O.* **Brunner**, constitution of physostigmine [eserine], i, 574.
Späth, *E.*, and *A.* **Dobrowsky**, alkaloids of *Corydalis cava*; corybulbine and *iso*corybulbine, i, 1085.
Späth, *E.*, and *R.* **Duschinsky**, alkaloids of the calumba root. III. Constitution of columbamine and jatrorrhizine, i, 1313.
Späth, *E.*, and *G.* **Koller**, synthesis of ψ-ephedrine, i, 1086.
new synthesis of ricinine. IV., i, 1446.
Späth, *E.*, and *E.* **Kunz**, jaborandi alkaloids. I. Pilocarpidine, i, 575.
Späth, *E.*, and *E.* **Mosettig**, corydalis alkaloids. V. Constitution of corypalmine, i, 1447.
Späth, *E.*, and *R.* **Seka**, constitution of tritopine, i, 1093.

Späth, *E.*, and *W.* **Stroh**, calycanthine, i, 1447.
Speakman, *H. B.*, biochemistry of acetone formation from sugars by *Bacillus acetoethylicum*, i, 1013.
Speakman, *J. B.*, wool as an amphoteric colloid. II. Chemical theory of dyeing, ii, 515.
Speakman, *J. B.*, and *A. E.* **Battye**, anomalous adsorption of dyes by wool and cotton, ii, 284.
Speer, *W.* See *H.* **Lecher**.
Spegazzini, *C. E.* See *C. A.* **Sagastume**.
Speidel, *P. E.* See *P.* **Rona**.
Speight, *E. A.*, *A.* **Stevenson**, and *J. F.* **Thorpe**, influence of substituents on the formation of derivatives of 1-hydrindone from β-phenylpropionic acids, i, 32.
Spek, *J. van der*. See *R. M.* **Barnette**, and *D. J.* **Hissink**.
Spence, *B. J.*, vibration–rotation spectrum of gaseous ammonia at 3 μ, ii, 350.
Spencer, *D. A.*, action of bromine on sodium and silver azides, ii, 416.
Spencer, *E.*, albite and other authigenic minerals in limestone from Bengal, ii, 1092.
Spencer, *G. C.* See *W. D.* **Collins**, and *R. M.* **Hann**.
Spencer, *L.* See *H. F.* **Coward**.
Spencer, *R. C.* See *F. K.* **Richtmyer**.
Spengler, *J. G. F. van*, determination of urobilin in urine and fæces; rôle of the liver in excretion of urobilin, i, 1351.
Spengler, *W.* See *C.* **Bülow**.
Sperfeld, *F.* See *F.* **Groebbels**.
Sperling, *L.* See *Erich* **Schmidt**.
Speyer, *E.*, and *K.* **Koulen**, α-methylmorphimethine and its isomerides, i, 59.
Speyer, *E.*, and *H.* **Rosenfeld**, preparation of monobromo- and monochloro-codeine and their behaviour on catalytic reduction, i, 961.
action of thionyl chloride on codeine and its isomerides, i, 961.
action of sodium hyposulphite on bromocodeinone, i, 961.
dihydrothebenine and its degradation, i, 961.
action of cyanogen bromide on thebaine, i, 962.
Spielmeyer, *G.* See *G.* **Heller**.
Spiers, *C. H.*, and *J. F.* **Thorpe**, influence of valency direction on the dissociation constants of dibasic acids, ii, 395.
Spiers, *C. W.* See *M.* **Nierenstein**.
Spilker, *G.* See *R.* **Fricke**.
Spinka, *J.*, effect of ultra-violet radiations on accessory food factors. I. Vitamin-*A*. II. Vitamin-*B*. III. Vitamin-*C*. IV. Vitamin-*D*., i, 212.
Spirescu, (*Mlle.*) *E.* See *A.* **Ionescu**.
Spitalsky, *E.*, and *N.* **Petin**, catalysis of hydrogen peroxide by iron salts, ii, 53.
Spitzin, *V. I.*, reduction of tungstates, ii, 1191.
Sponer, *H.*, spectral series of lead and tin, ii, 454.
Sponsler, *O. L.*, *X*-ray diffraction patterns from plant fibres, ii, 844.
Spoon, *W.*, occurrence of quebrachitol and sugar in *Hevea* latex under various conditions, i, 621.
Spooner, *T.*, effect of a superposed alternating field on apparent magnetic permeability and hysteresis loss, ii, 487.
Sporing, *P. A.*, equilibrium across a parchment membrane in the case of sodium chloride in presence of sodium caseinate, ii, 119.
Spreckels, *E.* See *D.* **Vorländer**.
Springer, *J. W.*, electrolytic determination of zinc [in the presence of copper], ii, 241.
Sprock, *G.* See *B.* **Helferich**.
Spuij, *M. J. van der*, determination of the phosphorus requirements of soils, i, 1524.
Squires, *B. T.* See *H. W.* **Kinnersley**.
Srikantia, *C.* See *M. G. S.* **Rao**.
Stadnichenko, *T.* See *H. S.* **Roberts**.
Stadnikov, *G.*, vapour pressure–water content diagrams and adsorption power of aniline black, ii, 771.
Stadnikov, *G.*, and *N. N.* **Gavrilov**, technical preparation of colloidal ferric hydroxide solutions, ii, 861.
Stählinger, *W.* See *R.* **Kunz**.
Stärkle, *M.*, formation of methyl ketones during the oxidative degradation of triglycerides and fatty acids by moulds with reference to the rancidity of coconut oil. I. Significance of methyl ketones in butter rancidity. II. Occurrence and significance of methyl ketones as odoriferous substances in Roquefort cheese, i, 205.
Staesche, *M.* See *G.* **Grube**.
Stafford, *J.* See *D. H.* **Bangham**.
Stahn, *R.* See *W.* **Traube**.
Stallmann, *O.* See *K.* **Brand**.
Stalony-Dabrovski, *J.*, scintillations in zinc sulphide, ii, 1027.
Stamm, *A. J.*, determination of the distribution of size of particles in emulsions, ii, 1153.

Stamm, *A. J.*, and *T.* **Svedberg**, use of scattered light in the determination of the distribution of size of particles in emulsions, ii, 774.
Stamm, *A. J.* See also *E. O.* **Kraemer.**
Stamm, *J.*, phenolphthalin as a reagent for hydrocyanic acid, ii, 75.
fluorescin as a reagent for hydrocyanic acid, ii, 76.
Stammreich, *H.*, proof of the formation of gold from mercury, ii, 1208.
Standenath, *F.*, effect of lecithin, cholesterol, and cholesterol derivatives on tryptic digestion, i, 473.
Standenath, *F.* See also *H.* **Pfeiffer.**
Stander, *H. J.*, *E. E.* **Duncan**, and *W. E.* **Sisson**, toxæmias of pregnancy, i, 1492.
Stanford, *R. V.*, and *A. H. M.* **Wheatley**, determination of calcium in blood, i, 1199.
determination of phosphorus compounds in blood, i, 1200.
distribution of phosphorus compounds in blood, i, 1200.
Stanley, *E.* See *F. L.* **Pyman.**
Stanley, *H. M.* See *G. T.* **Morgan.**
Stanoyévitch, *L.* See *F.* **Kehrmann.**
Stapelfeldt, *F.* See *H.* **Freundlich.**
Starczevska, (*Mlle.*) *H.* See *W.* **Swientoslawski.**
Starkenstein, *E.*, dependence of diuresis on the salt content and hydrogen-ion concentration of the water ingested, i, 327.
Starkey, *R. L.*, physiology of *Thiobacillus thio-oxidans*, an autotrophic bacterium oxidising sulphur under acid conditions, i, 1015.
carbon and nitrogen nutrition of *Thiobacillus thio-oxidans*, i, 1015.
Starkweather, *H. W.* See *G. P.* **Baxter.**
Starling, *E. H.*, and *E. B.* **Verney**, secretion of urine as studied on the isolated kidney, i, 458.
Starling, *E. H.* See also *F.* **Eichholtz.**
Starlinger, *W.*, and *K.* **Hartl**, determination of fibrinogen. III., i, 716.
Stary, *Z.*, brominated keratin and hydroxykeratin. II., i, 847.
Stary, *Z.*, and *I.* **Andratschke**, scleroproteins, i, 1480.
Starzevska, *M.*, influence of asparagine and ammonium nitrate on the nitrogen metabolism of ruminants, i, 1115.
effect of administration of sodium nitrate on the alkalinity of the urine of a ruminant, i, 1355.
Starzevska, *M.* See also *F.* **Rogozinski.**
Stas, *J.*, reducing action of organomagnesium compounds, i, 1052.
Stasiak, *A.*, action of santonin on blood-sugar, i, 1501.
Stassfurth, *T.* See *G.* **Tammann.**
Stather, *F.* See *M.* **Bergmann.**
Staub, *M.* See *P.* **Karrer.**
Staudinger, *H.*, highly polymerised compounds. V. Constitution of the polyoxymethylenes and other highly polymerised substances, i, 362.
autoxidation of organic compounds. V. Constitution of ozonides, i, 897.
autoxidation of organic compounds. III. Autoxidation of *as*-diphenylethylene, i, 898.
explosions with alkali metals, ii, 1181.
Staudinger, *H.* [with *F.* **Felix**, *E.* **Geiger**, *H.* **Harder**, *P.* **Meyer**, and *E.* **Stirnemann**], ketens. L. Additive and polymerisation reactions of dimethylketen. I. New compounds of dimethylketen and carbon dioxide, i, 786.
Staudinger, *H.*, *K.* **Dyckerhoff**, *H. W.* **Klever**, and *L.* **Ruzicka**, autoxidation of organic compounds. IV. Autoxidation of ketens, i, 933.
Staudinger, *H.*, and *W.* **Kreis**, experiments with a hot and cold quartz tube, ii, 316.
Staudinger, *H.*, and *M.* **Lüthy**, highly polymerised compounds. III. Constitution of the polyoxymethylenes, i, 360.
highly polymerised compounds. IV. Tri- and tetra-oxymethylenes, i, 361.
Staudt, *W.*, preparation of sarcosine ester, i, 1133.
Steacie, *E. W. R.*, and *F. M. G.* **Johnson**, viscosities of the liquid halogens, ii, 876.
Stearn, *A. E.* See *E. W.* **Stearn.**
Stearn, *E. W.*, and *A. E.* **Stearn**, chemical mechanism of bacterial behaviour. I. Factors controlling the gram reaction. II. Theory of the gram reaction. III. Bacteriostasis, i, 339.
chemical differentiation of bacteria, i, 1013.
Stedman, *Edgar*, and *G.* **Barger**, physostigmine [eserine]. III., i, 292.
Stedman, *Edgar*. See also (*Mrs.*) *Ellen* **Stedman.**
Stedman, (*Mrs.*) *Ellen*, and *Edgar* **Stedman**, hæmocyanin. I. Dissociation curves of the oxyhæmocyanin in the blood of some decapod *Crustacea*, i, 1199.

Steenbock, *H.*, and *A.* **Black**, fat-soluble vitamins. XXIII. Induction of growth-promoting and calcifying properties in fats by exposure to light, i, 1020.

Steenbock, *H.*, and *M. T.* **Nelson**, fat-soluble vitamins. XIX. Induction of calcifying properties in a rickets-producing ration by radiant energy, i, 107.

Steenbock, *H.*, *M. T.* **Nelson**, and *A.* **Black**, fat-soluble vitamins. XX. Modified technique for determination of vitamin-*A*, i, 107.

Steenbock, *H.* See also *E. B.* **Hart**, *E. M.* **Honeywell**, and *E. M.* **Nelson**.

Steenhauer, *A. J.* See *L. van* **Itallie**.

Stehle, *R. L.*, *W.* **Bourne**, and *E.* **Lozinsky**, pharmacological action of ethylene oxide, i, 333.

Steigerwald, *C.* See *S.* **Goldschmidt**.

Steigmann, *A.*, precipitation of gold and silver by metallic sulphides; [detection of traces of gold and silver in solution], ii, 719.

Stein, *H.* See *K.* **Brand**.

Steiner, *A.* See *W.* **Ostwald**.

Steinert, *H. E.* See *M. C.* **Crew**.

Steinheil, *M.* See *O.* **Hönigschmid**.

Steinherz, *R.* See *F.* **Eisenkolb**.

Steinkopf, *W.* [valency problem of sulphur], i, 657.

Steinkopf, *W.* [with *E.* **Zemisch**, *H.* **Winkler**, and *G.* **Pohl**], derivatives of *m*- and *o*-dicresol [dehydroxyditolyl], i, 1413.

Steinkopf, *W.*, and *R.* **Bessaritsch**, molecular compounds of iodoform and quaternary salts. II., i, 495.

Steinkopf, *W.*, *W.* **Ohse**, and *K.* **Buchheim**, laboratory apparatus, ii, 590.

Steinwehr, *H. von.* See *W.* **Jaeger**.

Stelling, *O.*, chemical constitution and *K* absorption spectra. II. Investigation of certain compounds of phosphorus, ii, 935.

chemical constitution and *K* absorption spectra. III. Röntgenspectroscopic method of determination of constitution, ii, 935.

chemical constitution and *K* absorption spectra. IV. Constitution of phosphorous acid and some derivatives, ii, 936.

Stenzl, *H.*, alkaloids of *Lobelia inflata*, i, 347.

Steopoe, *A.*, mechanism of the Liesegang phenomenon, ii, 1158.

Stepanov, *A.*, *N.* **Preobraschenski**, and *M.* **Schtschukina**, products of the bromination of paracetaldehyde, i, 1240.

Stepanov, *N. I.*, relation between the temperature and velocity of transformation of metastable non-variant systems, ii, 645.

Stephen, *H.*, synthesis of aldehydes, i, 1131.

Stephen, *H.* See also *E.* **Chapman**, and *J. T.* **Marsh**.

Stephens, *O. C.*, preparation of ethyl cyanoacetate, i, 121.

Stephenson, *G. E.* See *H. V. A.* **Briscoe**, and *P. L.* **Robinson**.

Stephenson, *M.* See *J. H.* **Quastel**.

Stephenson, *R. J.* See *J. A.* **Crowther**.

Stepp, *W.*, formation of vitamin-*A* during germination of seeds, i, 1220.

formation of vitamin-*D* in germinating seeds, i, 1221.

Steppuhn, *O.*, and *G.* **Pewsner**, extraction of *Adonis vernalis*, i, 762.

Steppuhn, *O.*, and *X.* **Utkin-Ljubovzov**, autolysis. III. Autolytic processes in liver pulp, i, 864.

Stěrba-Boehm, *J.*, and *M.* **Auerspergrová**, quadrivalent lead, ii, 699.

Stěrba-Boehm, *J.*, and *V.* **Matula**, volumetric determination of cerium, ii, 716.

Stern, *H.* See *W. D.* **Treadwell**.

Stern, *O.*, equilibrium between matter and radiation, ii, 926.

transformation of atoms into radiation, ii, 1021.

Stern, *R.*, uric acid. I., ii, 34.

uric acid. II. Hydrotropic action of uric acid, ii, 196.

supersaturated solutions of uric acid, ii, 504.

uric acid. III. Nature of the hydrotropic supersaturated solution of uric acid, ii, 1152.

Sterner-Rainer, *L.*, compound AuCu in gold alloys, ii, 651.

Stetter, *G.*, determination of mass of H-particles, ii, 1021.

Steubing, *W.*, simple demonstration screen for ultra-violet radiations, ii, 449.

continuous spectra of the halogens, ii, 452.

electromagnetic susceptibility of the iodine atom; change of intensity in the line spectrum, ii, 830.

Stevens, *H. C.*, and *E.* **Karrer**, non-polarisable electrodes for physiological purposes, ii, 1194.

Stevens, *T. S.* See *J. S.* **Buck**.

Stevenson, *A.* See *E.* **Rothstein**, and *E. A.* **Speight**.

Stewart, *A. W.* See *W. H.* **McVicker**.

Stewart, *C. P.*, metabolism of arginine and histidine. I. Arginine and histidine as precursors of purines, i, 730.

Stewart, *C. P.*, and *W.* **Archibald**, determination of phosphorus and magnesium, ii, 824.

Stewart, *C. P.*, and *H. E.* **Tunnicliffe**, glutathione; synthesis, i, 795.

Stewart, *C. P.*, and *A. C.* **White**, determination of fat in blood, i, 1485.

Stewart, *G. R.*, *E. C.* **Thomas**, and *J.* **Horner**, comparative growth of pineapple plants with ammonium and nitrate nitrogen, i, 1366.

Stewart, *H. J.*, oxygen and carbon dioxide contents of arterial and venous blood in dogs, i, 451.

Stewart, (*Miss*) *J.*, α-acenaphthaquinoline, i, 975.

Stewart, *J. Q.*, treatment of radiation-pressure and gas-pressure as due to intermolecular forces, ii, 1112.

Stewart, *L.* See *R. N.* **Pease**.

Stewart, *T. D.*, and *S.* **Maeser**, strength of trimethylamine oxide and trimethylalkoxyammonium hydroxides as bases; structure of ammonium compounds, i, 12.

Steyns, *M. E. J. M.* See *H.* **Zwaardemaker**.

Stiasny, *E.*, influence of neutral salts on some properties of gelatin, ii, 524.

Stiasny, *E.*, and *S. R. D.* **Gupta**, effect of neutral salts on gelatin. III. Influence on the action of trypsin on gelatin, i, 707.

effect of neutral salts on gelatin. I. Swelling action of neutral salts and the value of the Hofmeister series, ii, 392.

Stiasny, *E.*, *S. R. D.* **Gupta**, and *P.* **Tresser**, effect of neutral salts on gelatin. II. Their dispersive effect, ii, 393.

Stichel, *A.* See *J.* **Gadamer**.

Stickel, *F.* See *H. T.* **Bucherer**.

Stiegler, *H. W.* See *W. L.* **Lewis**.

Stieglitz, *J.*, theory of colour production, ii, 840.

Stier, *G.* See *G.* **Schroeter**.

Stiles, *H. R.*, *W. H.* **Peterson**, and *E. B.* **Fred**, fermentation products of mannitol-forming bacteria, i, 1216.

Stiles, *H. R.* See also *E. B.* **Fred**, and *W. H.* **Peterson**.

Stiles, *W.*, absorption of salts by storage tissues, ii, 31.

Stinson, *H. F.* See *N. S.* **Osborne**.

Stirnemann, *E.* See *H.* **Staudinger**.

Stix, *W.*, product with insulin action, i, 1218.

Stobbe, *H.*, and *E.* **Färber**, polymerides of indene, i, 19.

Stobbe, *H.*, *E.* **Färber**, and *F.* **Rau**, photodimerides of derivatives of γ-ketopentadienes, i, 1282.

Stobbe, *H.*, *A.* **Hensel**, and *W.* **Simon**, polymerisation of cinnamylidenemalonic acid, cinnamylideneacetic acid, cinnamylideneacetylacetone, and cinnamylideneacetone on exposure to light, i, 1067.

Stobbe, *H.*, and *F.* **Kuhrmann**, two photodimerides of α-phenylcinnamylideneacetonitrile, i, 253.

Stock, *A.*, fat-free, mercury valve with porous glass plates, ii, 1195.

Stock, *A.*, *A.* **Brandt**, and *Hans* **Fischer**, zinc arc as a means of reduction, ii, 570.

Stock, *A.*, and *E.* **Pohland**, tensimetric determination of molecular weight with liquid ammonia as solvent, ii, 489.

Stock, *A.*, *P.* **Praetorius**, and *O.* **Priess**, preparation of beryllium, ii, 1090.

Stock, *A.*, and *W.* **Wustrow**, thermal decomposition of carbonyl chloride, ii, 987.

Stock, *H.*, action of light on silver bromide, ii, 574.

Stockdale, *D.*, α-phase boundary in the copper–tin system, ii, 973.

Stocker, *E.* See *F.* **Fichter**.

Stocks, *H. B.*, and *C. V.* **Greenwood**, nature of the reaction between tannin and carbohydrates. I. Comparative study of the interaction of tannin with gelatin and certain carbohydrates, i, 1165.

Stöcklin, *P.* See *H.* **Lecher**.

Stoermer, *R.*, and *P.* **Klockmann**, ζ-truxinic acid. IX., i, 927.

Stoffella, *C. G.*, reversible system $PbI_2 + ZnSO_4 \rightleftharpoons PbSO_4 + ZnI_2$, ii, 1064.

Stoklasa, *J.*, influence of micro-organisms on the absorption of nutritive elements from soil, i, 765.

Stoklasa, *J.*, and *J.* **Penkava**, radioactivity of gases emitted from Vesuvius and the solfataras of Campania and their influence on the development of bacteria and higher plants, ii, 235.

Stolfi, *A.*, behaviour of lead containing radium-Ω in the formation of formaldehyde by Thunberg's method, ii, 1111.

Stoll, *L.* See *A.* **Thiel**.

Stoll, *W.* See *K.* **Freudenberg**, and *P.* **Pfeiffer**.

Stollé, *R.*, di(α-cyanobenzyloxy)phenylmethane, $CHPh(O\cdot CHPh\cdot CN)_2$, i, 815.
Stollé, *R.*, and *G.* **Adam**, addition of azodicarboxylic esters to aromatic hydrocarbons, i, 1469.
Stollé, *R.*, *W.* **Giesel**, and *W.* **Badstübner**, benz*iso*thiazole, i, 1466.
Stollé, *R.*, and *O.* **Orth**, 5-amino-2-phenyl-1:2:3:4-tetrazole, i, 1464.
Stoltenhoff, *W.* See *R.* **Anschütz**.
Stone, *S. B.* See *W. D.* **Harkins**.
Stoner, *E. C.*, distribution of electrons among atomic levels, ii, 85.
significance of spectroscopic magneton numbers, ii, 618.
Stoner, *E. C.*, and *L. H.* **Martin**, absorption of *X*-rays, ii, 257.
Stoppel, *A. E.*, *C. F.* **Sidener**, and *P. H. M.*-*P.* **Brinton**, iodometric determination of vanadium, ii, 73.
separation of molybdenum from vanadium as sulphide, ii, 718.
Stoppel, *A. E.* See also *P. H. M.*-*P.* **Brinton**.
Storm, *H. C.* See *P.* **Karrer**.
Storms, *L. B.* See *H. C.* **Sherman**.
Stosius, *K.*, and *E.* **Philippi**, action of ammonia on the esters of citraconic, mesaconic, and itaconic acids, i, 892.
action of ammonia on ethyl cinnamate, i, 918.
Stott, *V. H.*, viscosity of glass, ii, 1146.
Stott, *V. H.*, *E.* **Irvine**, and *D.* **Turner**, viscosity measurements with glass, ii, 503.
Stoyle, *F. W.* See *G. A.* **Edwards**, and *W. H.* **Perkin**, *jun.*
Strack, *E.* See *F.* **Wrede**.
Stranski, *I.*, rectifying action of contact detectors, ii, 55.
Strassmann, *S.* See *M.* **Kohn**.
Strathern, *R. C.* See *A.* **McKenzie**.
Stratton, *K.*, and *J. R.* **Partington**, latent heats of fusion. II. Palmitic acid and benzene, ii, 25.
Straubel, *R.*, geometry of the co-ordination number. I., ii, 362.
Strauch, *G.* See *A.* **Classen**.
Straus, *F.*, *O.* **Bernoully**, and *P.* **Mautner**, Δ^1-dihydronaphthalene. VI. *ac*-2-Hydroxy-1-ketotetrahydronaphthalene and β-naphthaquinol; autoxidation of polyhydric phenols, i, 1155.
Straus, *F.*, and *M.* **Ehrenstein**, distyryl ketone and triphenylmethane. XI. Diphenylstyrylcarbinol and the constitution of dimeric triphenylallene, i, 534.
Straus, *F.*, and *W.* **Ekhard**, Δ^1-dihydronaphthalene. V. Addition of nitrogen oxides and of nitrosyl chloride to Δ^1-dihydronaphthalene, i, 1138.
Straus, *F.*, and *W.* **Heyn**, distyryl ketone and triphenylmethane. XII. The dimethylacetal and methochloride of *p*-anisyl *p*-methoxystyryl ketone, i, 1430.
Strebel, *E.* See *F.* **Pollitzer**.
Strebel, *K.* See *H. de* **Diesbach**.
Strebinger, *R.*, and *J.* **Pollak**, microdetermination of chlorides, bromides, and iodides together, ii, 823.
Strenk, *C.* See *M.* **Centnerszwer**.
Stroh, *R. H.* See *J. S.* **Hepburn**.
Stroh, *W.* See *E.* **Späth**.
Strouts, *C. R. N.* See *F. D.* **Chattaway**.
Struensee, *R.*, apparatus for the extraction of solids, ii, 996.
Strutinski, *L.* See *N.* **Seljakov**.
Stscherbakov, *I.*, apparatus for anodic processes [dichromates, per-salts, chloroform], ii, 979.
Stschoukarev, *S. A.* See *I.* **Shukov**.
Stuart, *G. L.* See *M.* **Skene**.
Stuart, *H. A.*, extinction of resonance fluorescence of mercury, ii, 629.
Stuber, *B.*, and *P.* **Kuhn**, blood clotting. XII. Detection of so-called thrombin in circulating blood, i, 452.
Stuber, *B.*, and *S.* **Lee**, blood clotting. X. Detection of so-called thrombin in oxalate plasma, i, 94.
Stuckert, *G. V.*, action of bile salts on gelatin, ii, 392.
rhythmic reactions showing U-shaped bands, ii, 1061.
Stücklen, *H.*, absorption spectrum of the neutral and ionised cadmium atom in the spark discharge under water, ii, 338.
Stuhlman, *O.*, *jun.*, minimum velocity of impact to produce secondary electrons from tungsten, ii, 1104.
Stumper, *R.*, composition of rust, ii, 702.
Stumpf, *F.*, isotopes of mercury, ii, 619.
Sturges, *W. S.* See *L. B.* **Parsons**.
Sturgis, *R. D.* See *H. S.* **Harned**.
Sturkop, *S.* See *J.* **Snapper**.
Subrahmanyam, *G.* See *A. L.* **Narayan**.
Subramanyan, *V.* See *G. J.* **Fowler**.
Sucharda, *E.*, preparation of quinolinic acid and certain of its derivatives, i, 1317.
synthesis of "δ-pyrindigotin," i, 1331.
Suchariper, *A.* See *F.* **Feigl**.
Sudborough, *J. J.*, and *P. R.* **Ayyar**, dehydration of rectified spirit by means of anhydrous calcium chloride, i, 1125.

Sudborough, *J. J.*, *H. E.* **Watson**, and *B. T.* **Narayanan**, photochemical oxidation of aromatic hydrocarbons. I., i, 1136.

Sudborough, *J. J.* See also *B. V.* **Bhide**, *K. V.* **Hariharan**, *S. N.* **Iyer**, *B. S.* **Rao**, and *A. R.* **Yathiraja**.

Sudholt, *E.* See *A.* **Kratzer**.

Sugden, *S.*, determination of surface tension from the rise in capillary tubes, ii, 497.

Sugden, *S.*, *J. B.* **Read**, and *H.* **Wilkins**, the parachor and chemical constitution. I. Polar and non-polar valencies in unsaturated compounds, ii, 936.

Sugden, *S.*, and *H.* **Whittaker**, the parachor and chemical constitution. II. Geometrical isomerides, ii, 937.

Suginome, *H.* See *R.* **Majima**.

Sugiura, *K.* See *K. G.* **Falk**.

Sugiura, *Y.*, doublets and triplets in the spectra of different elements, ii, 726.

Sugiura, *Y.* See also *H.* **Nagaoka**.

Suhrmann, *R.*, red limit and work of escape of photo-electric electrons, ii, 831.

Suhrmann, *R.*, and *P.* **Huppert**, quantitative absorption measurements in the ultra-violet in very dilute solutions, ii, 773.

Suhrmann, *R.*, and *K. von* **Lüde**, specific heat of bromine at low temperatures and its chemical constant, ii, 96.

Sullivan, *M. X.*, tests for cystine and cysteine, ii, 1211.

Sultzaberger, *J. A.* See *F. B.* **Dains**.

Sulzer, *G.* See *K.* **Cherbuliez**.

Sumner, *J. B.*, determination of sugar in diabetic urine, i, 186.

reagent for determination of sugar in urine, i, 1491.

Sumner, *J. B.*, and *V. A.* **Graham**, globulins of the jack bean (*Canavalia ensiformis*). II. Content of cystine, tyrosine, and tryptophan, i, 1027.

Supniewski, *J.*, transformation of aromatic compounds by *Bacillus pyocyaneus*, i, 340.

benzene derivatives of bismuth, i, 1473.

Supniewski, *J.* See also *J. A.* **Collazo**.

Sur, *N. K.*, arc spectrum of phosphorus, ii, 1014.

Sur, *N. K.*, and *R. N.* **Ghosh**, absorption spectrum of potassium vapour at high temperatures, ii, 453.

Sure, *B.*, dietary requirements for reproduction. III. Existence of reproductive dietary complex (vitamin-*E*) in ethereal extracts of yellow corn [maize], wheat embryo, and hempseed, i, 212.

dietary requirements for reproduction. IV. Solubility of vitamin-*E* in organic solvents, i, 752.

Suszko, *J.*, *β-iso*quinine and niquine, i, 1448.

Suszko, *J.* See also *K.* **Dziewoński**.

Sutherland, (*Miss*) *M. M. J.*, and *F. J.* **Wilson**, action of hydrazines on semicarbazones. I., i, 42.

Sutter, *K.* See *C.* **Mannich**.

Sutton, *G. D.* See *I. M.* **Heilbron**.

Sutton, *T. C.*, and *H. R.* **Ambler**, absorption of carbon monoxide. I. Critical comparison of some methods employed in gas analysis. II. Advantages of using hot reagent, ii, 436.

Suzuki, *M.*, blood of the seal, i, 1345.

cetacea. XIV. Nature and constitution of ambergris, i, 1348.

cetacea. XVI. Whale's flesh, i, 1349.

cetacea. XX. Composition of the urine in the *Delphinidæ*, i, 1349.

cetacea. XXIII. Amniotic fluid of the sperm whale, i, 1350.

Suzuki, *U.*, *S.* **Odake**, and *T.* **Mori**, new sulphur-containing constituent of yeast, i, 338.

Svéda, *J.*, determination of combustible gases by combustion with cupric oxide. I. and II., ii, 154, 432.

simple apparatus for the distillation of mercury in a vacuum, ii, 428.

Švéda, *J.*, and *O.* **Procke**, elementary analysis of organic substances by combustion with copper oxide in a vacuum, ii, 719.

Svedberg, *T.*, recent advances in the field of colloids, ii, 196.

density and hydration in gelatin sols and gels, ii, 202.

centrifuging, diffusion, and sedimentation equilibria of colloids and substances of high molecular weight, ii, 528.

Svedberg, *T.*, and *H.* **Rinde**, ultracentrifuge, ii, 233.

Svedberg, *T.* See also *N. D.* **Scott**, and *A. J.* **Stamm**.

Svensson, *E.* See *E.* **Bengtsson**.

Swallow, *J. C.* See *E.* **Mathias**.

Swan, *E.*, use of long mercury manometers, ii, 707.

Swan, *E.* See also *F. D.* **Farrow**.

Swan, *T. H.*, and *E.* **Mack**, vapour pressures of organic crystals by an effusion method, ii, 951.

Swanson, *W. W.*, effect of sodium benzoate on composition of blood and urine; possible synthesis of glycine in the body, i, 465.
Swarts, *F.*, the significance of atomic constants in additive properties, ii, 744.
Swartz, *O.* See *H. von* **Euler.**
Swe, *N. K.* See *K.* **Majumder.**
Swe, *R. K.* See *M.* **Saha.**
Sweitzer, *C. W.*, light scattering in salt solutions, ii, 512.
Swientoslawski, *W.*, relation between the equilibrium constants in the gaseous and liquid phases, ii, 204.
thermochemistry of the α-oxides, ii, 364.
deviations from van't Hoff's law, ii, 388.
proposal to establish a secondary thermochemical standard, ii, 540.
classification of reactions taking place in the presence of a contact substance, ii, 562.
thermochemical researches on diazo compounds, ii, 1044.
errors introduced in certain thermochemical data and the correction coefficients of these data, ii, 1139.
Swientoslawski, *W.*, and (*Mlle.*) *Z.* **Blaszkovska**, thermochemical researches on the diazo derivatives of aminophenols, ii, 1044.
Swientoslawski, *W.*, and *M.* **Popov**, correction of the thermochemical data of P. Lemoult, ii, 1139.
Swientoslawski, *W.*, and *W.* **Romer**, ebullioscopic apparatus, ii, 319.
Swientoslawski, *W.*, and (*Mlle.*) *H.* **Starczevska**, correction of the thermochemical data of A. Valeur, ii, 1139.
Swientoslawski, *W.* See also *P. W.* **Zubov.**
Swift, *E. H.*, separation of gallium, ii, 71.
Swinne, *R.*, elements which are "electron-isomerides," ii, 922.
Sword, *J.*, action of hydrogen peroxide on limonene, i, 1163.
Syniewski, *V.*, non-reducing "limit dextrin I," i, 368.
oxidation of amylodextrin, i, 369.
diastase, i, 469.
action of α-diastase on the so-called amylopectin, i, 470.
source of error in the use of Lintner's starch solution for determining diastatic power, i, 470.
Szabó, *A.* See *A.* **Lottermoser.**
Szappanyos, *B.* See *Z.* **Ernst.**
Szegvari, *E.*, theory of elasticity of colloidal solutions, ii, 111.
Szemző, *B.* See *A.* **Schaarschmidt.**
Szendrö, *P.* See *E.* **Fromm.**
Szent-Györgyi, *A. von*, mechanism of oxidation of succinic acid and *p*-phenylenediamine; theory of cell respiration, i, 93.
cell respiration. II. Mechanism of oxidation of lactic acid. III. Reactivation experiments using artificial co-enzymes, i, 708.
Szent-Györgyi, *A. von.* See also *R. J.* **Hamburger.**
Szidon, *V.* See *H.* **Beehhold.**
Szilárd, *P.*, colorimetric method for the quantitative determination of bile salts in blood, i, 1485.
Szivessy, *G.*, Kerr effect in gases, ii, 15. Born's dipole theory of anisotropic liquids, ii, 1123.
Sztencel, *J.* See *J.* **Bielecki.**

T.

Tabern, *D. L.*, *W. R.* **Orndorff**, and *L. M.* **Dennis**, germanium. XII. Tetra-alkyl and tetra-aryl compounds of germanium; germanium tetraethoxide, i, 1108.
Tacchini, *G.*, thermal analysis of the system, lithium fluoride–magnesium fluoride, ii, 122.
Tacchini, *G.* See also *G. R.* **Levi.**
Tacke, *B.*, soil acidity and its determination, i, 875.
Tacke, *I.* See *W.* **Noddack.**
Täufel, *K.*, and *C.* **Wagner**, constitution of aqueous solutions of *o*-benzoicsulphinide (saccharin) and *p*-phenetylcarbamide (dulcin), i, 841.
oxidimetric determination of tartaric acid and other organic substances, ii, 1007.
Taeuffenbach, *G. von.* See *F.* **Kögl.**
Taffe, *M.*, *tert.*-trichlorobutyl alcohol and its esters, i, 2.
Taft, *R.* See *H. P.* **Cady.**
Tafuri, *G. B.* See *P.* **Leone.**
Tague, *E. L.*, isoelectric points of gliadin and glutenin, ii, 391.
Takahashi, *K.*, carbohydrate content of the brain, i, 1487.
Takahashi, *K.*, *Z.* **Makamiya**, *K.* **Kawakami**, and *T.* **Kitasato**, physical and chemical properties of biosterin (vitamin-*A*) and its physiological significance, i, 1365.
Takahashi, *K.* See also *L.* **Asher.**
Takahashi, *T.* See *P.* **Karrer.**
Takamine, *T.*, and *M.* **Fukuda**, mercury line 2270Å. ($1s-2p_1$), ii, 166, 725.

Takamine, *T.* See also *P. D.* **Foote.**
Takanosu, *S.*, nitrogen and chloride excretion in the urine following changes in the relations between blood and tissues, i, 185.
Takashima, *N.* See *P.* **Karrer.**
Takata, *M.*, cetacea. XI. Physiological significance of the compartments in the stomach of the whale, i, 1348.
cetacea. XXI. Enzymes of the pancreas, i, 1349.
Takei, *S.*, rotenone, an active principle of the derris root, i, 761.
Takehara, *K.* See *D.* **Holde.**
Takemura, *S.* See *Z.* **Matsuoka.**
Talen, *H. W.*, formation of *d*-sorbose and *d*-gulose by oxidation of *d*-sorbitol with bromine water, i, 1382.
Tallyn, *W. H.* See *C. D.* **Hurd.**
Talmud, *B.* See *P.* **Petrenko-Kritschenko.**
Talmud, *D.* See *P.* **Petrenko-Kritschenko.**
Tamaru, *K.*, equilibrium diagram of the system, iron–carbon–titanium, ii, 787.
Tamele, *M.* See *V.* **Bayerle.**
Tamm, *I.*, quantitative apprehension of the principle of correspondence and the calculation of the intensities of spectral lines. I., ii, 1023.
Tammann, *G.*, distribution of atoms in mixed crystals, ii, 20.
origin of free oxygen in the air, ii, 100.
extraction limit of the NaCl–AgCl mixed crystal, ii, 366.
reaction limits of some platinum alloys, ii, 378.
dissolution velocity and etched figures on crystals, ii, 942.
determination of crystal-orientation in conglomerates, ii, 1132.
glasses as supercooled liquids, ii, 1145.
Tammann, *G.*, and *H.* **Bredemeier**, hollow channels opening on to the surface of metals, ii, 388.
electrical conductivity of films, ii, 541.
Tammann, *G.*, and *O.* **Dahl**, silver–tin amalgams, ii, 502.
lead–zinc–antimony alloys, ii, 535.
Tammann, *G.*, and *C. F.* **Grevemeyer**, silicates. III. Action of magnesium, calcium, and barium oxides on silicates at high temperatures and the preparation of metallic iron from silicates, ii, 580.
Tammann, *G.*, and *G. T. R.* **Krige**, equilibrium pressures of hydrates of gases, ii, 869.
Tammann, *G.*, and *W.* **Krings**, orientation of etched figures and the distribution of the atoms in the space lattice, ii, 942.
Tammann, *G.*, and *G.* **Siebel**, temper-colours of iron–carbon alloys and of the mixed crystals Fe–Ni; Fe–V; Fe–Al, ii, 1169.
Tammann, *G.*, and *T.* **Stassfurth**, copper and silver amalgams, ii, 377.
Tanabe, *T.*, studies in the aluminium–zinc system, ii, 204.
Tanaka, *C.* See *S.* **Komatsu.**
Tanaka, *M.*, naphthalene derivatives, i, 1061.
hystazarindiquinone (2:3:9:10-anthradiquinone), i, 1077.
quinone diazides of the anthraquinone series, i, 1106.
9:10-anthraquinone-2:3- and -1:2-quinonediazides and their derivatives, i, 1434.
Tanaka, *T.*, wave-lengths of additional lines in the many-lined spectrum of hydrogen, ii, 909.
Tanaka, *T.* See also *O. W.* **Richardson.**
Tanaka, *Y.*, and *S.* **Nagai**, naphthenic acids. IV. Naphthenic acids derived from Kubiki kerosene distillates, i, 252.
naphthenic acids derived from Nishiyama petroleum, i, 1271.
Tanaka, *Y.*, *S.* **Nagai**, and *S.* **Ishida**, naphthenic acids. V. Naphthenic acids derived from Niitsu petroleum, i, 252.
Tananaev, *N. A.*, equilibrium $Fe^{\cdot\cdot} + Ag^{\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot} + Ag$, ii, 121.
qualitative "drop-analysis" of the elements in groups I. to III., ii, 324.
reaction between potassium permanganate and hydrogen peroxide in presence of ammonium sulphate, ii, 440.
gravimetric determination of iron and a rapid method for dissolving ignited iron oxide, ii, 603.
Tancov, *N. V.*, solubility of the crystallohydrates of nickel sulphate, ii, 852.
direction of spontaneous crystallisations and chemical transformations, ii, 868.
Tangl, *H.* See *L.* **Jendrassik.**
Tani, *Y.* See *M.* **Konishi.**
Tanner, *F. W.*, the "bios" question, i, 617.
Tanner, *W. F.* See *J.* **Goldberger.**
Tapley, *R. B.* See *W. H.* **Perkin**, *jun.*
Tarbett, *V. J.* See *F. M.* **Rowe.**
Tartakovski, *P.*, diamagnetism and the anomalous Zeeman effect, ii, 1016.
Tartar, *H. V.*, and *J. R.* **Lorah**, influence of hydrogen-ion concentration on the protective action of gelatin on Zsigmondy's standard gold sol, ii, 864.

Tartar, *H. V.* See also *C. Z.* **Draves.**
Tartarini, *G.* See *G.* **Scagliarini.**
Tasaki, *T.*, absorption spectra of vegetable dyes of the flavone series. II. Influence of methoxy-substitution on the absorption spectra of flavones and flavonols, i, 1444.
absorption spectra of vegetable dyes of the flavone series. III. Absorption spectra of certain flavone and flavonol glucosides, i, 1445.
absorption spectra of benzophenone derivatives, ii, 838.
Tate, *J. T.*, spectroscopic evidence of impact ionisation by positive ions in mercury vapour, ii, 1106.
Tatum, *W. W.* See *J.* **Baddiley**, and **British Dyestuffs Corporation, Ltd.**
Taub, *L.*, *L.* **Schütz**, and *K.* **Meisenburg**, allylcrotylbarbituric acid, i, 435.
Taube, *K.* See *H.* **Leuchs.**
Taubenhaus, *M.* See *J. K.* **Parnas.**
Taubmann, *G.*, accelerating influence of protein-free colloids on the hydrolysis of urea by soya bean urease, i, 744.
Tausson, *W. O.*, utilisation of paraffin by micro-organisms, i, 479.
Tavernier, *P.* See *P.* **Fleury.**
Tavola, *G.* See *L.* **Avogadro.**
Taylor, *B. S.* See *J. B.* **Conant.**
Taylor, *C. J. A.* See *G. T.* **Morgan.**
Taylor, *C. S.*, anode effect, ii, 548.
Taylor, *E. M.*, toxicity of acids towards yeast, i, 1011.
Taylor, *G. B.*, vapour pressure of aqueous solutions of nitric acid, ii, 767.
Taylor, *G. I.*, and *C. F.* **Elam**, plastic extension and fracture of aluminium crystals, ii, 488.
Taylor, *H.*, ionic nature of hæmoglobin, i, 93.
Taylor, *H. A.*, hydration and solution, ii, 858.
Taylor, *H. S.*, theory of the catalytic surface, ii, 562.
photosensitisation and the mechanism of chemical reactions, ii, 1078.
Taylor, *H. S.*, and *H. W.* **Close**, acid catalysis in lactone formation, ii, 1070.
Taylor, *H. S.*, and *A. L.* **Marshall**, reactions of hydrogen activated by excited mercury atoms, ii, 1078.
Taylor, *H. S.* See also *J. S.* **Beekley**, and *W. W.* **Russell.**
Taylor, *J. B.* See *W. H.* **Rodebush.**
Taylor, *M. C.*, *R. B.* **McMullin**, and *C. A.* **Gammal**, hypochlorous acid and the alkyl hypochlorites, i, 501.
Taylor, *N. W.*, and *G. N.* **Lewis**, paramagnetism of "odd molecules," ii, 945.
Taylor, *P. A.*, vibration of the carbonate group, ii, 1115.
Taylor, *W.*, photo-activation of chlorine, ii, 811, 1079.
Taylor, *W. W.* See *E.* **Ponder.**
Tazelaar, *M.* See *H.* **Chick.**
Teakle, *L. J. H.* See *C. B.* **Lipman.**
Tear, *J. D.* See *E. F.* **Nichols.**
Techoueyres, *E.* See *P. B.* **Varilla.**
Teichmann, *L.* See *G.* **Bredig.**
Telfer, *S. V.*, calcium and phosphorus metabolism. III. Absorption and fixation in the skeleton, i, 859.
Tendeloo, *H. J. C.* See *H. R.* **Kruyt.**
Tendick, *F. H.* See *A. M.* **Hjort.**
Teraoka, *M.*, taurine. I. Methylation and acetylation of taurine, i, 1390.
Terenin, *A.* See *E.* **Gross.**
Terentiev, *A. P.*, magnesium alkoxides and their application to the synthesis of alcohols, i, 110.
Terentiev, *A. P.*, and *V. V.* **Tschelincev**, bromination and iodination of some derivatives of pyrrole, i, 295.
Terlikowski, *F.*, action of soil solutions on root development, i, 1029.
Terrill, *H. M.*, absorption of cathode rays in aluminium foil, ii, 79.
Terroine, *E. F.*, *R.* **Bonnet**, and *A.* **Hee**, energy balance in development of various vegetable organisms and oxygen content of medium, i, 1517.
Terroine, *E. F.*, and *J.* **Roche**, causes of differences of intensity of the elementary respiration of tissues, i, 709.
Terroine, *E. F.*, *S.* **Trautmann**, and *R.* **Bonnet**, quantitative law of energy exchanges in formation of carbohydrates from proteins and fats in plants, i, 755.
energy balance during growth of micro-organisms and its dependence on composition of the nutrient medium, i, 1117.
Terry, *E. M.*, and *L.* **Eichelberger**, halogenation of fumaric and maleic acids; Walden inversion, i, 631.
catalytic transmutation of maleic acid into fumaric acid, i, 780.
Terry, *E. M.* See also *N. A.* **Milas.**
Tervaert, *D. G. C.*, determination of carbon monoxide in blood, i, 710.
determination of sugar in small quantities of blood, i, 1200.
Terwen, *A. J. L.*, determination of urobilin and urobilinogen in urine and fæces, i, 1351.
Teschner, *G.* See *C. G.* **Schwalbe.**
Teves, *M. C.* See *V.* **Henri.**
Thayer, *F. K.*, "butesin" picrate, a new type of anæsthetic-antiseptic, i, 467.

Theis, *R. C.*, and *S. R.* **Benedict**, inorganic constituents of the serum in cancer, i, 724.
Thelen, *C.* See *W.* **Dilthey**.
Thibaud, *J.*, large quantum γ-rays from the active elements of the thorium family, ii, 10.
γ-radiation of mesothorium II., ii, 85.
study of characteristic spectra of γ-rays by crystal diffraction, ii, 176.
absorption and diffusion of γ-radiation of great energy in light elements, ii, 257.
quantity of heat set free as γ-radiation in radioactive disintegration, ii, 464.
characteristic γ-ray spectra and their photo-electric effect, ii, 622.
Thibaud, *J.* See also *M. de* **Broglie**.
Thiel, *A.*, dual ions and internal salts, ii, 37.
Thiel, *A.*, and *L.* **Stoll**, lead nitrite, ii, 419.
Thiele, *H.* See *H.* **Kautsky**.
Thiele, *J.*, thermo-electricity of electrolytes, ii, 545.
Thiele, *J.* See also *H.* **Wieland**.
Thielmann, *F.* See *F.* **Holtz**.
Thierfelder, *H.*, and *E.* **Klenk**, behaviour of fatty-aromatic compounds in the animal body, i, 192.
behaviour of acetophenone and benzene in the animal body, i, 193.
preparation of the glucosamine-containing phosphatides of Fränkel and Kafka from brain, i, 997.
Thies, *O. J.*, *jun.* See *H. B.* **Arbuckle**.
Thiessen, *M.* See *J.* **Gadamer**.
Thiessen, *P. A.*, and *C.* **Carius**, method for measuring small changes of swelling, ii, 520.
Thiessen, *P. A.*, and *J.* **Heumann**, mobility of the particles in gold hydrosols, ii, 1157.
Thiessenhusen, *W.* See *H.* **Schlee**.
Thilo, *E.* See *F.* **Paneth**.
Thivolle, *L.*, and *J.* **Roche**, preparation of crystalline oxyhæmoglobin by ultrafiltration, i, 1111.
Thoenes, *F.*, "bound" water in colloids and animal tissues, i, 718.
Thomas, *A.*, and *A. W.* **Dox**, sodium salts of the nucleic acid from wheat embryo, i, 873.
Thomas, *A. W.*, and *M. W.* **Kelly**, thermolability of collagen, ii, 520.
Thomas, *A. W.*, and *E. R.* **Norris**, "irregular series" in the precipitation of albumin, i, 603.
Thomas, *C. H.*, soft *X*-rays from iron, ii, 336.
Thomas, *E. C.* See *G. R.* **Stewart**.
Thomas, *F.* See *O.* **Ruff**.
Thomas, *H.* See *J.* **Tröger**.
Thomas, *J.* See *E. G.* **Beckett**.
Thomas, *J. S.*, and *John Henry* **Jones**, polysulphides of the alkali metals. V. Lithium monosulphide and disulphide, ii, 58.
Thomas, *J. S.*, and *R. W.* **Riding**, organic polysulphides. II. Action of anhydrous potassium pentasulphide on allyl iodide and on some aromatic halogen compounds, i, 4.
organic polysulphides. III. Action of the disulphides of the alkali metals and of sodium tetrasulphide on some organic halogen compounds, i, 113.
Thomas, *J. S. G.* See *A. R.* **Pearson**.
Thomas, *K.*, and *F.* **Bettzieche**, action of Grignard reagents on amino-acids. I., i, 250.
action of Grignard reagents on amino-acids. IV. Acylamino-acids, i, 251.
action of Grignard reagents on amino-acids. II. Conversion of β-amino-$\alpha\alpha$-diphenylethan-α-ol into diphenylacetaldehyde, i, 257.
Thomas, *P.*, test for pentoses, ii, 604.
Thomas, *P.*, and *R.* **Imas**, detection of pentoses in plant glucosides, ii, 1209.
Thomas, *V.*, new type of organic magnesium compounds, i, 1055.
Thompson, *A. P.*, and *H. C.* **Kremers**, rare earths. XVIII. Preparation and properties of cerium-free "Misch metal," ii, 580.
Thompson, *F. C.*, and *W. H.* **Dearden**, experiment on solid diffusion and its possible bearing on the structure of solid solutions, ii, 29.
Thompson, *G.*, synthesis of *p*-thiolbenzoic acid, i, 815.
Thompson, *H. C.* See *D. W.* **Wilson**.
Thompson, *J. W.* See *C.* **Voegtlin**.
Thompson, *P. K.*, recovery of small amounts of zinc from biological material ashed by incineration, i, 1489.
Thompson, *T. J.*, and *R. H.* **Edee**, preparation of 6-methylcoumarin and its derivatives, i, 1442.
Thompson, *T. J.*, *H. L.* **Bedell**, and *G. M.* **Buffett**, preparation of substituted hydantoins, i, 699.
Thoms, *H.*, changes in the sweetening power of dulcin (*p*-phenetylcarbamide) by chemical modification, i, 538.
detection of ethyl phthalate in essential oils, ii, 1008.

Thoms, *H.* [with *B.* **Ambrus**, *H.* **Kahre**, and *M.* **Kemp**], odorants. I. Capacity for condensation of *iso*butaldehyde. II. New derivatives of eugenol. III. New asymmetric tertiary alcohols of high molecular weight, and the direction in which they lose water, i, 788.
Thoms, *H.*, and *K.* **Bergerhoff**, constitution of lupanine, i, 575.
Thomson, *G. P.*, physical interpretation of Bohr's stationary states, ii, 733.
Thomson, (*Sir*) *J. J.*, radiation given out by gases through which electric discharges are passing, ii, 461.
Thoræus, *R.*, *M*-series of tungsten, ii, 5.
Thoræus, *R.* See also *E.* **Bäcklin**.
Thorkelsen, *K.* See *C. N.* **Riiber**.
Thurlow, *S.* See *M.* **Dixon**.
Thorne, *P. C. L.* See *E.* **Hatschek**.
Thornton, *C. W.* See *C. N.* **Hinshelwood**.
Thornton, *H. G.* See *W. E.* **Brenchley**.
Thornton, *W. M.*, and *J. A.* **Harle**, electrolytic corrosion of ferrous metals, ii, 303.
Thornton, *W. M.*, *jun.*, and *D.* **Getz**, use of *p*-nitrobenzoic acid as an acidimetric standard, ii, 597.
Thorpe, *J. F.* See *J. P. C.* **Chandrasena**, *S.* **Dutt**, *F. R.* **Goss**, *W.* **Haerdi**, *G. A. R.* **Kon**, *E.* **Rothenstein**, *E. A.* **Speight**, and *C. H.* **Spiers**.
Thurlow, *S.*, xanthine oxydase. IV. Relation of xanthine oxydase and similar oxidising systems to Bach's oxygenase, i, 743.
Thurlow, *S.* See also *D. W.* **Wilson**.
Thwaites, *J. T.* See *J. K.* **Robertson**.
Tian, *A.* See (*Mlle.*) **Bérenger**.
Tideswell, *F. V.*, and *R. V.* **Wheeler**, fusain and its oxidation; composition of coal, i, 373.
banded bituminous coal; composition of coal, i, 373.
Tidmus, *J. S.* See *J. N.* **Friend**.
Tiede, *E.*, and *H.* **Tomaschek**, activating element in luminescent boron nitride, ii, 931.
Tiegs, *O. W.*, colour test for guanidine bases, with physiological applications, i, 97.
function of creatine in muscular contraction, i, 1003.
Tietze, *E.* See *L.* **Claisen**.
Tiffeneau, *M.*, and *A.* **Orékhov**, migratory tendencies of organic radicals. I., i, 378.
migratory tendencies of organic radicals. II. Comparison of *p*-anisyl and phenyl groups, i, 679.
Tiffeneau, *M.*, *A.* **Orékhov**, and *J.* **Lévy**, isomerism of ethylene oxides with migration [of groups]; mechanism of molecular transpositions, i, 544.
Timoféev, *W. F.*, *G. E.* **Muchin**, and *W. G.* **Gurevitsch**, influence of neutral salts on the reaction between ferric chloride and stannous chloride, ii, 586.
Timosuff, *V.*, oil from *Pistacia terebintus*, i, 1124.
Timpany, *C. R.* See *A. F. O.* **Germann**.
Tindal, *S. J.*, detection of cobalt, alone or in presence of nickel and other salts, in neutral solution, ii, 242.
Tischbein, *W.* See *M.* **Busch**.
Tistchenko, *D. V.*, organo-magnesium compounds; reaction between magnesium and acyl halides, i, 775.
Tocco-Tocco, *L.*, causes modifying the toxicity of strophanthin, i, 613.
Tödt, apparatus for direct reading of conductivity (and salt content) of a salt solution, ii, 898.
Tödt, *F.*, electrolytic separation of base radioactive elements, ii, 54.
Toia, *V.* See *G.* **Charrier**.
Tolksdorf, *S.* See *H.* **Mark**.
Tolman, *R. C.*, problem of the quantitative formulation of Bohr's correspondence principle, ii, 466.
mechanism of chemical reaction, ii, 799.
estimation of maximum coefficients of absorption, ii, 1112.
Tolman, *R. C.* See also *L.* **Pauling**, and *E. C.* **White**.
Tomaschek, *H.* See *E.* **Tiede**.
Tomaschek, *R.*, phosphorescent properties of the rare earths in alkaline-earth phosphors. I. and II., ii, 12, 354.
Tómasson, *H.* See *S.* **Holm**.
Tomiček, *O.*, use of titanous chloride in potentiometric titrations, ii, 243.
potentiometric determination of cerium, ii, 716.
Tomiček, *O.* See also *I. M.* **Kolthoff**.
Tominaga, *H.*, formation of ammonia in the oxyhydrogen flame, ii, 48.
Tominaga, *T.*, gravimetric microdetermination of cholesterol, i, 453.
Tomita, *T.*, adsorption and osmotic phenomena in gels, ii, 202.
Tomkeiev, *S. I.*, structure of aragonite, ii, 1035.
Tomkinson, (*Miss*) *M. G.*, condensation of acetylene and hydrogen sulphide in presence of catalysts, i, 58.
Tomkinson, (*Miss*) *M. G.* See also *W. H.* **Mills**.
Tomoda, *Y.*, production of glycerol by fermentation, i, 227.

Toni, *G. de*, preparation of enzymes; rennin from gastric mucous membrane, i, 200.
Tonn, *O.* See *O.* **Mumm.**
Tool, *A. G.*, and *E. E.* **Hill**, constitution and density of glass, ii, 1145.
Torti, *P.*, reactions of picric acid and of cignolin [1:8-dihydroxyanthranol], ii, 905.
Toul, *F.* See *H.* **Křepelka.**
Tounet, *J.* See *M.* **Loeper.**
Touplain, *F.* See *F.* **Bordas.**
Tourneux, *M.*, and (*Mlle.*) **Pernot**, aqueous and acetone solutions of potassium bromo- and iodo-mercurates, ii, 380.
Toussaint, *C.* See *J.* **Bardet.**
Toussaint, *L.* See *A.* **Schleicher.**
Townend, *D. T. A.* See *W. A.* **Bone.**
Townsend, *R. E.* See *A. R.* **Carr.**
Toy, *F. C.*, latent photographic image. I. Relation between light frequency and number of developable centres, ii, 143.
Toyama, *Y.*, unsaponifiable constituents (higher alcohols) of shark and ray liver oils. IV., i, 4.
Toyama, *Y.*, and *T.* **Tsuchiya**, separation of the highly unsaturated fatty acids in train oil, i, 1129.
Traill, *D.* See *E. L.* **Hirst**, and *A. K.* **Macbeth.**
Trapesnikov, *O.* See *P.* **Lukirsky.**
Traube, *J.*, and *E.* **Rackwitz**, action of protective colloids, ii, 968.
Traube, *J.*, and *S.* **Yumikura**, lipoids and the theory of surface action. II., i, 735.
Traube, *W.*, behaviour of sodium ethoxide solutions towards nitric oxide, i, 110.
Traube, *W.* [with *P.* **Baumgarten**, *L.* **Baermann**, *W.* **Lange**, and *R.* **Justh**], chlorosulphonic acid esters, i, 775.
Traube, *W.*, *E.* **Burmeister**, and *R.* **Stahn**, bivalent chromium, ii, 990.
Trautmann, *S.* See *E. F.* **Terroine.**
Trautz, *M.*, and *F.* **Geissler**, dissociation of chlorine into atoms, ii, 294.
Trautz, *M.*, and *W.* **Gerwig**, velocity of the reaction $2NO+Cl_2 \longrightarrow 2NOCl$ in the condensed state, ii, 878.
Trautz, *M.*, and *H.* **Schneter**, termolecular collisions resulting from bimolecular collisions considered from the physical and chemical points of view. I. Formation of nitrosyl chloride, ii, 552.
Travers, *A.*, reduction of permanganic acid by arsenious acid and mechanism of the oxidation of manganous salts to permanganic acid, ii, 585.
Traxler, *R. N.*, and *F. E. E.* **Germann**, decolorisation of carbon disulphide solutions of iodine by red phosphorus, ii, 1087.
Treadwell, *W. D.*, and *A.* **Köhl**, electrometric titration of fluorides, ii, 1197.
Treadwell, *W. D.*, and *C.* **Paoloni**, application of three-electrode valves in electrometric titrations, ii, 595.
Treadwell, *W. D.*, and *H.* **Stern**, determination of the decomposition potential of aluminium bromide in aqueous solution, ii, 41.
Trendtel, *F.*, combination of acids with insoluble albumin, i, 91.
Trénel, *M.*, simple apparatus for the electrometric measurement of hydrogen-ion concentration [of soil suspensions], i, 874.
apparatus for the determination of p_H, ii, 64.
Trénel, *M.*, and *R.* **Wilkendorf**, aliphatic nitro-alcohols. III., i, 112.
Tressler, *D. K.*, and *A. W.* **Wells**, iodine content of sea foods, i, 183.
Tresser, *P.* See *E.* **Stiasny.**
Triandafil, *S.*, influence of acidity on the polarisation of nickel, ii, 405.
Tricker, *R. A. R.*, determination of the variation of the mass of the electron with velocity, using homogeneous β-rays, ii, 1021.
Tricot, *E.* See *A.* **Kovache.**
Trillat, *J. J.*, molecular orientation of the fatty acids, ii, 195.
X-ray study of fatty acids and dibasic acids, ii, 489.
X-ray study of soaps and fats, ii, 752.
method of following the course of certain chemical reactions by means of *X*-rays; oxidation of unsaturated fatty acids, ii, 1127.
Trillat, *J. L.* See *L. de* **Broglie.**
Tritt, *C.* See *S.* **Fränkel.**
Tritton, *F. S.*, and *D.* **Hanson**, iron and oxygen, ii, 316.
Trocello, *E.* See *C.* **Serono.**
Tröger, *J.*, and *C.* **Brohm**, 8-*o*- and -*p*-anisolesulphonyl- and -phenetolesulphonyl-2-methylquinolines, their derivatives, and their behaviour towards nascent hydrogen, i, 1452.
Tröger, *J.*, and *J.* **Danehl**, condensation of *m*- and *o*-nitrobenzaldehyde with 8-methoxy-2-methylquinoline, i, 974.
Tröger, *J.*, and *E.* **Dunker**, condensation of hydroxy- and methoxy-2-methylquinolines, and 2-hydroxylepidine with aromatic aldehydes, i, 432, 975.
Tröger, *J.*, and *O.* **Philippson**, 2:4:5-triphenyloxazole or benzilam, i, 986.

Tröger, *J.*, and *H.* **Thomas**, 4:5-diphenyl-2-*m*-nitrophenylglyoxaline, 2:4:5-tri(*p*-nitrophenyl)glyoxaline, and some derivatives, i, 979.
Troensegaard, *N.*, and *Eugen* **Fischer**, composition of proteins. VI. Gliadin, i, 848.
Troje, *E.*, determination of hydroxymethylfurfuraldehyde, and Fiehe's reaction, ii, 1210.
Tropsch, *H.* See *F.* **Fischer.**
Trotman, *C. G.* See *D. L.* **Chapman.**
Trotman, *E. R.*, preparation of quaternary hydrocarbons, i, 382.
Trowbridge, *A.*, spectroscopy in the infra-red region of the spectrum, ii, 335.
Truffaut, *G.*, and *N.* **Bezssonoff**, predominance of activity of anaërobic nitrogen-fixing bacteria in the soil, i, 1227.
Truka, *A.* See *E.* **Fromm.**
Trumper, *M.* See *H.* **Leffmann.**
Trumpy, *B.* See *J.* **Holtsmark.**
Trusty, *A. W.* See *A. E.* **Wood.**
Tryhorn, *F. G.*, and *G.* **Jessop**, decomposition of hydrogen peroxide by cobaltic hydroxide, ii, 807.
Tsatsas, *T.* See *C.* **Dosios.**
Tscharner, *H. von.* See *E.* **Briner.**
Tschelincev, *V. V.*, higher valencies of onium compounds, ii, 480.
strengths of the higher valencies and their significance for assimilation, catalysis, and other chemical processes, ii, 481.
Tschelincev, *V. V.* See also *A. P.* **Terentiev.**
Tschernik, *G. P.*, calcio-ancylite and accompanying minerals from the Chibine Mountains [Russian Lapland], ii, 322.
Tschirch, *A.*, autoxidation of fats, resins, terpenes, and tannins, i, 356.
Tschirch, *A.*, and *H.* **Gfeller**, adipocere, i, 1203.
Tschirvinski, *P. N.*, tyuyamunite from the Tyuya-Muyun radium in Fergana, ii, 430.
Tschitschibabin, *A. E.*, tautomerism of 2-aminopyridine. III. Dicyclic derivatives of the tautomeric form of 2-aminopyridine with a glyoxaline nucleus, i, 158.
preparation of hydroxy derivatives of pyridine, quinoline, and their homologues, i, 299.
tautomerism of 2-aminopyridine. IV. Method for the preparation of pyriminazole and its homologues, i, 1328.
2-amino-3-methylpyridine and dinitro-2-aminopyridine, i, 1328.
Tschitschibabin, *A. E.*, and *I. G.* **Bylinkin**, 2-pyridylpyrrole, i, 1174.
Tschitschibabin, *A. E.*, and *R. A.* **Konovalova**, nitro derivatives of methylated forms of 2-aminopyridine, i, 1328.
Tschitschibabin, *A. E.*, *B. M.* **Kuindshi**, and *S. V.* **Benevolenskaja**, products of the nitration of 2- and 4-benzylpyridine, i, 1316.
Tschitschibabin, *A. E.*, and *G. P.* **Menschikov**, alkylation of pyridyl-2-nitroamine. I. New reaction analogous to that of Kishner and Wolff, i, 437.
Tschitschibabin, *A. E.*, and *E. D.* **Ossetrova**, tautomerism of 4-aminopyridine. II. Methylated derivatives of 4-aminopyridine, i, 1328.
Tschitschibabin, *A. E.*, *D. P.* **Vitkovski**, and *M. I.* **Lapschin**, nitration of 2- and 4-aminoquinoline, i, 838.
Tschörner, *W.* See *B. M.* **Margosches.**
Tschopp, *E.* See *H.* **Rupe.**
Tschugaev, *L. A.* [with *E.* **Fritzmann**], complex base of osmium, i, 1395.
Tschugaev, *L. A.*, *M.* **Skanavy-Grigorjeva**, and *A.* **Posnjak**, hydrazine carbylamine complexes of platinum, i, 1395.
Tschui, *J.* See *F.* **Kehrmann.**
Tsubura, *S.*, physiology of plain muscle; comparison of the reducing properties of plain and striated muscle, i, 1004.
Tsuchiya, *T.* See *Y.* **Toyama.**
Tsujimoto, *M.*, unsaponifiable matter of arctic sperm oil, i, 772.
occurrence of highly unsaturated acids in algæ, i, 778.
constitution of the tetradecenoic acid derived from sperm oil, i, 1128.
Tsukamoto, *R.*, dynamic action of ions on growth on a vitamin-rich diet, i, 210.
Tubandt, *C.*, and *H.* **Reinhold**, migration of ions in solid electrolytes, ii, 300.
Tudhope, *T. M. A.* See *A.* **McKenzie.**
Tuley, *W. F.* See *W. A.* **Noyes.**
Tunnicliffe, *H. E.*, glutathione; occurrence and determination of glutathione in tissues, i, 752.
glutathione; relation between the tissues and the oxidised dipeptide, i, 752.
Tunnicliffe, *H. E.* See also *C. P.* **Stewart.**
Turek, *O.* See *C.* **Krauz.**
Turley, *H. G.* See *J.* **Kenyon.**
Turner, *D.* See *V. H.* **Stott.**
Turner, *E. E.*, and *W. H.* **Patterson**, cryoscopy in sodium sulphate decahydrate, ii, 273.

Turner, *E. E.*, and *A. B.* **Sheppard**, 6-chlorophenoxarsine, i, 705.
Turner, *E. E.* See also *L. H. A.* **Holmes**, *A. F.* **Hunt**, and *E.* **Roberts**.
Turner, *L. A.*, relative sizes of the kernels of ten electrons of sodium, magnesium, aluminium, and silicon, ii, 349.
energies of multiple *X*-ray ionisation of light atoms, ii, 915.
Turner, *L. A.*, and *K. T.* **Compton**, absorption of a line of the principal series of singly ionised atomic mercury, ii, 613.
absorption and emission spectra of the Geissler discharge in mercury vapour and in mixtures of mercury and hydrogen, ii, 613.
nature of the iodine line 2062 Å., ii, 725.
Turner, *L. A.* See also *W. H.* **McCurdy**.
Turner, *W. A.*, and *A. M.* **Hartman**, non-volatile organic acids of alfalfa [lucerne], i, 1124.
Turner, *W. E. S.*, some physical properties of silicate glasses and their possible bearing on the history of igneous rocks, ii, 767.
nature and constitution of glass, ii, 1144.
Turova-Pollak, *M. B.* See *N. D.* **Zelinski**.
Tutin, *F.*, pectin content of normal and "silvered" apple leaves, i, 1028.
fruits and their products. I. Apple juice as a source of sorbitol, i, 1028.
fruits and their products. II. Fate of sugar during "cider sickness," i, 1028.
Tutton, *A. E. H.*, crystallographic and optical properties of iodosuccinimide, ii, 747.
monoclinic double sulphates containing thallium; thallium nickel and thallium cobalt sulphates, ii, 749.
Tuve, *M. A.*, impact ionisation by low-speed positive ions, ii, 1106.
Tweedy, *S. K.* See *J. R.* **Partington**.
Twist, *R. F.*, and *S.* **Smiles**, directing influence of the methanesulphonyl group, i, 894.
Tyndall, *A. M.* See *G. C.* **Grindley**.
Tyson, *P. L.* See *A. W. C.* **Menzies**.

U.

Ucko, *H.* See *H.* **Bernhardt**, and *H.* **Zondek**.
Ueberrack, *K.* See *F.* **Högler**.
Ueda, *H.* See *S.* **Komatsu**.
Ueki, *R.*, replacement of blood by solutions containing gum arabic, i, 177.
Uglow, *W.*, "dulcitol" as artificial sugar substitute from the hygienic point of view, i, 1356.
Uhlenbruck, *P.*, enzyme studies with colloidal gold, i, 742.
Ulich, *H.*, measurement of very high electrolyte resistances by Kohlrausch's method, ii, 671, 976.
dielectric constants of solutions of electrolytes, ii, 964.
Ulich, *H.* See also *P.* **Walden**.
Ulpts, *R.* See *P. A.* **Levene**.
Ulrich, *F.* See *K.* **Ziegler**.
Ulrich, *H. M.* See *R.* **Pummerer**.
Underhill, *F. P.*, and *G. T.* **Pack**, pharmacological behaviour of malic acid and its salts, i, 1211.
Underhill, *F. P.*, and *M. A.* **Sallick**, mechanism of water intoxication, i, 613.
Underwood, *H. W.*, *jun.*, [negative] catalysis, ii, 308.
Ungarelli, *A.*, a nitroprusside of bivalent iron, i, 526.
Unger, *K.* See *K.* **Schaum**.
Ungerer, *E.*, basic exchange with salts of organic nitrogen compounds, ii, 658.
Unmack, *A.* See *N.* **Bjerrum**.
Unsöld, *A.*, screening-doublets of the Bowen–Millikan ultra-violet spectra, ii, 1016.
Urazov, *G. G.*, nature of aluminium–magnesium alloys, ii, 786.
graphic methods of representing equilibria in systems of three components, ii, 788.
Urbach, *E.*, and *P.* **Fantl**, determination of chlorine in small amounts of tissue, i, 1203.
Urbain, *E.*, absorption of vapours by charcoal, ii, 191.
Urbain, *G.* See (*Mlle.*) *M.* **Marquis**.
Urbain, *P.* See (*Mlle.*) *M.* **Marquis**.
Urbschat, *E.* See *A.* **Binz**.
Urey, *H. C.*, disturbing influence of an electric field on the Zeeman effect in spectral lines, ii, 170.
structure of the hydrogen molecule ion, ii, 1105.
Urfer, *C.* See *L.* **Duparc**.
Urk, *H. W. van*, action of hydrochloric acid and of pepsin and hydrochloric acid on dissolved proteins, i, 1507.
effect of different ammonium salts in Rothera's reaction, ii, 162.
action of sodium nitroprusside on acetone and acetaldehyde, ii, 162.
Urquhart, *A. R.*, and *A. M.* **Williams**, moisture relations of cotton. I. Taking up of water by raw and soda-boiled cotton at 20°, ii, 780.

Urquhart, *A. R.*, and *A. M.* **Williams**, moisture relations of cotton. II. Absorption and desorption of water by soda-boiled cotton at 25°, ii, 780.
moisture relations of cotton. III. Effect of temperature on the absorption of water by soda-boiled cotton, ii, 780.
moisture relations of cotton. IV. Absorption of water by cotton mercerised without tension, ii, 781.
Usher, *F. L.*, interaction of nitrogen sulphide and sulphur: nitrogen persulphide, ii, 581.
Usher, *F. L.* See also *M.* **Iyer**.
Uthe, *H.* See *E.* **Wedekind**.
Utida, *Y.*, and *M.* **Saitô**, influence of metallic elements on the corrosion of iron and steel, ii, 1069.
Utkin-Ljubovzov, *L.*, proteolytic enzymes of the liver, i, 864.
Utkin-Ljubovzov, *X.* See *O.* **Stepphuhn**.
Utzino, *S.* See *P. P. von* **Weimarn**.
Uzac, *R.*, lead resinates, i, 1295.

V.

Vági, *I.* See *D.* **Fehér**.
Vági, *S.*, reactions for nitrates and nitrites, ii, 599.
Vági, *S.* See also *D.* **Fehér**.
Vail, *J. G.*, silicate solutions and some silicious gels, ii, 661.
Vail, *W. E.* See *A. B.* **Lamb**.
Vaillant, *P.*, electrical conductivity of solid salts at high temperatures, ii, 40.
law of variation with temperature of the conductivity of solid salts, and possible relationship to the characteristic spectrum of the metal of the salt, ii, 165.
Valasek, *J.*, dielectric anomalies in Rochelle salt crystals, ii, 23, 1118.
Valdiguié, *A.* See *J.* **Aloy**.
Valentin, *J.*, and *G.* **Chaudron**, solidification of ternary alloys of aluminium, magnesium, and cadmium, ii, 205.
Valk, *J. H. A. P. van der.* See *W. P.* **Jorissen**.
Valkenburgh, *H. B. van*, and *J. C.* **Bailar**, *jun.*, nitrogen tetrasulphide and nitrogen tetraselenide, ii, 993.
Valkó, *E.* See *W.* **Pauli**.
Vallarta, *M. S.*, Sommerfeld's theory of fine structure [of spectral lines] from the point of view of general relativity, ii, 449.
Valton, *P. A.*, detection of methylamine in presence of excess of ammonia, ii, 446.
Vanderhook, *G.* See *L. A.* **Congdon**.
Vandervelde, *J.* See *R.* **Brinkman**.
Vandevelde, *A. J. J.*, halogenated proteins. III. Bromogluten, i, 91.
halogenated proteins. IV. Bromofibrin, i, 707.
halogenated proteins. V. Bromocasein, i, 1477.
Vanino, *L.*, and *F.* **Herzer**, preparation of acetylsalicyloyl peroxide, i, 139.
Vanselow, *A. P.* See *M.* **Randall**.
Vanstone, *E.* [with *W. G.* **Messenger**], reactivity of antimony halides with certain aromatic compounds. II., i, 662.
Vanzetti, *B. L.*, action of arsenious anhydride on alkali carbonates, ii, 421.
existence of alkali ortho-arsenites, ii, 421.
Varilla, *P. B.*, and *E.* **Techoueyres**, induced antisepsis: bactericidal action of sodium hypochlorite without contact with the bacteria, i, 863.
Varma, *P. S.*, and *D. A.* **Kulkarni**, nitration by means of a mixture of nitrosulphonic and fuming nitric acids, i, 238.
Vartejeanu, *E.*, determination of urea in the blood of a normal dog, i, 1113.
Vásárhelyi, *B.* See *F.* **Verzár**.
Vaucher. See *L.* **Ambard**.
Vavilov, *S. J.*, extinction of fluorescence of dyes at high concentration, ii, 474.
polarised fluorescence of dyes. V., ii, 739.
Vavon, *G.*, and *A. L.* **Berton**, mechanism of the catalytic hydrogenation of phenols, i, 806.
Vavon, *G.*, and *P.* **Peignier**, preparation of active *iso*borneol, i, 1079.
Vecchiotti, *L.*, and *A.* **Michetti**, action of mercuric acetate on *o*-chloroaniline, i, 1058.
Vecchiotti, *L.*, and *A.* **Capodacqua**, reaction between phenylhydrazine and mercuric acetate, i, 1106.
Véchot, *J.* See *M.* **Battegay**.
Vegard, *L.*, luminescence of solid nitrogen and the auroral spectrum, ii, 630.
Vegard, *L.*, *H. K.* **Onnes**, and *W. H.* **Keesom**, emission of light by solidified gases at the temperature of liquid helium and the origin of the spectrum of the aurora, ii, 474.
Vegesack, *A. von*, graphic representation of ternary iron–carbon alloys, ii, 535.
Vehalgo, *M. L.* See *L. A.* **Congdon**.

Veil, (*Mlle.*) *S.*, evolution of the molecule of nickelic hydroxide in contact with water, ii, 183.
decomposition of hydrogen peroxide in presence of nickel hydroxide ii, 412.
Vellinger, *E.* See *F.* **Vlès**.
Vén, *I.* See *L.* **Moser**.
Venable, *C. S.*, plasticity as applied to viscose and artificial silk, ii, 1058.
Venkatesachar, *B.* See *E. P.* **Metcalfe**.
Venn, *H. J. P.*, yield of β-glucosan obtained from low-pressure distillation of cellulose, i, 887.
Verbruggen, *L.* See *P.* **Bruylants**.
Verchovski, *V.* See *V.* **Ipatiev**.
Vercillo, *A.* See *A.* **Mazzucchelli**.
Verge, *J.* See *L.* **Panisset**.
Vergnaud, *P.* See *A.* **Job**.
Verkade, *P. E.*, manganous salts of comenic and meconic acids; intramolecular wandering of metal atoms, i, 421.
effect of boric acid on the solubility in water and on the conductivity of γ-pyronecarboxylic acids, ii, 128.
amendment to the Lyons decisions (1922) regarding the thermochemical standard substance, ii, 871.
Verkade, *P. E.*, and *J.* **Coops**, calorimetric researches. VI. Determination of heat of combustion of salicylic acid; proposed adoption of this substance as secondary standard in calorimetry, ii, 39.
Verkade, *P. E.*, *J.* **Coops**, *jun.*, and *H.* **Hartman**, molecular heat of combustion of successive terms of homologous series, ii, 364.
calorimetric researches. VIII. The paraffin oil method: an aid in the determination of the heats of combustion of difficultly combustible and hygroscopic substances, ii, 490.
Verley, *A.*, [oxidation of eugenol, methylheptenone, and citral with ozone], i, 406.
exchange of functional groups between two molecules; passage of the alcoholic function into the aldehydic function and inversely, i, 783.
exchange of functional groups between two molecules; passage of alcoholic into ketonic groups and inversely, i, 1034.
Verley, *A.*, and (*Mlle.*) *J.* **Beduwé**, general method of preparation of substituted indoles, i, 578.
Vermelin, *H.* See *P.* **Lasseur**.
Vernadski, *V.*, representation of the chemical composition of living matter, i, 606.
distribution of the chemical elements in the earth's crust, ii, 996.
hydrogen sulphide in limestone and dolomite, ii, 997.
Verney, *E. B.* See *E. H.* **Starling**.
Vernon, *C. C.* See *H.* **Gilman**.
Vernon, *W. S.* See *H. E.* **Buckley**.
Verzár, *F.*, and *B.* **Vásárhelyi**, carbon dioxide content of capillary blood and its determination, i, 178.
Veselý, *V.*, and *L. K.* **Chudožilov**, reduction of aromatic nitro derivatives by means of sulphides, i, 654.
preparation of isonuclear bromonitronaphthalenes from corresponding derivatives of tetrahydronaphthalene [tetralin], i, 1056.
Veselý, *V.*, and *J.* **Kapp**, nitro derivatives of 2-methylnaphthalene, i, 246, 804.
Vesterberg, *K. A.*, α-paltreubyl alcohol, an inactive form of β-amyrin, i, 1062.
Vesterberg, *K. A.*, and *E.* **Borge**, terpenes, phytosterols, and resins. III. Pyrogenic decomposition of abietic acid, i, 252.
Vesterman, *A.* See *V.* **Grignard**.
Vickery, *H. B.*, nitrogenous constitution of the juice of the alfalfa [lucerne]. IV. Betaine fraction, i, 1370.
Vickery, *H. B.*, and *C. S.* **Leavenworth**, nitrogenous constituents of the juice of the alfalfa [lucerne]. III. Adenine in alfalfa, i, 873.
Vickery, *H. B.*, and *C. G.* **Vinson**, nitrogenous constituents of the juice of the alfalfa [lucerne]. V. Basic lead acetate precipitate, i, 1370.
Vidic, *E.* See *O.* **Ruff**.
Viel, *E.* See *E.* **Caille**.
Viel, *J. E.* See *C.* **Dufraisse**.
Vieweg, *W.*, action of aqueous and aqueous-alcoholic solutions of sodium hydroxide on cellulose, i, 12.
absorption of sodium hydroxide by cellulose from solutions, i, 119.
Vigneaud, *V. du.* See *C. S.* **Marvel**.
Vila, *A.*, reduction of sulphuric acid to hydrogen sulphide, ii, 148.
Vilbrandt, *F. C.*, elimination of surface devitrification on laboratory quartzware, ii, 1091.
Vilon, *E.* See *E.* **Carrière**.
Vilsmeier, *A.* See *O.* **Fischer**.
Vincent, *G. P.*, potassium dichromate as depolariser, ii, 882.

Vincent, *P. D.*, effect of treatment with sulphuric acid on the breaking load of cotton, ii, 783.
Vinney, *S. S. de.* See *L. R.* **Ingersoll.**
Vinogradski, *S.*, measurement of the nitrogen-fixing capacity of soils, i, 623.
soil microbiology, i, 765.
Vinson, *C. G.* See *H. B.* **Vickery.**
Vio, *W.* See *F. X.* **Erben.**
Viol, *C. H.*, *G. D.* **Kammer**, and *A. L.* **Miller**, decay and regeneration of radio-luminescence, ii, 474, 1117.
Virli, *G.* See *F.* **Zetzsche.**
Virtánen, *A. I.*, insulin, i, 753.
lactic acid fermentation. I., i, 866.
influence of colloids in the reductase test, ii, 76.
Visco, *S.*, enzymes present in the latex of *Ficus carica*. I. Esterases, i, 471.
Visscher, *M. B.*, nature of the sugar in blood, i, 1343.
Visser, *J. C. S. de.* See *G.* **Hertz.**
Vita, *N.* See *M.* **Padoa.**
Vitale, *C.* See *G.* **Charrier.**
Viterbi, *E.*, ultra-violet absorption of aqueous potassium permanganate solutions, ii, 352.
Vitha, *J.* See *J.* **Frejka.**
Vitkovski, *D. P.* See *A. E.* **Tschitschibabin.**
Vivario, *R.* See *A.* **Desgrez.**
Vixseboxse, *H.*, influence of solvent on the equilibrium of isomerides, ii, 396.
Vlădescu, *R.*, determination of chloride in animal tissue, i, 1113.
inorganic phosphates in milk, i, 1114.
Vleck, *J. H. van*, specific heat of an elastic gyroscopic model of the hydrogen molecule, ii, 1138.
Vlès, *F.*, spectrophotometric determination of p_H, ii, 595.
Vlès, *F.*, and (*Mlle.*) *M.* **Gex**, ultra-violet absorption as a function of p_H of some organic acids, considered as ultra-violet indicators, ii, 472.
behaviour of benzene in aqueous solutions; ultra-violet absorption as a function of p_H, ii, 1115.
Vlès, *F.*, and *E.* **Vellinger**, physico-chemical properties of gelatin; rotatory power, ii, 292.
variations in the rotatory power of tartaric acid as a function of p_H, ii, 356, 964.
hydrogen electrode, ii, 817.
Vlès, *S. I.* See *W.* **Reinders.**
Voegtlin, *C.*, *H. A.* **Dyer**, and *C. S.* **Leonard**, specificity of the so-called arsenic receptor in the higher animals, i, 861.
Voegtlin, *C.*, *J. M.* **Johnson**, and *H. A.* **Dyer**, reducing power of normal and cancer tissue, i, 99.
protoplasmic action of copper and gold, i, 1116.
Voegtlin, *C.*, *J. W.* **Thompson**, and *E. R.* **Dunn**, hyperglycæmia produced by glycerol, i, 1211.
Voeller, *F.* See *R.* **Anschütz.**
Voge, *C. I. B.* See *W. O.* **Kermack.**
Vogel, *F.* See *H.* **Niklas.**
Vogel, *I.*, constitution of the thionic acids, ii, 1189.
Vogel, *I.*, and *J. R.* **Partington**, sulphur sesquioxide, ii, 890.
Vogel, *I.* See also *A.* **Ferguson.**
Vogel, *L.* See *L.* **Kalb.**
Vogel, *R.*, structure of iron–nickel meteorites, ii, 709.
Vogel, *W.*, nitrosomethylurethane as a reagent for pyrocatechol tannins, ii, 827.
Vogler, *H.* See *P. P.* **Koch.**
Vogt, *A.* See *S.* **Goldschmidt.**
Vogt, *M.* See *E.* **Mislowitzer.**
Voigt, *A.* See *R.* **Lorenz.**
Voit, *K.* See *R.* **Feulgen.**
Volbert, *F.* See *H.* **Ley.**
Vollenbruck, *O.* See *O.* **Bauer.**
Vollmann, *H.*, colloid-chemistry of linseed oil, ii, 517.
Vollmer, *H.*, *W.* **Schmidt**, and *J.* **Serebrijski**, anti-lipolytic effect of iodine, i, 335.
Volmar, photolysis of ethylenic dibasic acids, i, 1378.
photolysis of dibasic acids, ii, 575.
Volmer, *M.*, thermodynamic deductions from the equation of state for adsorbed substances, ii, 539.
Volmer, *M.*, and *P.* **Kirchoff**, vapour pressures of solid and liquid benzophenone between 0° and 48°, ii, 494.
Volmer, *M.*, and *P.* **Mahnert**, solution of solids in liquid surfaces, and the properties of the resulting films, ii, 508.
Volmer, *T.*, slow corpuscular radiations from salts, ii, 7.
Voltolin, *P. M.* See *L.* **Cambi.**
Volwiler, *E. H.*, alkylallylbarbituric acids, i, 1173.
Volwiler, *E. H.* See also *R.* **Adams.**
Vonaesch, *F.* See *H.* **Rupe.**
Vondraček, *R.*, and *J.* **Izák-Krizko**, influence of impurities in zinc on its solubility in acids, ii, 686.
Voorhees, *V.*, and *G. S.* **Skinner**, derivatives of barbituric acid, i, 837.
Voorhis, *C. C. van*, diffusion of helium through different glasses, ii, 1143.
Voorhis, *C. C. van.* See also *K. T.* **Compton.**

Vorländer, *D.* [with *K.* **Büchner**, *E.* **Spreckels**, *E.* **Schroedter**, *O.* **Meissner**, *F.* **Caesar**, *E.* **Fischer**, *Walter* **König**, and *H.* **Hoffmann**], conception of internal molecular strain and the directing of substituents in benzene, II., i, 1255.

Vorländer, *D.* [with *H.* **Hiemesch**, *K.* **Schoenemann**, *W.* **Schade**, and *K.* **Kunze**], acid, salt, ester, and adduct, i, 267.

Vorländer, *D.*, and *K.* **Büchner**, fission of *p*-iodoxynitrobenzene by alkali hydroxide, i, 1055.

Vorländer, *D.*, *Ernst* **Fischer**, and *K.* **Kunze**, ε-phenyl-$\Delta^{\beta\delta}$-pentadien-α-al and η-phenyl-$\Delta^{\beta\delta\zeta}$-heptatrien-α-al, i, 1068.

Vorländer, *D.*, and *K.* **Kunze**, green modification of *pp'*-dihydroxyazobenzene, i, 1106.

Vorländer, *D.*, *W.* **Selke**, and *S.* **Kreiss**, doubly-refractive white phosphorus, ii, 1086.

Vorländer, *D.*, and *R.* **Walter**, double refraction of amorphous liquids and molecular constitution, ii, 183.

Vortmann, *G.*, generally applicable method of conducting an elementary organic analysis by the wet way, ii, 827.

Vosburgh, *W. C.*, conditions affecting the reproducibility and constancy of Weston standard cells, ii, 672.

decrease in electromotive force of unsaturated Weston cells, ii, 1066.

saturated standard cell with small temperature coefficients, ii, 1164.

Vosnessenski, *S.*, thermodynamic potential difference at the boundary of two liquid phases, ii, 673.

Voswinckel, *H.*, preparation of dyes, i, 572.

Votoček, *E.*, and *P.* **Jirů**, halogenated aromatic hydrazines. I. 3:4-Dibromophenylhydrazine, i, 317.

Votoček, *E.*, and *R.* **Lukes**, oxidation of the sugar alcohols from the stereochemical point of view, i, 773.

Vrevski, *M.*, equilibrium between vapour and liquid of aqueous solutions of ammonia, ii, 102.

equilibrium between liquid and gaseous phases of aqueous solutions of hydrogen chloride and of hydrogen bromide, ii, 102.

specific heats of aqueous solutions of hydrogen chloride and ammonia at various temperatures, etc. I.–V., ii, 126.

Vrevski, *M.*, and *A.* **Kaigorodov**, specific heats of aqueous solutions of hydrogen chloride and ammonia at various temperatures, ii, 125.

Vrevski, *M.*, and *N.* **Savaritzki**, heats of formation of aqueous solutions of hydrogen chloride and ammonia at different temperatures, ii, 126.

Vrevski, *M.*, *N.* **Savaritzki**, and *L.* **Scharlov**, determination of the vapour pressures and of the composition of the vapour phases in equilibrium with aqueous solutions of hydrogen chloride and hydrogen bromide at different temperatures, ii, 101.

Vries, *T. de.* See *W. H.* **Rodebush**.

Vrtiš, *M.*, tervalent copper, ii, 694.

Vürtheim, *A.*, determination of potassium in potassium salts as perchlorate, ii, 437.

Vuillaume, *M.* See *A.* **Boutaric**.

Vuilleumier, *E. A.*, determination of acetone in presence of alcohol by a vapour pressure method, ii, 246.

Vyle, *L. R.*, and *F. S.* **Kipping**, organic derivatives of silicon; action of mercuric oxide on diaryldichlorosilicanes, i, 172.

W.

Waard, *R. H. de*, Weiss's theory of ferromagnetism, ii, 751.

Wache, *X.*, and *G.* **Chaudron**, influence of thermal and mechanical treatment on the rate of dissolution of aluminium in hydrochloric acid, ii, 687.

Wachendorff, *E.* See *E.* **Berl**.

Waddell, *J.* See *E. B.* **Hart**.

Wade, *F. B.*, detection of traces of iodides, ii, 598.

Waele, *A. de*, alteration of viscosity of disperse systems with the velocity of shear, ii, 777.

Waelsch, *E.*, calculation with pole-systems: crystal groups and crystal dynamics, ii, 485.

Waelzel, *O.*, determination of hydrofluoric acid, ii, 433.

Wagenhofer, *A.*, *p*-orsellinic acid, i, 550.

Wagler, *K.* See *F.* **Hein**.

Wagner, *C.*, mechanism of the oxidation of the iodine ion by the ferricyanide and ferric ion, ii, 49.

surface tension of dilute electrolytes, ii, 387.

calculation of reaction velocity coefficients, ii, 406.

influence of temperature on reaction velocity in solution, ii, 407.

Wagner, *C.*, Trouton's rule as a criterion of association, ii, 762.
Wagner, *C.* See also *K.* **Täufel.**
Wagner, *E.*, *K. F.* **Meyer**, and *C. C.* **Dozier**, metabolism of *Bacillus botulinus*. XXVI., i, 1510.
Wagner, *E. C.*, evaluation of chlorates, ii, 1196.
Wagner, *R.* See *W.* **Hieber.**
Wagner, *W.*, experiments with the local anæsthetics psicaine and tutocaine, i, 1503.
Wagner-Jauregg, *T.* See *R.* **Kuhn.**
Wahl, *A.*, preparation of esters, i, 880.
Wahl, *A.*, and *T.* **Faivret**, derivatives of 7-methylisatin, i, 588.
Wahl, *A.* See also *R.* **Lantz.**
Wahl, *A. R.* See **Société Anonyme des Matières Colorantes, et Produits Chimiques de St. Denis.**
Wahl, *R.* See *E.* **Cherbuliez.**
Wahl, *W. A.*, valency relations of boron, carbon, and nitrogen from the standpoint of the Bohr atomic model, ii, 937.
problems of boron chemistry, ii, 938.
Wahlin, *C. S.* See *A.* **Biester**, and *J. J.* **Willaman.**
Wahlin, *H. B.*, mobilities of the positive ions in helium, ii, 170.
relative mobility of initial positive ions in gas mixtures at low pressures, ii, 615.
Waibel, *F.* See *C.* **Füchtbauer.**
Waksman, *S. A.*, what is humus? i, 1528.
Waksman, *S. A.*, and *S.* **Lomanitz**, decomposition of proteins and amino-acids by various groups of micro-organisms, i, 867.
Walcker, *R.* See *R.* **Schwarz.**
Waldbauer, *L. J.* See *O.* **Maass.**
Walden, *P.*, fifty years of stereochemical theory and investigation, i, 849.
Walden, *P.*, and *H.* **Ulich**, conductivity determinations in non-aqueous salt solutions, ii, 209.
Walden, *P.*, *H.* **Ulich**, and *F.* **Laun**, electrical conductivity measurements in dilute methyl- and ethyl-alcoholic solution at 0°, 25°, and 56°, ii, 208.
Walden, *P.*, *H.* **Ulich**, and *O.* **Werner**, dielectric constants of solutions of electrolytes. I. and II., ii, 512, 773.
Waldie, (*Miss*) *A. T.*, impact experiments in compound gases; ammonia, ii, 1106.
Waldmann, *E.* See *K.* **Dziewoński.**
Waldmann, *H.* See *G.* **Weissenberger.**
Waldschmidt-Leitz, *E.*, and *A.* **Hartenech**, tryptic and ereptic activity of the pancreas, i, 1360.
Waldschmidt-Leitz, *E.*, and *A.* **Schäffner**, specific nature of animal proteases. I. Importance of diketopiperazines in the synthesis of proteins, i, 1110.
Waldschmidt-Leitz, *E.*, and *F.* **Seitz**, rôle of oxygen in catalytic hydrogenation by means of platinum, ii, 411.
Waldschmidt-Leitz, *E.* See also *R.* **Willstätter.**
Wales, *H.* See *O. A.* **Nelson**, and *S.* **Palkin.**
Walker, *A. C.* See *J.* **Johnston.**
Walker, *A. J.* See *F. D.* **Chattaway.**
Walker, *E.*, oxidations in turpentine and olive oil, i, 990.
Walker, *G. H.*, and *I. M.* **Heilbron**, styrylbenzopyrylium salts. IV. γ-Styryl derivatives of 5:7-dihydroxy- and 5:7-dimethoxy-2-phenyl-4-methylbenzopyrylium chlorides, i, 693.
Walker, *G. H.* See also *W. H.* **Cooke**, and *I. M.* **Heilbron.**
Walker, *H.*, influence of different substances on the diastatic activity of saliva, i, 738.
Walker, *J. C.*, *C. C.* **Lindegren**, and *F. M.* **Bachmann**, toxicity of juice extracted from succulent onion scales, i, 872.
Walker, *M.*, and *D. N.* **Eldred**, decomposition of liquid hydrocyanic acid, i, 1393.
Walker, *O. J.*, solubility of bi-bivalent salts in solutions containing a common ion, ii, 769.
Walker, *T. K.*, synthesis of arylazoaldoximes, i, 1193.
the preservative principles of hops, i, 1479.
Walker, *T. R.*, nomenclature of the hop resin constituents, i, 1479.
Walker, *W. B.*, colorimetric determination of small amounts of iron, ii, 717.
Walker, *W. J.*, critical pressure-ratio for gases as affected by variable specific heat, ii, 100.
Walker, *W. M.*, *J. H.* **Sorrels**, and *J. M.* **Breckenridge**, potentials of copper and zinc in cyanide solutions, ii, 1066.
Wallach, *G.* See *A.* **Smits.**
Walter, *B.*, wave-length and width of the *K*-absorption limit of zinc, ii, 611.
Walter, *O.*, enzyme dialysis, i, 1357.
decomposition of arginine in *Lupinus luteus* by means of enzymes, i, 1358.
Walter, *R.* See *D.* **Vorländer.**

Walters, *F. M., jun.*, regularities in the arc spectrum of cobalt, ii, 334.
regularities in the arc spectrum of nickel, ii, 335.
Walters, *F. M., jun.* See also *W. F.* **Meggers.**
Walters, *J. E.*, and *A. G.* **Loomis**, cryostat for precision measurements at temperatures extending to −180°, ii, 1091.
Walters, *W.* See *J. P.* **Bowler.**
Walther, *T.* See *L.* **Dede.**
Walton, *J. H.*, and *R. V.* **Wilson**, equilibrium in the system, carbamide-methyl alcohol, ii, 505.
Wander, *G.* See *O. A.* **Oesterle.**
Wang, *C.* See *W. R.* **Orndorff.**
Wang, *C. C.*, and *A. R.* **Felsher**, effect of hæmolysis on the calcium and inorganic phosphorus content of serum and plasma, i, 995.
Wang, *D. G.* See *M.* **Nierenstein.**
Wangler, *J. G.* See *S. L.* **Jodidi.**
Wankell, *F.* See *E.* **Boden.**
Wanner, *E.*, influence of methyl and sulphonic acid groups as well as other substituents on the colour of azo dyes, i, 841.
Warburg, *E.*, theory of chemical action in Siemens ozone tubes, ii, 706.
quantum laws in photochemistry, ii, 984.
Warburg, *E.*, and *W.* **Rump**, production of ozone by silent discharge at low pressures, ii, 706.
Warburg, *O.*, method of measuring respiration and glycolysis, i, 321.
[mechanism of oxidation processes], i, 374.
iron, the oxygen-carrying component of the oxidative enzyme, i, 471.
metabolism of carcinoma cells, i, 1206.
iron, the oxygen-carrier of respiration-ferment, i, 1481.
lactic acid formation during growth, i, 1492.
Warburton, *F. W.*, and *F. K.* **Richtmyer**, *X*-ray absorption coefficients in the neighbourhood of *K*-limits, ii, 1103.
Ward, *A. M.* See *G.* **Senter.**
Ward, *L. A.* See *N. A.* **Lange.**
Wardlaw, *W.*, and *F. H.* **Nicholls**, molybdenum pentoxide, ii, 817.
Wardlaw, *W.*, and *W. H.* **Parker**, compounds of tervalent molybdenum. III. Oxalates, i, 893.
Wardlaw, *W.*, and *R. L.* **Wormell**, compounds of tervalent molybdenum. II. Molybdenum monochloride, ii, 61.
Ware, *A. H.*, detection of plant phenols by the use of nitrites or nitric acid, i, 1122.
use of Mitchell's ferrous tartrate reagent in qualitative analysis, ii, 444.
modifications of the ferric citrate precipitation test for tannins, ii, 905.
identification of drugs containing tannins, ii, 1209.
Waris, *G.*, equilibrium in the ternary system, bismuth oxide, hydrochloric acid, water, ii, 786.
Warkany, *J.*, behaviour of the reserve carbohydrate of yeast in assimilation and dissimilation, i, 105.
Warnat, *K.* See *A.* **Skita.**
Warr, *J. C.* See *M.* **Nierenstein.**
Wartenberg, *H. von*, ozone from flames, ii, 147.
osmium tetroxide, ii, 231, 276.
chemistry of high temperatures, ii, 576.
action of some gases on silicates, ii, 699.
Wartenberg, *H. von*, and *G. von* **Podjaski**, ozone [determination and solubility], ii, 1198.
Wartenberg, *H. von*, and **Lerner-Steinberg**, heat of formation of formaldehyde, ii, 745.
Wartenberg, *H. von*, and *D.* **Weigel**, dissociation of chlorine, ii, 668.
Waser, *E.*, catalytic hydrogenation with hydrogen and platinum, i, 584.
Waser, *E.*, and *K.* **Sander**, oxalic acid as an agent for splitting off alcohol groups, i, 536.
Washington, *H. S.*, radial distribution of certain elements in the earth, ii, 234.
chemical composition of the earth, ii, 591.
Washington, *H. S.* See also *F. W.* **Clarke**, and *R. W. G.* **Wyckoff.**
Wasser, *E.*, photo-electric effect for submicroscopic mercury drops, ii, 80.
effect of adsorption of gases on the density of mercury droplets, ii, 80.
Wassermann, *A.* See *R.* **Kuhn.**
Wasteneys, *H.*, and *H.* **Borsook**, fractional analysis of incomplete protein hydrolysates, i, 97.
enzymic synthesis of protein. I. Synthesising action of pepsin, i, 102.
enzymic synthesis of protein. III. Effect of p_H on peptic synthesis, i, 472.
enzymic synthesis of protein. V. Synthesising action of trypsin, i, 865.

Wasteneys, *H.* See also *H.* **Borsook.**
Wastl, *H.* See *L.* **Berczeller.**
Watase, *T.* See *S.* **Mitsukuri.**
Waterman, *H. I.*, and *J. N. J.* **Perquin**, decomposition of paraffin wax at 450° in presence and in absence of hydrogen under high pressure, i, 1125.
Watkins, *H. R.* See *S.* **Palkin.**
Watson, *D. L.*, thermal decomposition of derivatives of ethyl oxalacetate; a unimolecular reaction, ii, 556.
Watson, *E. C.* See *J. A.* **Becker.**
Watson, *F. S.* See *J. B.* **Firth.**
Watson, *H. B.*, reaction of bromine with aliphatic acids; catalytic effect of acyl halides, i, 1232.
Watson, *H. E.* See *B. S.* **Rao**, and *J. J.* **Sudborough.**
Watson, *W. H.*, absorption of superposed *X*-radiations, ii, 458.
Watson, *W. H.* See also *S. R.* **Khastgir.**
Watson, *W. W.*, emission spectrum of water vapour, ii, 349.
Watt, *J. S.*, mobility of negative ions in flames by the Hall effect method, ii, 170.
Wattiez, *N.*, presence of β-methylglucoside in the leaves of *Scabiosa succisa*, L. (*Dipsaceæ*), i, 1521.
Wayman, *M.* See *J. Howard* **Mueller.**
Wayne, *E. J.*, and *J. B.* **Cohen**, addition of ethyl malonate to anils, i, 550.
Weatherby, *L. S.*, *L.* **McIlvaine**, and *D.* **Matlin**, butyrin, i, 1128.
Weatherill, *P. F.*, atomic weight of antimony, ii, 23.
filling mercury manometers, ii, 896.
Weaver, *S. D.* See *C. K.* **Ingold.**
Webb, *T. J.*, third law of thermodynamics and calculation of entropies, ii, 867.
Weber, *A. P.*, suitability of the Seemann "edge-method" for measurements of *X*-ray standards, ii, 458.
non-existence of the Clark–Duane secondary spectra from faultless crystals, ii, 1034.
Weber, *B.* See *G.* **Jander.**
Weber, *C. J.* See *W. C.* **Rose.**
Weber, *E.* See *K.* **Freudenberg.**
Weber, *F.*, effect of cold rolling on structure of cubic crystals, ii, 93.
Weber, *F.* See also *P.* **Karrer.**
Weber, *G.* See *H.* **John**, and *R.* **Kremann.**
Weber, *H.* See *F.* **Auerbach.**
Weber, *H. H.*, colloidal characteristics of muscle proteins. I. Isoelectric point and stability of myogen. II. Isoelectric point and solubility of myosin, i, 995.
Weber, *J.*, significance of ions in muscular function. VIII. Action of different alkali salts on the fermentative breakdown of glycogen in frog's muscle pulp, i, 1004.
Weber, *J.* See also *H.* **Meerwein.**
Webster, *D. L.*, and *P. A.* **Ross**, Compton effect, ii, 92.
Compton effect with hard *X*-rays, ii, 1034.
Webster, *D. L.* See also *P. A.* **Ross.**
Webster, *E. R.* See *R. C.* **Frederick.**
Webster, *L. T.*, acid agglutination of mixtures of oppositely charged bacterial cells, i, 749.
Webster, *T. A.*, *L.* **Hill**, and *A.* **Eidinov**, measurement of ultra-violet light by means of an acetone methylene-blue solution, i, 750.
Webster, *T. A.* See also *J. C.* **Drummond.**
Webster, *W. L.*, magnetic properties of iron crystals, ii, 369.
Wecher, *E. J.* See *V.* **Lenher.**
Weckering, *A.* See *A.* **Dewael.**
Wedekind, *E.*, asymmetric nitrogen atom. LIII. Activation problem in the case of quaternary ammonium bases with a double linking at the nitrogen atom, i, 678.
relations between chemical constitution and camphor-like physiological action in compounds not of the camphor series, i, 684.
Wedekind, *E.*, *M.* **Miller**, and *C.* **Weinand**, action of triethylamine on adipyl and β-methyladipyl chlorides, i, 510.
Wedekind, *E.*, and *F.* **Uthe**, asymmetric nitrogen atom. LII. Dependence of the rate of decomposition of an optically active aminoammonium nitrate on the presence of primary, secondary, and tertiary amines, i, 536.
asymmetric nitrogen atom. LIV. Function of solvate formation in the decomposition of asymmetric amine-ammonium salts, i, 1059.
Weeks, *E. J.*, production of antimony hydride (stibine) at an antimony cathode in alkaline solution. II. and III., ii, 415, 882.
formula of cerium hydride, ii, 1186.
Weeks, *E. J.*, and *J. G. F.* **Druce**, solid antimony hydride, ii, 760.
bismuth dihydride, ii, 988.
bismuth trihydride and silver bismuthide, ii, 1188.
Weeldenburg, *J. G.*, determination of nickel by means of dimethylglyoxime in presence of iron and cobalt, ii, 72.

Wegner, *A.* See *W.* **Herz.**
Wegner, *W.* See *E.* **Rupp.**
Wegscheider, *R.*, kinetics of coupled reactions, ii, 47.
Wehmer, *C.*, conversion of lignin, cellulose, and wood into humic substances by fungi, i, 521.
supposed poisonous action of carbon monoxide on green plants, i, 1029.
Wehrmann, *O.* See *A.* **Gehring.**
Weidemann, *A. W.* See *M. M.* **McCool.**
Weidemann, *G.* See *E.* **Poulsson.**
Weiderpass, *N.*, Esthonian oil of peppermint, i, 687.
Weigel, *D.* See *H. von* **Wartenberg.**
Weigel, *O.*, properties and occurrence of zeolites, ii, 709.
Weigert, *F.*, and *L.* **Brodmann**, confirmation of Einstein's law of the photochemical equivalent in a very simple photochemical reaction, ii, 1075.
Weigert, *F.*, and *G.* **Käppler**, polarised fluorescence in solutions of dyes, ii, 1026.
Weiglé, *J. J.*, heat of evaporation of electrons, ii, 253.
Weiglé, *J. J.* See also *C. E.* **Guye.**
Weil, *H.*, and *M.* **Adler**, boric acid compounds of pyrocatechol, i, 136.
Weil, *R.*, microscopic study of the $\alpha\beta$-transformation of natural cristobalite, ii, 757.
synthesis of cristobalite in the wet way, ii, 1193.
Weil, *S.*, local anæsthetics, i, 157.
Weil, *S.* See also *M.* **Grabowska.**
Weimarn, *P. P. von*, dispersoid synthesis of gold. II., ii, 196.
stability of dispersoid silver solutions, ii, 198.
colloidal sugar. I. and II., ii, 290, 390.
jelly state of matter. I., ii, 390.
disperse systems, giving all the spectrum colours in order on temperature changes, ii, 390.
connexion between the dispersion process and the production of chemical compounds, ii, 395.
dispersoid study of cellulose, ii, 515.
general structure of matter in the colloidal state. I. Form and chemical composition of disperse particles in suspensoids and precipitates, ii, 660.
dispersion of different kinds of cellulose by mechanical means and by the action of aqueous salt solutions, ii, 782.
Weimarn, *P. P. von*, precipitates with stratified structures. I., ii, 959.
influence of added substances on the life of dispersoids. I., ii, 969.
structure of true solutions and the nature of the changes occurring therein, ii, 1055.
precipitation laws, ii, 1064.
Weimarn, *P. P. von*, and *S.* **Utzino**, effect of added substances on the stability of dispersoids. II., ii, 664.
Wein, *W.* See *W.* **Biltz.**
Weinand, *C.* See *E.* **Wedekind.**
Weinberg, *M.*, spark-spectra of indium and gallium in the extreme ultraviolet region, ii, 249.
Weinmann, *F.* See *M.* **Bergmann.**
Weinstock, *M.* See *A. F.* **Hess.**
Weir, *A. B.*, coagulation of a colloidal solution by hydrogen ions, ii, 1155.
Weir, *J. F.*, thyroxin and tryptophan content of the diseased thyroid gland, and the iodine compounds in desiccated thyroid, i, 1491.
Weiser, *H. B.*, adsorption by precipitates, ii, 108.
adsorption and Schulze's law, ii, 855.
Weiss, *H.*, application of *X*-rays to the study of alloys, ii, 940.
Weiss, *H.* See also *R.* **Schwarz.**
Weiss, *R.*, and *E.* **Freund**, action of organo-magnesium compounds on phthalonitrile. I., i, 139.
Weiss, *R.*, and *J.* **Korczyn**, triphenylmethane compounds with linked benzene nuclei. I. Trimethylenetriphenylmethane triketone, i, 560.
Weiss, *R.*, and *L.* **Sonnenschein**, *o*-phenylacetyldeoxybenzoin, its conversion into substituted naphthalenes and attempted preparation of further *o*-phenylene derivatives, i, 937.
Weiss, *S.* See *J.* **Holló.**
Weissbach, *H.* See *C.* **Drucker.**
Weissberg, *M.* See *M.* **Kohn.**
Weissenberg, *K.*, crystal structure and chemical constitution. I Transformation properties of matter, ii, 1129.
crystal structure and chemical constitution. II. Structural theory of crystals, ii, 1129.
crystal structure and chemical constitution. III. Analysis of crystal structure, ii, 1130.
Weissenberg, *K.* See also *R. O.* **Herzog.**
Weissenberger, *G.*, and *L.* **Piatti**, molecular compounds of phenols. I. Behaviour of the cresols towards alcohol, ether, and acetone, i, 538.

Weissenberger, *G.*, and *L.* **Piatti**, molecular compounds of phenols. II. Behaviour of cresols towards aromatic hydrocarbons, i, 539.

Weissenberger, *G.*, and *F.* **Schuster**, molecular compounds of phenols. III. Behaviour of binary systems with hydrogenated phenols, ii, 648.

molecular compounds of the phenols. V. Vapour pressure curves, ii, 765.

Weissenberger, *G.*, *F.* **Schuster**, and *N.* **Mayer**, molecular compounds of phenols. VI. Behaviour of the naphthols, the *ar*-tetrahydronaphthols, and related substances, ii, 766.

Weissenberger, *G.*, *F.* **Schuster**, and *K.* **Schuler**, molecular compounds of phenols. IV. Binary systems with phenol and its ethers, ii, 649.

Weissenberger, *G.*, and *H.* **Waldmann**, adsorption from viscous media by charcoal, ii, 655.

Weitz, *E.*, preparation of oxidoketones, i, 408.

solubility of ammonium salts in presence of ammonia, ii, 1147.

Weitz, *E.*, and *Herbert* **Müller**, action of ammonia on aqueous solutions of ferrous salts, ii, 317.

Welker, *W. H.*, fractionation of the proteins of rattlesnake venom, i, 998.

Welker, *W. H.* See also *L.* **Hektoen**.

Wellcome Foundation, Ltd., and *W. H.* **Gray**, therapeutic compound [sodium *p*-aminophenylstibinate glucoside], i, 991.

Wellcome Foundation, Ltd., *W. H.* **Gray**, and *T. A.* **Henry**, therapeutic compounds [esters of benzoyl-*l*-ecgonine and similar compounds], i, 1446.

Wellcome Foundation, Ltd., *T. A.* **Henry**, and *T. M.* **Sharp**, therapeutic compounds [mercuri compounds of phenols], i, 1154.

Welling, *W. F.* See *O. L.* **Brady**.

Wells, *A. H.*, and *F.* **Garcia**, chemical and pharmacodynamic investigation of *Strophanthus lutei*, Merrill, i, 614.

Wells, *A. W.* See *D. K.* **Tressler**.

Wells, *R. C.*, reaction between ferrous salts and cuprous salts, ii, 148.

Welo, *L. A.*, magneton numbers of iron in some complex salts, ii, 943.

Welo, *L. A.*, and *O.* **Baudisch**, two-stage transformation of magnetite into hæmatite, ii, 845.

valency theories and the magnetic properties of complex salts, ii, 1031.

Welo, *L. A.*, and *O.* **Baudisch**, catalytically active and inactive forms of ferric oxide, ii, 1071.

Welo, *L. A.* See also *O.* **Baudisch**.

Weltmann, *O.* See *H. K.* **Barrenscheen**.

Weltzien, *W.*, ethers of polysaccharides with hydroxy-acids, i, 12.

Weltzien, *W.* See also *K.* **Hess**.

Wendehorst, *E.*, colorimetric determination of molybdenum, ii, 718.

Wendehorst, *E.* See also *G.* **Jander**.

Wendlandt, *R.*, detonation limits of gaseous mixtures, ii, 135.

detonation limits in explosive gas mixtures, ii, 801.

Wendt, *G. L.*, and *M.* **Farnsworth**, equilibrium of carbon dioxide with carbon monoxide and oxygen in the corona discharge, ii, 1158.

Wengefeld, *E.* See *A.* **Kurtenacker**.

Wenger, *P.*, and *M.* **Müller**, separation of zirconium from iron, ii, 1207.

Wenger, *P.* See also *L.* **Duparc**.

Wenner, *W.* See *K.* **Freudenberg**.

Wentzel, *G.*, complex structure of Röntgen-spark spectra, ii, 251.

the term problem of doublet spectra, with particular reference to *X*-ray spectra, ii, 728.

Wenzel, *E.* See *R.* **Willstätter**.

Werner, *G.*, calculations for and calibration of the Haber–Löwe gas interferometer, ii, 1091.

Werner, *H.* See *H.* **Schmalfuss**.

Werner, *O.* See *G.* **Klein**, and *P.* **Walden**.

Werner, *S.*, excitation of spark spectra, ii, 165.

spark spectrum of lithium, ii, 1013.

Wertheimer, *E.*, kinetic and electromagnetic definition of the thermodynamic temperature of a gas, ii, 784.

Wertheimer, *E.*, and *H.* **Paffrath**, permeability and physiological action of compounds of the choline group, i, 1211.

Wesly, *W.* See *A.* **Schleicher**.

Wesolowski, *W. A.* See *F. O.* **Rice**.

Wessel, *W.*, evaluation of the grating energy of crystals, ii, 640.

surface potential in solutions of inorganic electrolytes, ii, 795.

Wessel, *W.* See also *H.* **Lindemann**.

Wessely, *F.*, anhydrides of *N*-carboxylic derivatives of α-amino acids, i, 1151.

Wesson, *L. G.*, relationship of arachidonic acid to saturated fatty acids in metabolism, i, 1353.

West, *E. S.*, interference of ammonia with the hypochlorite reaction for aniline, ii, 168.

West, *J.* See *W.* **Mandell**.

West, *R. M.* See *J. J.* **Willaman.**
West, *R. W.*, quantitative reduction by hydriodic acid of halogenated malonyl derivatives. IV. Influence of substitution in the amide group on the reactivity of the halogen atom in bromomalonamide, i, 524.
reduction of aromatic nitro compounds, i, 535.
West, *W.*, and *E. B.* **Ludlam**, ionisation of iodine vapour by ultra-violet light, ii, 476.
West, *W.* See also *E. B.* **Ludlam.**
Westgarth, *G. C.* See *W. N.* **Haworth.**
Westgren, *A.*, and *G.* **Phragmén**, structure of alloys, ii, 502.
X-ray analysis of copper–zinc, silver–zinc, and gold–zinc alloys, ii, 746.
crystal structure of manganese, ii, 1035.
Westling, *G.* See *H. von* **Euler.**
Weston, *F. R.*, flame spectra of carbon monoxide and water-gas. I., ii, 928.
Westphal, *W.*, equilibrium between radiation and matter, ii, 926.
Wettstein, *H.* See *W.* **Manchot.**
Wetzel, *J.*, mercury distillation apparatus, ii, 589.
Wetzel, *M.* See *H.* **Schmalfuss.**
Wever, *F.*, constitution of technical iron, ii, 503.
Weygand, *C.*, and *L.* **Frieling**, simplest *O*-alkyl ethers of benzoylacetone and phenylmethyl*iso*oxazole, i, 1288.
Whalen, *H. F.*, and *L. W.* **Jones**, action of hydroxylamine on sulphinic acids and their derivatives, i, 802.
Whalen, *H. F.* See also *L. W.* **Jones.**
Wheatley, *A. H. M.* See *R. V.* **Stanford.**
Wheatley, *J. H.*, martensite and troostite, ii, 488.
Wheeler, *A. S.*, and *R. W.* **Bost**, 4-*p*-tolylsemicarbazide and certain derivatives, i, 317.
Wheeler, *A. S.*, and *F. P.* **Brooks**, action of phenylsemicarbazide on acetylacetone, i, 1459.
Wheeler, *A. S.*, and *C. R.* **Harris**, occurrence of borneol in spruce turpentine, i, 1437.
Wheeler, *A. S.*, and *M.* **Morse**, chlorination of *p*-xylidine, and certain new azo dyes, i, 22.
Wheeler, *R. V.*, ignition of gases. V. Ignition by induction sparks; mixtures of the paraffins with air, ii, 408.
Wheeler, *R. V.* See also *O. C. de C.* **Ellis**, *W.* **Francis**, *V. H.* **Legg**, and *F. V.* **Tideswell.**
Whelan, *M.*, effect of intravenous injection of inorganic chorides on composition of blood and urine, i, 860.
Whetham, *M. D.* See *J. H.* **Quastel.**
Whiston, *J. R. H.*, preparation of 4-chloro-6-nitro-*m*-anisidine, i, 136.
preparation of naphthalic acid by oxidation of acenaphthaquinone, i, 140.
preparation of *iso*diphenetidine, i, 156.
Whitaker, *H.*, physical properties of nacreous sulphur, ii, 486.
purification of phosphoric oxide, ii, 1195.
Whitby, *G. S.*, and *G. L.* **Matheson**, heavy-metal salts of disubstituted dithiocarbamic acids, i, 644.
Whithy, *G. S.* See also *A. D.* **Macallum.**
White, *A. C.* See *C. P.* **Stewart.**
White, *A. G.*, limits for the propagation of flame in inflammable gas-air mixtures. I. Mixtures of air and one gas at ordinary temperature and pressure, ii, 48.
limits for the propagation of flame in inflammable gas-air mixtures. II. Mixtures of more than one gas and air, ii, 408.
limits for the propagation of flame in inflammable gas-air mixtures. III. Effect of temperature on the limits, ii, 553.
White, *E. C.*, and *R. C.* **Tolman**, initial rate of decomposition of nitrogen pentoxide, ii, 682.
White, *E. C.* See also *S. M.* **Rosenthal.**
White, *J. F.* See *J.* **Kendall.**
White, *H. L.*, comparison of the polarimeter and copper reduction values of dextrose solutions, ii, 1006.
White, *J. W.*, and *F. J.* **Holben**, chromic acid method for determining organic carbon, ii, 240.
Whitehead, *H. R.*, *J.* **Gordon**, and *A.* **Wormall**, "third component" or heat-stable factor of complement, i, 1202.
Whitehorn, *J. C.*, determination of lipoid phosphorus in blood and plasma, i, 95.
Whitford, *E. L.*, decomposition of malic acid by sulphuric acid, ii, 559.
Whitman, *J. L.* See *S.* **Popov.**
Whitman, *W. G.*, and *D. S.* **Davis**, comparative absorption rates for various gases, ii, 106.
Whitman, *W. G.*, and *R. P.* **Russell**, acid corrosion of metals; effect of oxygen and velocity, ii, 689.

Whitman, *W. G.*, *R. P.* **Russell**, and *G. H. B.* **Davies**, solubility of ferrous hydroxide and its effect on corrosion, ii, 505.
Whitman, *W. G.* See also *W. K.* **Lewis**.
Whitmore, *M. R.* See *F. T.* **Sisco**.
Whitney, *G. W.* See *E. D.* **Campbell**.
Whitney, *W. R.*, corrosion of iron [erosion], ii, 688.
Whittaker, *H.* See *W. J.* **Powell**, and *S.* **Sugden**.
Whittier, *E. O.*, lactose, i, 792.
Whitworth, *A. B.* See *I. M.* **Heilbron**.
Wibaut, *J. P.*, additive compound of triethylphosphine and carbon disulphide, i, 527.
Wibaut, *J. P.*, and *A.* **Coppens**, *C*(α-pyridyl)-1-methylpyrrole. II., i, 75.
Wibaut, *J. P.*, *J. J.* **Diekmann**, and *A. J.* **Rutgers**, addition of gaseous hydrogen chloride and hydrogen bromide to ethylene and propylene under the influence of catalysts, i, 494.
Wichers, *E.* See *W. D.* **Collins**.
Wichert, *E.*, and *H.* **Donat**, decomposition of [2:4:6-]trinitrotoluene by the action of sunlight, i, 803.
Wick, *F. G.*, and *J. M.* **Gleason**, effect of heat treatment upon the cathode luminescence of fluorite, ii, 262.
Widder, *W.*, elasticity modulus, temperature, and m. p., ii, 1043.
Widdowson, *W. P.*, and *A. S.* **Russell**, period of mesothorium-2, ii, 463.
Widell, *H.* See *H. von* **Euler**.
Widgoff, *L.* See *E. R.* **Riegel**.
Widmark, *E. M. P.*, and *O.* **Carlens**, influence of the intensity of lactation on the blood-sugar concentration of cows, i, 608.
Widmark, *E. M. P.*, and *K.* **Jensen-Carlen**, effect of carbohydrate metabolism on the synthesis of hippuric acid, i, 331.
Widmer, *R.* See *P.* **Karrer**.
Wieckowski, *W.* See *K.* **Jablczyński**.
Wiedbrauck, *E.* See *R.* **Lorenz**.
Wiederholt, *W.* See *E.* **Liebreich**, and *E.* **Maass**.
Wiegner, *G.*, dispersion and base exchange (ion exchange), ii, 527.
Wiegner, *G.*, *R.* **Galley**, and *H.* **Gessner**, retention of water in soils, ii, 36.
Wieland, *H.*, bile acids. XXII. Some unexplained results, i, 1065.
Wieland, *H.* [with *A.* **Baumann**, *C.* **Reisenegger**, *W.* **Scherer**, *J.* **Thiele**, *J.* **Will**, *H.* **Haussmann**, and *W.* **Frank**], fulminic acid. VII. Polymerisation of the fulminic acids; *iso*cyanilic and erythrocyanilic acids, i, 1048.
Wieland, *H.* [with *H.* **Haussmann**, and *H.* **Lövenskiold**], mechanism of oxidation processes. IX., ii, 1171.
Wieland, *H.* [with *Walter* **Schneider**, and *E.* **Martz**], chemical nature of the resin acids of hops. I., i, 276.
Wieland, *H.*, and *E.* **Dorrer**, Gattermann's synthesis of aldehydes in the case of enols, i, 779.
Wieland, *H.*, and *R.* **Jacobi**, bile-acids. XXIII. Components of human and ox bile; constitution of anthropodeoxycholic acid, i, 1488.
Wieland, *H.*, and *H.* **Jung**, so-called "dibromonitroethylene" and the mechanism of the formation of bromo- and chloro-picrins from polynitrophenols, i, 1374.
Wieland, *H.*, and *E.* **Krause**, fluorene compounds, i, 902.
Wieland, *H.*, *E.* **Martz**, and *H.* **Hoek**, chemical nature of the resin acids of hops. II., i, 1422.
Wieland, *H.*, and *G.* **Reverey**, bile acids. XXI. Human bile, i, 181.
Wieland, *H.*, and *C.* **Schöpf**, the yellow dye of the wing of the lemon butterfly (*Gonepteryx rhamni*), i, 1464.
Wieland, *H.*, *C.* **Schöpf**, and *W.* **Hermsen** [with *O.* **Dragendorff**], *Lobelia* alkaloids. II., i, 1087.
Wieland, *H.*, and *M.* **Kotake**, morphine alkaloids. III., i, 1090.
Wieland, *H.*, and *M.* **Kotake**, morphine alkaloids. IV. Constitution of thebaine, i, 1448.
Wien, *M.*, dependence on temperature of the internal friction and electrical conductivity of aqueous solutions, ii, 931.
Wien, *W.*, recent researches in positive rays, ii, 921.
Wiener, *B. S.* See *A. W.* **Rowe**.
Wierda, *J.*, and *H. C.* **Kremers**, concentration of praseodymium material and the preparation and properties of metallic praseodymium, ii, 993.
Wieringa, *H.* See *A. A. H. van den* **Bergh**.
Wiesen, *J.* See *M.* **Kohn**.
Wiesner, *S.*, specific heats, ii, 275, 757.
Wiessmann, *H.*, has silicic acid an influence on the morphological and anatomical structure of rye straw, where there is a deficiency of phosphatic food? i, 488.
influence of light on the absorption of nutrients by young plants, i, 757.
Wiessmann, *H.* See also *O.* **Lemmermann**.
Wiggers, *F. A.*, laboratory apparatus, ii, 319.

Wigglesworth, *V. B.*, ketosis. I. Relation between alkalosis and ketosis, i, 191.
Wigglesworth, *V. B.*, ketosis. II. Oxidation of ketone bodies by the isolated liver of the rat, i, 191.
Wightman, *E. P.* See *R. H.* **Lambert.**
Wightman, *W. A.*, spatial structure of *cyclo*paraffins. I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene, i, 894.
Wigner, *E.* See *M.* **Pólányi.**
Wijs, (*Miss*) *H. J. de*, composition and stability of complex metal–ammonium ions, ii, 889.
Wijs, (*Miss*) *H. J. de.* See also *F. E. C.* **Scheffer.**
Wilbur, *O. C.* See *W. S.* **Calcott.**
Wilcke, *G.* See *P.* **Günther.**
Wilcoxon, *F.*, *A. E.* **McKinney**, and *A. W.* **Browne**, azido-carbon disulphide. II. Reaction of azido-carbon disulphide and of free thiocyanogen with hydrogen trinitride [azoimide] in certain non-aqueous solvents, i, 1051.
Wild, *G.* See *F.* **Kehrmann.**
Wilde, *H. D.*, *jun.*, and *H. L.* **Lochte**, rapid determination of carbon in organic compounds, ii, 600.
Wilhelm, *R. M.* See *J. L.* **Finck.**
Wilke, *E.*, and *O.* **Kieniger**, activity coefficients, ii, 790.
Wilke, *E.*, and *H.* **Kuhn**, oxidation of hydrogen by potassium permanganate, ii, 51.
Wilke-Dörfurt, *E.*, and *M.* **Deker**, use of tap water as the outer liquid in dialysis, ii, 528.
Wilken, *D.* See *F.* **Krauss.**
Wilkendorf, *R.* See *M.* **Trénel.**
Wilkins, *H.* See *S.* **Sugden.**
Wilkinson. *J. A.*, and *W.* **Hoff**, adsorption of dyes by soils, i, 1227.
Wilkinson, *J. A.* See also *G. N.* **Quam.**
Wilkinson, *J. F.* See *F.* **Challenger.**
Will, *J.* See *H.* **Wieland.**
Willaman, *J. J.*, *C. S.* **Wahlin**, and *A.* **Biester**, carbohydrates. II. Relative sweetness of invert-sugar, i, 1499.
Willaman, *J. J.*, and *R. M.* **West**, composition of potato tubers, i, 1522.
Willcox, *J. S.*, and *E. B. R.* **Prideaux**, dissociation constants of selenious acids, ii, 867.
Willerding, *U.* See *A.* **Windaus.**
Williams, *A. M.*, surface tension, surface energy, and the surface layer. I., ii, 386.
Williams, *A. M.* See also *G. E.* **Collins**, and *A. R.* **Urquhart.**
Williams, *E. C. P.*, chemical composition of blood during labour, i, 713.
Williams, *E. G.* See *E. K.* **Rideal.**
Williams, *E. J.*, effect of a magnetic field on the electrical resistance of liquid metals and alloys, ii, 753.
electrical conductivity of some dilute amalgams, ii, 946.
Williams, *H. A.* See *H. N.* **Holmes.**
Williams, *J. R.*, and *G. U.* **Casey**, rapid determination of small amounts of dextrose in the urine in diabetes, i, 998.
Williams, *J. W.*, and *F.* **Daniels**, specific heats of binary mixtures, ii, 765.
Williams, *M. D.*, *H. C.* **Fogg**, and *C.* **James**, solubilities of rare earth salts. I., ii, 504.
Williams, *N. H.* See *A. W.* **Hull.**
Williams, *R.* See *G. W.* **Robinson.**
Williams, *R. R.*, ultra-violet light and the antineuritic vitamin, i, 751.
Williams, *R. R.* See also *W. H.* **Eddy.**
Williams, *W.* See *H. J.* **Page.**
Williams-Gardner, *A.*, "cracking" of paraffins, i, 1229.
Williamson, *R. V.*, and *J. H.* **Matthews**, rate of absorption and equilibrium of carbon dioxide in alkaline solutions, ii, 105.
Williamson, *W. T. H.* See *W. O.* **Kermack.**
Willimott, *S. G.*, apparatus for the catalytic dehydrogenation of alcohols, ii, 151.
Willimott, *S. G.*, and *F.* **Wokes**, vitamin content of *Cortex limonis*, B.P., i, 1220.
Wills, *G. O.* See *A.* **McKenzie.**
Willstätter, *R.*, synthesis of "psicaine," i, 424.
specific nature of lipases with respect to configuration, i, 1008.
Willstätter, *R.*, *F.* **Haurowitz**, and *F.* **Memmen**, pancreatic enzymes. IX. Specificity of lipases from different organs, i, 201.
Willstätter, *R.*, *H.* **Kraut**, and *E.* **Wenzel**, invertase. VII. Enzyme adsorption. II., i, 739.
Willstätter, *R.*, and *H.* **Kumagawa**, taka-esterase; comparison with pancreatic lipase and hepatic esterase, i, 1213.
Willstätter, *R.*, *C. D.* **Lowry**, *jun.*, and *K.* **Schneider**, increase of invertase content of yeast, i, 1214.
Willstätter, *R.*, and *H.* **Persiel**, pancreatic enzymes. XII. Determination of trypsin, i, 741.
Willstätter, *R.*, and *O. T.* **Schmidt**, synthesis of new anthocyanidins, i, 54.
Willstätter, *R.*, and *K.* **Schneider**, invertase. VIII., i, 739.

Willstätter, *R.*, *K.* Schneider, and *E.* Bamann, invertase. X., i, 1359.
Willstätter, *R.*, *F.* Seitz, and *J. von* Braun, hydrogenation of indole to perhydroindole [octahydroindole] and to *o*-ethylhexahydroaniline, i, 428.
Willstätter, *R.*, and *E.* Waldschmidt-Leitz, pancreatic enzymes. XI. Enterokinase, i, 741.
Willstätter, *R.*, *E.* Waldschmidt-Leitz, and *A. R. F.* Hesse, pancreatic enzymes. X. Adsorption behaviour of pancreatic amylase, i, 736.
Willstätter, *R.*, *L.* Zechmeister, and W. Kindler, syntheses of pelargonidin and cyanidin, i, 54.
Wilsdon, *B. H.*, chemical affinity and electronic structure. I. The non-polar band, ii, 481.
chemical affinity and electronic structure. II. The polar link, ii, 481.
magnetic properties of atoms and molecules, ii, 641.
Wilson, *B. D.* See *T. L.* Lyon.
Wilson, *C. P.* See *J. A.* Hall.
Wilson, *D. W.*, *W. L.* Long, *H. C.* Thompson, and *S.* Thurlow, changes in the composition of the urine after muscular exercise, i, 1115.
Wilson, *D. W.* See also *S. H.* Liljestrand.
Wilson, *F. J.*, and *A. B.* Crawford, action of amines on semicarbazones. II., i, 818.
Wilson, *F. J.*, and *E. C.* Pickering, derivatives of semioxamazide. III., i, 935.
Wilson, *F. J.* See also (*Miss*) *M. M. J.* Sutherland.
Wilson, *H. C.*, osmotic pressure of hæmoglobin; explanation of the effect of acetic acid, based on Donnan's theory of membrane equilibrium, ii, 292.
Wilson, *H. E. C.*, relation between sulphur and nitrogen metabolism, i, 729.
Wilson, *J. H.* See *H. H.* Hodgson.
Wilson, *K.* See *O.* Collenberg.
Wilson, *R. E.* See *W. H.* Bahlke.
Wilson, *R. V.* See *J. H.* Walton.
Wiltshire, *H. G.* See *H. B.* Newham.
Wimmer, *J.*, determination of methyl and ethyl alcohol, ii, 1006.
Winchell, *A. N.*, composition of melilite, ii, 152.
mica group, I. and II., ii, 592.
atoms and isomorphism, ii, 1122.
Wind, *F.*, oxidation of dihydroxyacetone and glyceraldehyde in phosphate solutions and acceleration of oxidation by heavy metals, ii, 1174.
Windaus, *A.*, and *A.* Bohne, thermal decomposition of γ- and δ-ketonic acids and their esters, i, 552.
Windaus, *A.*, *A.* Bohne, and *E.* Schwarzkopf, chenodeoxycholic acid, i, 405.
Windaus, *A.*, and *J.* Brunken, sterol of scopolia root, i, 108.
sitosterol, i, 394.
stigmasterol, i, 394.
presence of gitogenin in digitalis leaves, i, 873.
Windaus, *A.*, and *W.* Eickel, synthesis of certain dihydrophenanthrene derivatives, i, 32.
Windaus, *A.*, and *R.* Hossfield, conversion of cholesterol into 4-hydroxycholanic acid, i, 1066.
Windaus, *A.*, *H.* Jensen, and *A.* Schramme, synthesis of 9-methylphenanthrene, i, 19.
Windaus, *A.*, and *O.* Linsert, gitonin and its degradation products, i, 1438.
Windaus, *A.*, and *G.* Schwarte, gitoxin, a glucoside insoluble in chloroform from digitalis leaves, i, 1295.
Windaus, *A.*, and *U.* Willerding, digitonin and its degradation products, i, 1082.
Windhausen, *O.* See *R.* Fricke.
Windheuser, *C.* See *A.* Morgen.
Wing, *H. J.*, constant-level water baths, ii, 707.
Winkler, *H.* See *W.* Steinkopf.
Winkler, *L. W.*, gravimetric determination of the iodine–bromine number, ii, 446.
Nessler's reagent without potassium iodide, ii, 713.
preparation of bromine–acetic acid solution for determination of iodine–bromine number [of fats and oils], ii, 1009.
detection of sodium as oxalate, ii, 1095.
Winter, *F. A.* See *L. A.* Congdon.
Winter, *H.* See *H.* Funk.
Winter, *R. M.* See *T.* Barratt.
Winterer, *E. V.*, percolation of water through soils, i, 1527.
Winterfeld, *K.* See *J.* Gadamer.
Winters, *N. E.*, soil conditions which promote nitrogen fixation, i, 767.
Winterstein, *H.*, and *E.* Hirschberg, formation of ammonia in the nervous system, i, 607.
glycogen and cerebroside metabolism of the central nervous system, ii, 1495.
Wintgen, *R.*, and *E.* Meyer, action of colloidal and semi-colloidal ferric hydroxide on aqueous gelatin solutions. I., ii, 524.

Winther, *C.*, oxidation of hydrogen iodide. II., ii, 56.
relation between quantum sensitivity and intensity of radiation, ii, 1074.
relation between velocity of photochemical reactions and dielectric constant, ii, 1082.
Winzer, *K.* See *H.* **Leuchs.**
Wirzmüller, *A.* See *W.* **Manchot.**
Wismer, *K. L.* See *F. B.* **Kenrick.**
Wisniewski, *F. J. von*, doublets of the alkali metals, ii, 77.
possible structure of the hydrogen halides, ii, 361.
s-term, ii, 449.
arc spectrum of sodium, ii, 451.
theory of the spark spectra of aluminium, ii, 451.
absorption limits of *K*-series, ii, 457.
Witkovsky. See **Vitkovski.**
Witmer, *E. E.*, theory of the decay of α-ray luminescence, ii, 89.
Witt, *H.*, spectrometric methods of investigation of the infra-red, ii, 335.
series in absorption spectrum of water vapour, ii, 352.
Witte, *C.* See *M.* **Bergmann.**
Wittekindt, *W.* See *K. von* **Auwers.**
Wittig, *G.*, action of ammonia on *o*-hydroxyphenyl-1:3-diketones, i, 279.
simple apparatus for the determination of carbon dioxide, ii, 1094.
Wittig, *R.* See *H.* **Reihlen.**
Wittka, *F.* See *A.* **Grün.**
Wittkower, *E.* See *P.* **Rona.**
Wittner, *L.* See *E.* **Glaser.**
Wlodek, *J.*, spectrum of chlorophyll in the living leaf, ii, 258.
Wöhler, *L.*, and *P.* **Balz**, chlorides of ruthenium, ii, 424.
Wöhler, *L.*, *P.* **Balz**, and *L.* **Metz**, ruthenium oxides, ii, 149.
Wöhlisch, *E.*, clotting of blood and settling of blood-corpuscles as a problem of the physical chemistry of fibrinogen; does the stability of plasma proteins depend on their isoelectric points? i, 452.
theory of the action of thrombin, i, 452.
thrombin of Alexander Schmidt. X. Blood-clotting, i, 1486.
theoretical stoicheiometry of the intermolecular forces and the space occupied by the molecules of organic compounds. I.—II., ii, 269.
theoretical stoicheiometry of molecular volume, intermolecular attraction, viscosity, and ionic mobility of liquid organic compounds, ii, 277.
Wöhlisch, *E.*, measurements in series with the gas cell, ii, 301.
Wöhlisch, *E.*, and *H.* **Schriever**, isoelectric points of muscle proteins, i, 1488.
Wöhlisch, *E.*, and *E.* **Schütz**, human blood groups. II. Physical chemistry of *iso*hæmagglutination, i, 717.
Wölfel, *E.* See *O.* **Fischer.**
Wöllmer, *W.*, bitter principles of hops, i, 690.
Wohl, *A.*, and *K.* **Freudenberg**, [nomenclature of steric series], i, 366.
Wohl, *K.*, chemical constants of chlorine, bromine, and iodine in the monatomic and diatomic states, ii, 98.
atomic dissociation of chlorine and hydrogen. I. Dissociation of chlorine, ii, 395.
Wohlgemuth, *J.*, and *E.* **Klopstoke**, enzymes of the skin. II. Distribution of enzymes in the skin; the presence of a nucleotidase, i, 203.
Wohlgemuth, *J.*, and *Y.* **Yamasaki**, enzymes of the skin, i, 472.
Wokes, *F.*, determination of small amounts of reducing sugars in urine, i, 1205.
Wokes, *F.* See also *S. G.* **Willimott.**
Wolf, *A.*, theory of electrical conduction in metals, ii, 942.
Wolf, *A.* See also *K.* **Freudenberg.**
Wolf, *C. G. L.* See *L.* **Lawn**, and *G. S.* **Lund.**
Wolf, *H.* See *F. L.* **Hahn.**
Wolf, *J.* See *P.* **Pfeiffer.**
Wolf, *K. L.* See *K. F.* **Herzfeld**, and *H.* **Schüler.**
Wolf, *L.* See *A.* **Hantzsch.**
Wolfbauer, *O.* See *A.* **Zinke.**
Wolfes, *O.* See *E.* **Merck.**
Wolff, *C. J. de*, determination of invert sugar, ii, 245.
Wolff, *J.* See *K.* **Jellinek.**
Wolff, *P.*, halogen-alkylated aromatic amines and a new pyrrolidine ring closure, i, 428.
Wolfke, *M.*, and *H. K.* **Onnes**, dielectric constants of liquid and solid hydrogen, ii, 630.
dielectric constant of liquid helium, ii, 631.
Wolkenberg, *A.* See *L.* **Kofler.**
Wolkoff, *M. I.*, determination of sulphur in soil, i, 224.
Wollheim, *E.* See *K.* **Dresel**, and *F.* **Kraus.**
Wollman, (*Mme.*) *E.*, and *E.* **Wollman**, use of *Bacillus coli* in the detection of tryptophan and its application to the tubercle bacillus, i, 205.

Wollman, *E.* See (*Mme.*) *E.* **Wollman.**
Woltjer, *H. R.*, magnetic researches. XXVII. Magnetic properties of some paramagnetic chlorides at low temperatures, ii, 1038.
Woltjer, *H. R.*, and *H. K.* **Onnes**, further experiments with liquid helium; magnetic researches. XXVIII. Magnetisation of anhydrous chromium, cobalt, and nickel chlorides at very low temperatures, ii, 1038.
Woltjer, *J., jun.*, influence of radiation on ionisation equilibrium, ii, 343.
Woo, *Y. H.*, Compton effect and tertiary *X*-radiation, ii, 368.
Woo, *Y. H.* See also *A. H.* **Compton.**
Wood, *A. E.*, preparation of alkyl sulphides, i, 1034.
Wood, *A. E.*, *C.* **Sheely**, and *A. W.* **Trusty**, corrosion effect of naphtha solutions of sulphur and sulphur compounds, ii, 980.
Wood, *C. E.*, and *M. A.* **Comley**, rotatory dispersion of certain normal alkyl hexahydromandelates, ii, 264.
Wood, *C. E.*, and *H. S.* **Lilley**, transformation of mandelonitrile to mandelo*iso*nitrile, i, 400.
Wood, *F. C.* See *H. F.* **Coward.**
Wood, *J. G.*, selective absorption of chlorine ions, and the absorption of water by the leaves in the genus *Atriplex*, i, 1024.
Wood, *J. K.*, and *A.* **Wooller**, behaviour of hydrated aluminium oxide towards dyes, ii, 285.
Wood, *M. W.* See *A.* **Biester.**
Wood, *R. W.*, controlled orbital transfers of electrons in optically excited mercury atoms, ii, 8.
structure of the mercury line, 2536 Å., ii, 339.
fine structure, absorption, and Zeeman effect of the 2536 mercury line, ii, 1015.
optical excitation of the mercury spectrum, with controlled orbital transfers of electrons, ii, 1015.
Woodhouse, *D. L.* See *E. A.* **Cooper.**
Woodman, *D.*, effects of parathyroid feeding on calcium and creatine metabolism, i, 1210.
Woodman, *H. E.*, and *F. L.* **Engledon**, chemical study of the development of the wheat grain, i, 217.
Woodman, *H. E.*, and *J.* **Hammond**, mucous secretion of the cervix of the cow, i, 721.
Wooldridge, *W. R.* See *J. H.* **Quastel.**
Wooller, *A.* See *J. K.* **Wood.**
Wooster, *W. A.* See *C. D.* **Ellis.**
Work, *P.*, sodium nitrate in the nutrition of the tomato, i, 1366.
Worley, *F. P.* See *R. W.* **Harman.**
Wormall, *A.*, constituents of the sap of the vine (*Vitis vinifera*, L.), i, 215.
Wormall, *A.* See also *H. S.* **Raper**, and *H. R.* **Whitehead.**
Wormell, *R. L.* See *W.* **Wardlaw.**
Worrall, *D. E.*, addition of ethyl sodioacetoacetate to substituted aromatic mustard oils [thiocarbimides], i, 244.
action of hydroxylamine and of hydrazine on the aryl monothioamides of ethyl acetylmalonate. II., i, 308.
Worthing, *A. G.*, temperature scale and m. p. of molybdenum, ii, 759.
Worthing, *A. G.*, and *R.* **Rudy**, line spectra of tungsten and nickel in the afterglow of a discharge through a mixture of nitrogen and argon, ii, 1102.
Wosnessensky. See **Vosnessenski.**
Wrede, *F.*, and *E.* **Strack**, pyocyanine, the blue pigment of *Bacillus pyocyaneus*. I. and II., i, 174, 844.
Wrede, *F.*, and *W.* **Zimmermann**, synthesis of dissaccharides from sugar derivatives containing sulphur and selenium and their oxidation products, i, 1384.
Wrenshall, *R.*, and *A. L.* **Dean**, leprosy. XXXVII. Fractionation of chaulmoogra oil. II. Evidence of the existence of a highly unsaturated optically active acid, i, 1414.
Wrenshall, *R.* See also *A. L.* **Dean.**
Wright, *C. H.* See *O.* **Maass.**
Wright, *F. E.* See *J.* **Parry.**
Wright, *R.*, selective solvent action. IV. Cryoscopy in mixed solvents, ii, 1144.
Wright, *S.* See *F.* **Dickens.**
Wright, *W. M.* See *E. K.* **Rideal.**
Wróbel, *A.*, polarimetric determination of inactive substances; potassium, ii, 240.
Wu, *D. Y.* See *H.* **Wu.**
Wu, *H.*, modification of Duboscq–Pellin colorimeter for biocolorimetric work, ii, 899.
Wu, *H.*, and *D. Y.* **Wu**, heat denaturation of proteins, i, 1110.
Wüst, *J.*, and *E.* **Lange**, heat of solution of alkali halides, ii, 38.
heats of solution and dilution of salts. I., ii, 791, 976.
Wulf, *O. R.*, possible limits for the heat of dissociation of oxygen, ii, 848.

Wunschendorff, *H.*, removal of proteins from body fluids with colloidal ferric hydroxide; indirect determination of proteins in cerebro-spinal fluid, etc., i, 1346.
Wunstorf, *O.* See *F.* **Boedecker**.
Wurmser, *R.*, activity of various radiations in photosynthesis, ii, 1082.
Wurmser, *R.* See also *E.* **Aubel**, and *C.* **Fromageot**.
Wustrow, *W.* See *A.* **Stock**.
Wuyts, *H.*, preparation of ethers, i, 501.
Wyatt, *K. S.*, supersaturation of gases in liquids, ii, 504.
Wyatt, *K. S.* See also *F. B.* **Kenrick**.
Wyck, *H. B. van* See *V. J.* **Harding**.
Wyckoff, *R. W. G.*, orthorhombic space group criteria and their application to aragonite, ii, 484.
crystal structure of the high temperature form of cristobalite [SiO_2], ii, 638.
crystal structure of silver phosphate and silver arsenate, ii, 1037.
Wyckoff, *R. W. G.*, *F. L.* **Hunt**, and *H. E.* **Merwin**, *X*-ray diffraction effects from solid fatty acids, ii, 1129.
Wyckoff, *R. W. G.*, and *H. E.* **Merwin**, crystal structure of dolomite, ii, 94.
space group of barite ($BaSO_4$), ii, 485.
space group of diopside, ii, 485.
Wyckoff, *R. W. G.*, *H. E.* **Merwin**, and *H. S.* **Washington**, *X*-ray diffraction measurements on the pyroxenes, ii, 1126.
Wyckoff, *R. W. G.*, and *G. W.* **Morey**, *X*-ray diffraction measurements on some soda-lime-silica glasses, ii, 1146.
Wyckoff, *R. W. G.* See also *R. E.* **Gibson**.
Wyss, *F.*, biochemical determination of insulin, i, 1220.

Y.

Yabusoe, *M.*, iron and blood pigment determinations in normal tissues and in tumours, i, 724.
Yaitschnikov, *I. S.*, hydrolysis of peptones, albumoses, and proteins with hydrochloric acid. I., i, 320.
Yajnik, *N. A.*, and *B.* **Ilahi**, emulsifying power of sodium stearate and sodium palmitate, ii, 968.
Yajnik, *N. A.*, *M. P.* **Jain**, and *D.* **Nath**, influence of electrolytes on the solubilities of some organic acids, ii, 1147.
Yajnik, *N. A.*, and *K. S.* **Malik**, viscosities of aqueous solutions of pure soaps and their variations with temperature, ii, 779.
Yakubchik, *A. O.* See *S. V.* **Lebedev**.
Yamada, *M.*, crystal form and the crystal lattice, ii, 94.
Yamada, *N.*, long-range particles from polonium, ii, 255.
long-range particles emitted by the active deposits of radium, ii, 834.
Yamada, *N.* See also (*Mme.*) *I.* **Curie**.
Yamada, *S.* See *S.* **Komatsu**.
Yamaga, *N.*, equilibrium of gases in the reaction of explosives, ii, 294.
Yamaguchi, *S.*, Beckmann's rearrangement. XIII. Catalytic action of reduced copper on benzaldoximes, i, 1278.
Yamamoto, *R.*, insecticidal principle of *Chrysanthemum cinerariæfolium*, i, 1522.
Yamasaki, *Y.* See *J.* **Wohlgemuth**.
Yamauchi, *M.*, lipoids of the ovarian follicles in human beings and cattle, i, 457.
Yannakis, *N. C.*, total vapour pressure of cuprous or lithium chloride solutions in hydrochloric acid, ii, 401.
partial pressures of aqueous solutions of hydrochloric acid at 50°, ii, 514.
Yant, *W. P.*, and *F. E.* **Frey**, apparatus for preparing vapour–air mixtures of constant composition, ii, 897.
Yardley, (*Miss*) *K.*, *X*-ray examination of calcium formate, ii, 480.
X-ray examination of iodosuccinimide, ii, 746.
X-ray methods of supplementing and correcting crystallographic data, ii, 1033.
X-ray examination of maleic and fumaric acids, ii, 1126.
Yarsley, *V. E.* See *G. T.* **Morgan**.
Yasuda, *K.*, preparation of pure calcium cyanamide, i, 377.
Yates, *W. W.* See *H. G.* **Miller**.
Yathiraja, *A. R.*, and *J. J.* **Sudborough**, hydrolysis of amides of Δ^{α}-unsaturated acids and of their saturated analogues, i, 1184.
Yensen, *T. D.*, magnetic properties of the 50% iron–nickel alloy, ii, 372.
Yoda, *G.* See *A. G.* **Perkin**.

Yoe, *J. H.*, adsorption of arsenious acid by hydrated aluminium oxide, ii, 107.
perchloric acid as an analytical reagent, ii, 902.
Yokoyama, *T.* See *R. W.* **Seuffert.**
Yonge, *C. M.*, hydrogen-ion concentration in the gut of certain lamellibranchs and gastropods, i, 1489.
Yoshikawa, *K.* See *B.* **Kubota.**
Yoshimatsu, *N.* See *Z.* **Matsuoka.**
Yoshine, *S.*, effect of ultra-violet light on protein metabolism, i, 1356.
Young, *A. F. A.* See *O. W.* **Richardson.**
Young, *J.*, Thomson effect in copper, iron, and carbon steels, ii, 490.
Young, *J. F. T.* See *J. C.* **McLennan.**
Young, *R. C.* See *J. F.* **Norris.**
Youngburg, *G. E.*, and *G. W.* **Pucher**, organic phosphorus of the urine, i, 98.
Youtz, *M. A.*, rapid preparation of cetyl alcohol, i, 1125.
Yovanovitch, *A.*, micro-determination of ammonia in urine, i, 1114.
determination of ammonia and ammonium salts in urine, i, 1204.
Yovanovitch, *A.* See also *M.* **Nicloux.**
Yovanovitch, *D. K.*, and *J.* **D'Espine**, magnetic spectrum of β-rays of high velocity from mesothorium II., ii, 85.
magnetic spectrum of the high speed β-rays of thorium-B+C, ii, 176.
Yovanovitch, *D. K.* See also (*Mme.*) *M.* **Curie.**
Yovitchitch, *M. Z.*, deficit of the condensed substances obtained by the action of the electric discharge, ii, 406.
Yukitomo, *T.* See *S.* **Komatsu.**
Yumikura, *S.*, osmosis in aqueous gels with and without addition of lipoids, i, 785.
osmosis of certain anæsthetics in aqueous and lipoid-containing gels, i, 785.
osmosis of certain acids in a gelatin gel, i, 785.
Yumikura, *S.* See also *J.* **Traube.**
Yung, *C. C.* See *R. N.* **Pease.**
Yvon, syntheses by means of the sodium and magnesium derivatives of propinine, i, 514.

Zabrodin, *A.* See *S.* **Nametkin.**
Zacharias, *P. D.*, metachemistry and metachemical processes (a nomenclature and system of colloids), ii, 196.
Zachrisson, *C. G.*, proteolytic enzymes of the liver, i, 335.
Zadek, *F.* See *G.* **Schroeter.**
Zahn, *C. T.* See *K. T.* **Compton**, and *C. P.* **Smith.**
Zahn, *H.*, dielectric constant of water in [the presence of] strong electrolytes, ii, 263.
Zahn, *H.* See also *H.* **Hellmann.**
Zajdel, *R.* See *S.* **Sierakovski.**
Zakarias, *L.*, colloid filtration, ii, 862.
Zakowski, *J.* See *K.* **Jellinek.**
Zaleski, *J.*, and *K.* **Lindenfeld**, esterification of hæmin, i, 88.
Zambonini, *F.*, and *V.* **Caglioti**, double sulphates of rare earth and alkali metals. II. Neodymium and potassium, ii, 222, 315.
sulphates of neodymium and thallous thallium, ii, 1185.
Zambonini, *F.*, and *G.* **Carobbi**, isomorphous relations between beryllium and magnesium compounds, ii, 144.
double sulphates of rare earth and alkali metals. I. Lanthanum and potassium, ii, 222.
isomorphism between tervalent thallium and rare earth metals, ii, 272.
lanthanum thallous sulphates, ii, 579.
chromates of the metals of the cerium group, ii, 700.
presence of the compound $K_2Mn_3(SO_4)_3$ among the products of activity on Vesuvius, ii, 898.
Zambonini, *F.*, *O. de* **Fiore**, and *G.* **Carobbi**, lead sulphobismuthite of volcanic origin, ii, 709.
Zambonini, *F.*, and *R. G.* **Levi**, isomorphism of the molybdates of the rare earths with those of calcium, strontium, barium, and lead, ii, 1133.
Zamparo, *A.*, variations in physiological action of morphine derivatives with diverse substituent groups, i, 1116.
differentiation of the naphthols, and condensation product of α-naphthol with formaldehyde, ii, 444.
identification of the alkyl derivatives of barbituric acid, ii, 907.
Zanda, *G. B.*, significance of copper in the animal organism, i, 719.
Zanetti, *J. E.*, esters of furfuryl alcohol, i, 567.
furfuryl furfuroate, i, 953.
Zechmeister, *L.* See *N.* **Bjerrum**, and *R.* **Willstätter.**
Zechner, *K.* See *R.* **Kremann.**
Zee, *H. van der.* See *S. C.* **Bokhorst.**
Zeeman, *P.*, radiating atoms in magnetic fields, ii, 614.
Zeeman, *P.* See also *T. L. de* **Bruin**, and *S.* **Goudsmit.**
Zeh, *H. P.* See *H.* **Freundlich.**

Zeilinger, *F.*, theory of Brownian movement, ii, 389.
Zeisberg, *F. C.*, partial vapour pressures of aqueous hydrogen chloride solutions, ii, 401.
Zelinski, *N. D.*, irreversible catalysis of unsaturated cyclic hydrocarbons. II., i, 122.
irreversible catalysis of unsaturated cyclic hydrocarbons. III. Contact transformation of limonene, i, 146.
mechanism of catalytic hydrogenation and dehydrogenation, i, 237.
irreversible catalysis of unsaturated cyclic hydrocarbons. IV. Contact transformation of α-pinene: dihydropinene, i, 821.
Zelinski, *N. D.* [with *M.* **Gavedovskaja**], isomerisation of decahydronaphthalene, i, 123.
Zelinski, *N. D.*, and *P.* **Borissov**, octahydroindene and its behaviour towards catalytic dehydrogenation, i, 122.
Zelinski, *N. D.*, and *E.* **Rjachina**, 1:3-dimethyl*cyclo*pentane-3-carboxylic acid, i, 28.
conversion of naphthenic acids into ketones with the aid of catalysts, i, 39.
Zelinski, *N. D*, and *V. A.* **Smirnov**, action of aluminium chloride on heptanaphthene, i, 1125.
Zelinski, *N. D.*, and *M. B.* **Turova-Pollak**, noble metals as catalysts of hydrogenation and dehydrogenation, i, 1052.
isomerisation of decahydronaphthalene; transformation of *cis*- into *trans*-decahydronaphthalene and dehydrogenation of decahydronaphthalene, i, 1053.
Zellner, *J.*, chemical components of native medicinal plants. II., i, 763.
chemistry of heterotrophic phanerogams. V., i, 1025.
Zemčužny, *S. F.* See *N. S.* **Kurnakov**.
Zemiattschenski, *P. A.*, hydrolysis of mica, ii, 814.
Zemisch, *E.* See *W.* **Steinkopf**.
Zemplén, *G.*, and *G.* **Braun**, ethers of salicin, i, 1081.
Zepter, *H.* See *W.* **Manchot**.
Zerban, *F. W.*, specific rotation of invert-sugar and the Clerget divisor, ii, 479.
Zerbe, *C.* See *R.* **Anschütz**.
Zervas, *L.* See *M.* **Bergmann**.
Zetzsche, *F.*, and *O.* **Arnd**, influence of phosphorus oxychloride on the catalytic reduction of acid chlorides, i, 1415.
Zetzsche, *F.*, *H.* **Silbermann**, and *G.* **Virli**, formation of metallic phenoxides by metals, i, 1411.
Zeynek, *R.*, halogen compounds of tyrosine, i, 920.
Ziegler, *K.*, polyarylated vinylcarbinols and their derivatives. V. Anomalous etherification in the triphenylallyl series, i, 395.
Ziegler, *K.*, *H.* **Grabbe**, and *F.* **Ulrich**, polyarylated vinylcarbinols and their derivatives. IV. Course of the dimerisation of triphenylallene, i, 131.
Ziegler, *K.*, *K.* **Richter**, and *B.* **Schnell**, polyaryl-substituted vinylcarbinols and their derivatives. VI. True derivatives of diphenylstyrylmethane, i, 915.
Ziegler, *O.* See *K.* **Brass**.
Zilva, *S. S.*, influence of ultra-violet radiations on accessory food factors, i, 485.
antiscorbutic fraction of lemon juice, III., i, 1220.
Zilva, *S. S.* See also *E. H.* **Lepper**.
Zimmermann, *M.* See *G.* **Embden**.
Zimmermann, *W.* See *F.* **Wrede**.
Zinke, *A.*, *K.* **Funke**, and *A.* **Pongratz**, perylene and its derivatives. IX., i, 819.
Zinke, *A.*, and *K.* **Funke** [with *J.* **Matscher**, *O.* **Wolfbauer**, and *N.* **Lorber**], perylene and its derivatives. X., i, 1436.
Zinke, *A.*, and *F.* **Hanselmayer**, perylene and its derivatives. VI., i, 564.
Zinke, *A.*, *F.* **Linner**, and *O.* **Wolfbauer**, perylene and its derivatives. VII., i, 383.
Zinke, *A.*, *A.* **Pongratz**, and *K.* **Funke**, perylene and its derivatives. VIII., i, 384.
Zinsser, *H.* See *J. Howard* **Mueller**.
Zintl, *E.*, and *A.* **Rauch**, theory of constitutive colour, ii, 182.
electrometric titration of bismuth alone and together with lead, ii, 442.
standardisation of titanous chloride solutions, and potentiometric titration of copper, ii, 1003.
potentiometric titration of bismuth in presence of other metals, ii, 1004.
potentiometric titration of gold, ii, 1005.
Zintl, *E.* See also *O.* **Hönigschmid**.
Zipf, *K.* See *E.* **Bissinger**.
Zobel, *F.* See *J. von* **Braun**.
Zocher, *H.*, spontaneous structure-formation in sols (new type of anisotropic liquid media), ii, 966.

Zocher, *H.*, and *K.* **Coper**, production of optical activity in silver by circularly polarised light, ii, 935.
Zocher, *H.* See also *H.* **Freundlich**.
Zondek, *H.*, and *H.* **Ucko**, two-phase action of hormones; antagonistic endocrine action, i, 1513.
Zondek, *S. G.* See *F.* **Kraus**.
Zschiegner, *H. E.*, determination of palladium, ii, 443.
Zsigmondy, *R.*, and *E.* **Hückel**, reduction velocity and growth of particles in the preparation of colloidal gold solutions, ii, 775.
Zsigmondy, *R.*, and *E.* **Joël**, protection and precipitation of gold by proteins, ii, 35.
Zubov, *P. W.*, and *W.* **Swientoslawski**, heats of combustion of three oxides [α-propylene oxide, α-trimethylethylene oxide, and γδ-hexylene oxide], ii, 364.
Zumstein, *F.* See *R.* **Kuhn**.
Zumstein, *O.* See *K.* **Lehmstedt**.
Zumstein, *E. V.*, absorption spectra of copper, silver, and gold vapours in the ultra-violet, ii, 453.
tungsten *X*-ray emission and absorption spectra, ii, 725.
absorption spectrum of lead vapour in the ultra-violet, ii, 914.
Zurbriggen, *G.* See *H. de* **Diesbach**.
Zuskine, *N.*, preparation of nitroxyl chloride and bromide and their action on Grignard's reagent, ii, 587.
Zwaardemaker, *H.*, *T. P.* **Feenstra**, and *M. E. J. M.* **Steyns**, emanation and calcium, i, 193.
Zweiglówna, *I.*, equilibrium in solutions of the isomorphous salts, $(NH_4)_2SO_4,MgSO_4,6H_2O$, and $(NH_4)_2SO_4,FeSO_4,6H_2O$, ii, 189.
Zwiçky, *F.*, theory of the specific heats of electrolytes, ii, 1138.
Zwikker, *C.*, characteristics of tungsten and the candle power of a black body, ii, 1041.
Zyl, *G. van*. See *A. L.* **Ferguson**.

INDEX OF SUBJECTS.

ABSTRACTS, 1925.

A.

Abietic acid, constitution of (FREJKA and BALAŠ), i, 669.
pyrogenic decomposition of (VESTERBERG and BORGE), i, 252.
oxidation and anhydride formation of (RUZICKA and PFEIFFER; RUZICKA, MEYER, and PFEIFFER), i, 1419.
hydrochlorides of, and hydroxy-, and its silver salt and methyl ester (RAO and SIMONSEN), i, 687.
sodium salt, oxidation of (FREJKA and BALAŠ), i, 1422.
methyl ester, oxidation of, and its ozonide (RUZICKA, MEYER, and PFEIFFER), i, 1420.
Abietic acids, salts and derivatives of (KNECHT and HIBBERT), i, 1421.
Absorption coefficients, estimation of (TOLMAN), ii, 1112.
Absorption spectra. See under Spectra.
Acacetin, and its derivatives (HATTORI), i, 1443.
Acaciin, and its derivatives, from the leaves of *Robinia pseudacacia* (HATTORI), i, 1443.
Acanthias vulgaris (dog-fish), action of pancreatic extract of (DUCLOUX and CORDIER), i, 1364.
Acatenango in Guatemala, volcanic ash from (GUTBIER, BRINTZINGER, and BUBAM), ii, 1195.
Accumulator, lead, reactions in (LOTTERMOSER and GRÜTZNER), ii, 312.
α-Acenaphthaquinoline, and its salts (STEWART), i, 975.
Acenaphthaquinone, oxidation of (WHISTON), i, 140.
Acenaphthene, hydrogenation of (GOSWAMI), i, 127.
derivatives of (LORRIMAN), i, 672.
Acenaphthene, 1-amino-, and its salts and derivatives, and 1-nitro- (MORGAN and SHEASBY), i, 1144.
2- and 3-amino-, 2-nitro-3-amino-, iodonitro-, and their derivatives (MORGAN and STANLEY), i, 133.
Acenaphthene series (MORGAN and STANLEY), i, 133; (MORGAN and SHEASBY), i, 1144.
Acenaphthenquinoneanil (SANDER), i, 982.
4-Acenaphthoic acid, ethyl and methyl esters (LORRIMAN), i, 673.
o-(**4-Acenaphthoyl**)-**benzoic acid**, acetyl derivative (LORRIMAN), i, 672.
4-Acenaphthylphthalide (LORRIMAN), i, 673.
Acetals, catalytic preparation of (ADAMS and ADKINS), i, 784, 785.
acyclic, and their azeotropic properties (BÉDOWÉ), i, 513.
Acetaldehyde, occurrence of, in plants (GRIEBEL), i, 763.
formation of, in animal organs (NEUBERG and GOTTSCHALK), i, 199.
formation of, in frog's muscle (NEUBERG and GOTTSCHALK), i, 859.
oxidation of (REINER), ii, 213.
use of nickel in catalytic reduction of (NEGOSHI), i, 1375.
action of sodium nitroprusside on (VAN URK), ii, 162.
as an intermediate in carbohydrate metabolism (GOTTSCHALK), i, 191.
determination of, together with lactic acid (LEONE and TAFURI), ii, 907.
determination of, in blood (FABRE), i, 852.
Acetaldehyde, bromo-, derivatives of (STEPANOV, PREOBRASCHENSKI, and SCHTSCHUKINA), i, 1240.
bromonitro-, phenylhydrazone (WIELAND and JUNG), i, 1374.
α- and β-*tri*thio-, and their derivatives (FROMM and ENGLER), i, 1231.
Acetaldol, heat of formation of (SHAW), ii, 644.
Acetaldoxime, thermochemistry of (DORABIALSKA), ii, 1140.
Acetamide, cyano-, *C*-*di*sulphide (NAIK and PATEL), i, 121.
Acetanilide, influence of acetyl chloride on nitration of (CHRZASZCZEWSKA and BIATA), i, 1058.

Acetanilide, 2:4-*di*nitro-5-chloro- (KEHRMANN and STANOYÉVITCH), i, 1331.
Acetanilides, oximino-, preparation and reactions of (KARRER, DIECHMANN, and HAEBLER), i, 243.
Acetanilide-*p*-sulphinic acid (BERE and SMILES), i, 22.
2-Acetanilido-1:4-naphthaquinone, 3-amino-, and 3-chloro- (FRIES and BILLIG), i, 939.
α-2-Acetanilido-1:4-naphthaquinonyl-3-acetic acid, ethyl ester (FRIES and BILLIG), i, 940.
Acethydroxamic acid, hydroxy-, and its salts and derivatives (JONES and POWERS), i, 13.
Acetic acid, latent and specific heats of (PARKS and KELLEY), ii, 949.
adsorption of, from solution by silica (JONES), ii, 382.
sorption of the vapour of, by sugar charcoal (BAKR and MCBAIN), ii, 193.
viscosity of solutions of (DE KOLOSOVSKI), ii, 859.
molecular film of, between water and benzene (HARKINS and MCLAUGHLIN), ii, 771.
equilibrium of acetic anhydride and (POVARNIN and MARKOV), ii, 851.
equilibrium of aniline, water, and (ANGELESCU and MOTZOC), ii, 854.
equilibrium in the system, water and (POVARNIN and MARKOV), ii, 851.
oxidation of (KNOOP and GEHRKE), i, 1131.
and its derivatives, reduction of (POVARNIN and KALJE), i, 1034.
catalytic decomposition of, by charcoal (KULTASCHEV and KUDRJASCHEVA), ii, 881.
action of benzoyl peroxide on (GELISSEN and HERMANS), i, 664.
and *mono-* and *tri*-chloro-, additive compounds of esters with (KENDALL and BOOGE; KENDALL and KING), ii, 972.
Acetic acid, alkali salts, electrolysis of, in methyl alcohol solution (SALAUZE), i, 504.
alkali copper salts of (BÜTTGENBACH), i, 1035.
ammonia salt, as source of nitrogen for fungi (BACH), i, 216.
double salts of rare earth metals and carbamide or guanidine (CANNERI), i, 525.
mercuric salt, compounds of *o*-chloroaniline with (VECCHIOTTI and MICHETTI), i, 1058.
Acetic acid, mercuric salt, reaction of phenylhydrazine with (VECCHIOTTI and CAPODACQUA), i, 1106.
acid uranyl salt (COLANI), i, 5.
Acetic acid, alkoxymethyl esters (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
p-carboxybenzyl and *o*-cyanobenzyl esters (BARKENBUS and HOLTZCLAW), i, 1148.
cellulose esters (HESS, SCHULTZE, and MESSMER), i, 1245.
cinnamyl ester (ENDOH), i, 1428.
ethyl ester, preparation of (ROBERTS), i, 114.
surface tension of, and its mixtures with *cyclo*hexanol (WEISSENBERGER and SCHUSTER), ii, 648.
effect of, on nitrogen excretion (BYLSMA), i, 1356.
and amino-, ethyl ester, compounds of stannic and titanic chlorides with (FICHTER and REICHART), ii, 193.
4-hydroxy-*tert.*-butylbenzene-3:5-dimercuric ester (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1154.
substituted derivatives, menthyl esters (RULE and SMITH), ii, 1120.
methyl ester, density and compressibility of solutions of (RICHARDS and CHADWELL), ii, 1049.
4-nitro-2:6-dinitroso-3-acetoxybenzyl ester (SCHULTZ and GANGULY), i, 647.
triarylmethyl esters (SCHOEPFLE), i, 811.
and *tri*bromo-, tribromoethyl esters (NAKAI), i, 360.
Acetic acid, amino-, hydroxylamine salt (OESPER and BALLARD), i, 1233.
bromonitro-, chlorobromonitro-, and chloronitro-derivatives, ethyl esters (MACBETH and TRAILL), i, 629.
chloro-, phenylethyl ester (WEIL), i, 157.
*di*chloro-, preparation and properties of (DOUGHTY and BLACK), i, 628.
amine salts of, and *tri*chloro-, aniline salts of (DOUGHTY), i, 805.
*tri*chloro-, conductivity of, in methyl alcohol (GOLDSCHMIDT and AARFLOT), ii, 976.
equilibria in binary organic systems with (KITRAN), ii, 533.
trichloromethyl ester, mechanism of the synthesis of (GIBSON), ii, 312.

Acetic acid, cyano-, ionisation of, in alcohol–water mixtures (BRADLEY and LEWIS), ii, 868.
ethyl ester, preparation of (STEPHENS), i, 121.
Acetic anhydride, preparation of (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1233.
interaction of tellurium tetrachloride with (MORGAN and DREW), i, 530.
analysis of (CALCOTT, ENGLISH, and WILBUR), ii, 1007.
***o*-Acetoacetanisidide**, 4-chloro-5-nitro- (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 598.
Acetoacetic acid, effect of carbohydrates on oxidation of, by hydrogen peroxide (ERNST and FORSTER), ii, 684.
action of, on nitrogen metabolism (LABBÉ and LAVAGNA), i, 191.
catalytic decomposition of, by strong acids and bases (v. EULER and OLANDER), ii, 1069.
esters, hydrolysis of (SKRABAL, PFAFF, and AIROLDI), ii, 139.
action of hydrazine on halogen derivatives (HIRST, MACBETH, and TRAILL), i, 1251.
ethyl ester, preparation of (ROBERTS), i, 114.
reactions of, with *o*-hydroxydistyryl ketones (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
sodium derivative, addition of, to substituted aromatic thiocarbimides (WORRALL), i, 244.
determination of, in urine (GOLDBLATT), i, 1204.
6-Acetoacetyl-*o*-cresol, and its semicarbazone (WITTIG), i, 279.
Acetoacetyldehydrothiotoluidide (CHEMISCHE FABRIK GRIESHEIM ELEKTRON), i, 989.
Acetobenzylmethylamide (HOLMES and INGOLD), i, 1144.
Aceto-3:5-*di*bromo-*o*-anisidide and its hydrochloride (ELION and JANSSEN), i, 389.
Acetodibenzylamide (HOLMES and INGOLD), i, 1144.
Acetoethylanilide, action of phosphoryl chloride on (FISCHER, MÜLLER, and VILSMEIER), i, 439.
Acetohexadecylamide (ADAM and DYER), i, 354.
Acetoin, enzymic synthesis of (NEUBERG and SIMON), i, 737.
Acetomesitylene, oxidation of, with permanganate (PERKIN and TAPLEY), i, 42.
Acetomethylanilide, action of phosphoryl chloride on (FISCHER, MÜLLER, and VILSMEIER), i, 439.
Aceto-α-naphthylamide, 4-bromo- and 4-chloro-3-nitro-, and 3-nitro-4-amino- (PANIZZON-FAVRE), i, 145.
Acetone, formation of, from mahua flowers (GOKHALE), i, 1216.
formation of, from sugars (SPEAKMAN), i, 1013; (MOSKOVITS), i, 1511.
production of, by bacilli (FOWLER and SUBRAMANYAN), i, 1216.
latent and specific heats of (PARKS and KELLEY), ii, 949.
latent heat of fusion of (MAASS and WALDBAUER), ii, 492.
surface tension of, and its mixtures with *cyclo*hexanol (WEISSENBERGER and SCHUSTER), ii, 648.
properties of mixtures of water and (SANDONNINI), ii, 765.
action of mixtures of nitric and hydrochloric acids on (BOYD), i, 788.
effect of nitrogen and carbon dioxide dilutions on the explosion of, and its mixtures with methyl alcohol (CROUCH and CARVER), ii, 682.
oxidation of (KNOOP and GEHRKE), i, 1131.
reaction of glycols with (HERMANS), ii, 50.
action of sodium nitroprusside on (VAN URK), ii, 162.
and β-hydroxybutyric acid in urine (LUBLIN), i, 459.
m- and *p*-methoxyphenylhydrazones (SPÄTH and BRUNNER), i, 574.
4-methylthiosemicarbazone (BOSE), i, 1466.
4-phenylthiosemicarbazone (BOSE), i, 1465.
semicarbazones (WILSON and CRAWFORD), i, 318.
4-*p*-tolylsemicarbazone (WHEELER and BOST), i, 318.
detection and determination of (BÜLOW), ii, 1210.
detection and determination of, in urine (ENGFELDT), i, 1490.
determination of, in presence of alcohol (VUILLEUMIER), ii, 246.
determination of, colorimetrically, in urine (SITSEN), i, 855.
Acetone, *di*amino-, acetyl derivative, phenylhydrazone (MANN and POPE), i, 374.
*s-di*chloro-, reduction of, by yeast (SEN), i, 337; (SEN and BARAT), i, 1241.

Acetone, *as-di*chloro-, biochemical conversion of, into αγ-dichloropropan-β-ol (SEN), i, 203.
chloro-oximino-, benzoyl derivative (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
*di*hydroxy-, condensation of thiocarbamide and (SJOLLEMA and SEEKLES), i, 1175.
oxidation of, in presence of phosphates (WIND), ii, 1174.
fermentation of (NEUBERG and GOTTSCHALK), i, 337.
effects of administration of (ISAAC and ADLER), i, 343.
effect of ingestion of, on blood-sugar (RABINOVITSCH), i, 1352.
Acetone oil, constituents of (PRINGSHEIM and BONDI), i, 1072.
Acetonitrobenzylmethylamides (HOLMES and INGOLD), i, 1144.
Aceto*di*nitro*di*benzylamides (HOLMES and INGOLD), i, 1144.
Aceto-octadecylamide (ADAM and DYER), i, 354.
Acetophenone, behaviour of, in the body (THIERFELDER and KLENK), i, 193.
δ-anilinosemicarbazone (SUTHERLAND and WILSON), i, 42.
carbethoxyhydrazone (v. AUWERS and DANIEL), i, 1181.
2:4-*di*chlorophenylhydrazone (HUMPHRIES, HUMBLE, and EVANS), i, 989.
p-methoxyphenylhydrazone, and *p*-hydroxy*di*bromo-, *p*-bromophenylhydrazone (KORCZYNSKI and KIERZEK), i, 973.
4-*p*-tolylsemicarbazone (WHEELER and BOST), i, 318.
Acetophenone, *p*-amino-, condensation of formaldehyde with (GRABOWSKA and WEIL), i, 260.
ω-bromo-, condensation of thiosemicarbazide with (BOSE), i, 167, 1465.
o-chloro-, and *o*-iodo-, and its oxime (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
2:4:6-*tri*nitro-, and its phenylhydrazone (SONN and BÜLOW), i, 1268.
Acetophenoneaminobenzazimide (HELLER, GÖRING, KNOSS, and KÖHLER), i, 1323.
Acetophenones, chloro-oximino-, and their derivatives (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
Acetophenone-*p*-arsenious oxide, and its semicarbazone (MARGULIES), i, 447.
Acetophenone-*p*-arsinic acid (OGDEN and ADAMS), i, 707.
derivatives of (MARGULIES), i, 448.
Acetophenoneoxalyldihydrazone (WILSON and PICKERING), i, 935.
Acetopyrocatechol dibenzyl ether, preparation of (MERCK), i, 1431.
o-Aceto-*p*-thiocresol, and its derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
Aceto-*o*-toluidide, 3:5-*di*bromo- and nitroso- (v. AUWERS and LOHR), i, 75.
Aceto-*p*-toluidide, solubility of, in mixed solvents (PLEUGER), ii, 283.
Acetoxime chlorostannate (SONN and MEYER), i, 932.
Acetoxime, *di*amino-, dihydrochloride (MANN and POPE), i, 373.
7′-Acetoxy-3′-coumaryl-4-α-naphthapyrone (DEY and ROW), i, 149.
Acetoxydihydro-*p*-cymene, bromo- (HENRY and PAGET), i, 1163.
3-Acetoxy-5:5′-dimethyl-2′-aldehydo-2:3′-dipyrrole-4:4′-dicarboxylic acid, ethyl ester, and its *p*-nitrophenylhydrazone (FISCHER and HEYSE), i, 78.
Aceto-*p*-2-xylidide, 5-*mono*- and *di*chloro- (WHEELER and MORSE), i, 22.
Acetoxymercuriethoxychaulmoogric acid, ethyl ester (DEAN, WRENSHALL, and FUJIMOTO), i, 546.
α-Acetoxy-α-methylpropionamide, β-chloro- (LES ÉTABLISSEMENTS POULENC FRÈRES), i, 601.
α-Acetoxy-α-methylpropionyl chloride, β-chloro- (LES ÉTABLISSEMENTS POULENC FRÈRES), i, 601.
***p*-Acetoxyphenyl-3-acetoxyxanthhydrol** (GOMBERG and SNOW), i, 660.
Acetyl groups, determination of (FREUDENBERG and WEBER), ii, 446.
Acetylacetone, decomposition of (HURD and TALLYN), i, 885.
action of phenylsemicarbazide on (WHEELER and BROOKS), i, 1459.
vanadyl salt, and its derivatives (ROSENHEIM and MONG), i, 1412.
Acetylalanine, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
5-Acetyl-2-anisyl-4-methylpyrimidine (MITTER and PALIT), i, 1320.
α-Acetyl-β-benzoyl-2:4-*di*bromophenylhydrazine (CHATTAWAY and WALKER), i, 929.
3-Acetylbornylene. See α-Bornylene methyl ketone.
δ-Acetylbutyl alcohol, δ-hydroxy-, anhydride of a disaccharide from (BERGMANN, MIEKELEY, and STATHER), i, 227.
3-Acetylcamphane. See α-Camphanyl methyl ketone.
5-Acetyl-5:10-dihydrophenarsazine, 10-chloro- (BURTON and GIBSON), i, 84.

3-Acetyl-2:8-dimethylbenzopyrone (WITTIG), i, 279.

β-3-Acetyl-2:2-dimethyl*cyclo*pentyl*iso*propyl alcohol, and its semicarbazone (HALLER and LEGAGNEUR), i, 924.

β-3-Acetyl-2:2-dimethyl*cyclo*pentylpropylene, and its derivatives (HALLER and LEGAGNEUR), i, 925.

3-Acetyl-1:6-dimethylpyridone (MUMM), i, 965.

3-Acetyl-1:6-dimethyl-α-pyridone-5-carboxylic acid, and its ethyl ester, and phenylhydrazone and their derivatives (MUMM), i, 965.

5-Acetyl-2:4-dimethylpyrrole-3-carboxylic acid, ethyl ester (KALLE & Co.), i, 297.

(3-Acetyl-2:4-dimethylpyrrolenyl)-(4-hydroxy-3-carbethoxy-2-methylpyrryl)methene (FISCHER and HEYSE), i, 77.

3-Acetyl-2:4-dimethylpyrryldi-(3-carbethoxy-2:4-dimethylpyrryl)-methane (FISCHER and HEYSE), i, 77.

(3-Acetyl-2:4-dimethylpyrryl)(4-hydroxy-3-carbethoxy-2-methylpyrrolenyl)methene, and its hydrochloride (FISCHER and HEYSE), i, 77.

α-Acetyl-β-diphenylacetylphenylhydrazide (VAN ALPHEN), i, 81.

5-Acetyl-2-β-naphthyl-4-methylpyrimidine (MITTER and PALIT), i, 1320.

Acetylene, solubility of, in electrolytes (MANCHOT, JAHRSTORFER, and ZEPTER), ii, 282.
dielectric constant of (SMITH and ZAHN), ii, 1118.
compressibility of (HOWARTH and BURT), ii, 818.
polymerisation of, by means of radium emanation (MUND and KOCH), ii, 1173.
condensation of (KOVACHE and TRICOT), i, 799.
condensation of, with hydrogen sulphide in presence of catalysts (TOMKINSON), i, 58.
explosion of mixtures of nitrogen and (GARNER and SAUNDERS), ii, 627.
as a narcotic (KNIPPING), i, 176.
*di*chloride. See Ethane, αβ-*di*chloro-.

Acetylene, *di*iodo-, preparation of, electrolytically (DUSSOL), i, 350.

Acetylenic compounds, synthesis of (LESPIEAU), i, 225; (BERT), i, 803.
hydrogenation of (BOURGUEL), i, 883.

α-Acetylhexoic acid, ethyl ester, condensation of aldehydes with (RYAN and SHANNON), i, 558.

Acetylmalonic acid, ethyl ester, thioamides, action of hydrazine and hydroxylamine on (WORRALL), i, 308.

Acetylmethylcarbinol, formation of, in sugar fermentation (KLUYVER and DONKER), i, 1215.
in vinegar (VAN'T HOOFT), i, 772.

1-Acetyl-2-methylindole, 3-cyano- (SEKA), i, 67.

2-Acetyl-α-naphthol, magnesium salt (ZETZSCHE, SILBERMANN, and VIELI), i, 1411.

***N*-Acetylphenarsazinic acid** (BURTON and GIBSON), i, 84.

Acetylphenylarsenious oxides, and hydroxy- and nitrohydroxy-derivatives of (MARGULIES), i, 448.

Acetylphenylarsinic acids, hydroxy-, and nitrohydroxy-, derivatives of (MARGULIES), i, 448.

β-Acetyl-α-phenyl-α-2-diketohydrindenylbutan-γ-one (JONESCU), i, 1154.

Acetylphenylmalonic acid, methyl ester, and its phenylhydrazone (VOORHEES and SKINNER), i, 837.

β-*o*-Acetylphenylpropaldehyde disemicarbazone (SCHROETER, ZADEK, and HOFFMANN), i, 678.

β-*o*-Acetylphenylpropionic acid, and its derivatives (v. AUWERS), i, 241.

1-Acetyl-4-phenylthiosemicarbazide (BOSE), i, 1465.

Acetyl*cyclo*propanecarboxylic acid, derivatives of (KÜSTER), i, 922.

Acetylpyrocatechol, *di*nitro- (KEHRMANN and PRUNIER), i, 304.

2-Acetylpyrrole, 3:4-*di*iodo- (TERENTIEV and TSCHELINCEV), i, 295.
di- and *tri*-iodo- (PIERONI and NOCENTINI), i, 1097.

Acetylsalicyloyl *per*oxide, preparation of (VANINO and HERZER), i, 139.

Acetylsuccinic acid, ethyl ester, bromo- and chloro-derivatives (MACBETH and TRAILL), i, 782.

Acetylsuccinyl *per*oxide, and its thermal decomposition (BRUNNER), i, 1236.

Acetyltaurine, sodium salt (TERAOKA), i, 1390.

Acetyltropic acid, β-piperidinoethyl ester hydrochloride (CHEMISCHE WERKE GRENZACH), i, 31.

Acetylvaline, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.

Acid, $C_9H_{14}O_5$, and its salts, from chenopodium oil (HENRY and PAGET), i, 1162.

$C_{10}H_{14}O_4$, from *Pimenta officinalis* oil (KEMP), i, 565.

$C_{10}H_{16}O_3$, and its salts and oxime, from oxidation of sodium abietate (FREJKA and BALAŠ), i, 1422.

Acid, $C_{12}H_{18}O_6$, from action of ozone on methyl abietate (RUZICKA, MEYER, and PFEIFFER), i, 1420.
$C_{13}H_{14}O_4$, from *Pimenta officinalis* oil (KEMP), i, 565.
$C_{13}H_{22}O_2$ (two), from hydrogenation of diphenyl-*o*-carboxylic acid (RANEDO and LEÓN), i, 666.
$C_{14}H_{12}O_6$, and its ethyl ester, from ethyl dibromocinnamate and ethyl sodiomalonate (HAERDI and THORPE), i, 924.
$C_{15}H_{30}O_4$, from oxidation of rottlerin (DUTT), i, 1297.
$C_{15}H_{30}O_2$, from fractionation of chaulmoogra oil (WRENSHALL and DEAN), i, 1414.
$C_{19}H_{36}O_6$, and its derivatives, from plant cuticle (LEGG and WHEELER), i, 1026.
$C_{19}H_{22}O_2N_2$, from strychnos alkaloids, and its derivatives (LEUCHS and TAUBE), i, 1314.
$C_{20}H_{28}O_3$, and its semicarbazone, by action of acetic anhydride on oxidation product of methyl abietate (RUZICKA, MEYER, and PFEIFFER), i, 1420.
$C_{20}H_{33}O_4$, and its semicarbazone, from oxidation product of methyl abietate (RUZICKA, MEYER, and PFEIFFER), i, 1429.
$C_{26}H_{19}O_3N_2S$, from diphenylethylamine hydrochloride and diazotised sulphanilic acid (ELBS), i, 165.
$C_{32}H_{26}O_2$, and its bromo derivative from algæ (TSUJIMOTO), i, 778.
$C_{24}H_{46}O_3$, from nervone and sulphuric acid (KLENK), i, 1347.
$C_{27}H_{44}O_4$, and its methyl ester, from oxidation of 4:7-diacetoxycholestan (WINDAUS and HOSSFELD), i, 1066.
Acids, thermochemistry and constitution of solutions of (KARVE), ii, 633.
adsorption of, by filter paper (MOKRUSCHIN), ii, 957.
displacement of, by diffusion (DEMOUSSY), ii, 654.
osmosis of, in gels (YUMIKURA), i, 735.
dissociation of (v. HALBAN), ii, 511; (HANTZSCH), ii, 512.
liquid-crystalline properties of salts, esters, and (VORLÄNDER), i, 267.
additive compounds of esters and (KENDALL and BOOGE; KENDALL and KING), ii, 972.
electrometric titration of (AUERBACH and SMOLCZYK), ii, 118.
aliphatic, Röntgen ray spectra of (DE BROGLIE and TRILLAT), ii, 640.
Acids, aliphatic, action of bromine on (WATSON), i, 1232.
and their derivatives, chromic acid oxidation of (SIMON), i, 778.
decomposition of, with metallic chlorides (MAILHE), i, 503.
esterification of, in glycerol (KAILAN and RAUPENSTRAUCH), i, 880.
ammonium salts, oxidation of (CLUTTERBUCK and RAPER), i, 882.
carboxylic (PHILIPPI, SEKA, HAGER, and LANDAU), i, 511.
higher, surface tensions of (FRUMKIN), ii, 856.
aromatic, metabolism of. See Metabolism.
glycol esters of (CRETCHER and PITTENGER), i, 1415.
*mono*basic, neutralisation of, by means of viscosity (SIMON), ii, 512.
*di*basic, photolysis of (VOLMAR), i, 1378; ii, 575.
dissociation of (LARSSON), ii, 294.
second dissociation constants of (PAUL), ii, 116.
influence of valency direction on dissociation constants of (SPIERS and THORPE), ii, 895.
carboxylic, dissociation contents of (EBERT), i, 230.
*mono*carboxylic, and their esters, electric moments of (SMYTH), ii, 846.
*di*carboxylic, nephropathic action of (ROSE, WEBER, CORLEY, and JACKSON; ROSE and DIMMETT), i, 733.
fatty, structure of (GIBBS), ii, 269; (FRIEDEL), ii, 272.
from ceresin (MARCUSSON), i, 349.
molecular orientation in films of (TRILLAT), ii, 195.
and their esters, spreading of, on the surface of water (CARY and RIDEAL), ii, 388.
emulsions of, as insecticides (SIEGLER and POPENOE), i, 489.
and *di*basic, *X*-ray study of (TRILLAT), ii, 489.
*mono*basic, change in molecular volume of (GARNER and RYDER), ii, 355.
saturated, anhydrides of, and their stability (HOLDE and GENTNER), i, 1035.
solid, Röntgen ray diffraction of (WYCKOFF, HUNT, and MERWIN), ii, 1129.
unsaturated, constitution of (ARMSTRONG and HILDITCH), i, 355, 778.

Acids, fatty, unsaturated, oxidation of (BAUER and KUTSCHER), i, 630; (GRÜN and WITTKA), i, 1377; (TRILLAT), ii, 1127.
higher, structure of, and their salts (KLIMONE), i, 505.
sulphonation of (POMERANZ), i, 1380.
free, determination of, in presence of aluminium (SABALITSCHKA and REICHEL), ii, 602.
higher saturated, determination of, in mixed acids (LAPWORTH and MOTTRAM), i, 1129.
inactive, and inactive bases, mutual resolution of (INGERSOLL), i, 814.
organic, structure of, and their behaviour on sulphochromic oxidation (ARMSTRONG, ALLAN, and MOORE), i, 505; (SIMON), i, 511.
preparation of, by the Grignard reaction (IVANOV), i, 503.
ultra-violet absorption spectra of (VLÈS and GEX), ii, 472.
conductivity of, in methyl alcohol (GOLDSCHMIDT and AARFLOT), ii, 976.
effect of electrolytes on solubilities of, in water (YAJNIK, JAIN, and NATH), ii, 1147.
adsorption of, from solutions (RUFF and HOHLFELD), ii, 192; (PATRICK and JONES), ii, 193.
and their salts, comparative adsorption of (FROMAGEOT and WURMSER), ii, 384.
velocity of esterification of, with ethyl alcohol (BHIDE and SUDBOROUGH), i, 1127.
action of magnesium phenyl bromide on (PETERS, GRIFFITH, BRIGGS, and FRENCH), i, 543.
displacement of, from their sodium salts (BUREAU), ii, 792.
volatile, determination of (BOHANES), ii, 605.
polycarboxylic, esters, compounds of stannic chloride with (HIEBER and BECKER), i, 1325.
stereoisomeric, transformation of, and their esters (HÜCKEL and GOTH), i, 402.
unsaturated, $\alpha\beta$–$\beta\gamma$ change in (KON and LINSTEAD), i, 506.
α-unsaturated, synthesis of, from malonic acid (DUTT), i, 882.
weak, indicator for determination of (CHABOT), ii, 899.
determination of, volumetrically (HARRIS), ii, 155.
Acid chlorides, catalytic decomposition of (MAILHE), i, 629.
Acid chlorides, action of aluminium organic compounds with (LEONE), i, 937.
decomposition of, with metallic nickel (MAILHE), i, 1232.
aromatic, action of diazomethane on (LEWIS, NIERENSTEIN, and RICH), i, 935.
Acidity, origin of (LOWRY), ii, 15.
Acidosis (HASTINGS, SENDROY, and ROBSON), i, 1490.
production of (BLUM and DELAVILLE; HALDANE), i, 723.
Acipenser sturio (sturgeon), constituents of (FLÖSSNER and KUTSCHER), i, 720.
Acocantherine (MOIR and LEWIS), i, 833.
Acocanthic acid, benzoyl derivative (MOIR and LEWIS), i, 833.
Aconite alkaloids (SCHULZE and BERGER), i, 282; (MAJIMA and SUGINOME), i, 1447.
Aconitine *perchlorate* (SCHULZE and BERGER), i, 283.
Aconitum anthora, alkaloids from (GORIS and MÉTIN), i, 761, 762.
Aconitum napellus, alkaloids from (SCHULZE and BERGER), i, 282; (GORIS and MÉTIN), i, 762.
Acraldehyde (*acrolein*), formation of, from glycerol, by bacilli (HUMPHREYS), i, 340.
activation of, by light, and its deactivation by quinol (MOUREU and DUFRAISSE), i, 362; (MOUREU, DUFRAISSE, and BADOCHE), i, 362, 363.
Acridine, constitution of (v. AUWERS and KRAUL), i, 578.
derivatives, preparation of (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 429.
Acridine, 3:9-*diamino*- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
Acridone, derivatives of (LINNELL and PERKIN), i, 62.
Acriflavine, effect of, on infusoria (ROBERTSON), i, 1012.
Actinium, mobility of ions in active deposit of (ERIKSON), ii, 79.
Actinometers, electrochemical (ATHANASIU), ii, 1067.
with mercury electrodes, sensitiveness of (ATHANASIU), ii, 415.
Actinoscopic reactions (REYCHLER), ii, 1180.
Activity coefficients (WILKE and KIENIGER), ii, 790.
Acyl chlorides, aromatic, action of diazomethane on (NIERENSTEIN, WANG, and WARR), i, 34.

O-**Acyl compounds**, catalytic isomerisation of, into *C*-alkyl compounds (SCHEIBLER), i, 918.
Acylindazoles, labile and stable, constitution of (V. AUWERS), i, 1460.
O- and *N*-**Acylsalicoylimides**, isomeric (ANSCHÜTZ, ASCHENBERG, KUCKERTZ, KRONE, RIEPENKRÖGER, and ZERBE), i, 666.
Addition to cyclic double linkings (NAMETKIN), i, 250.
Additive reactions and tautomerism (INGOLD), i, 357.
Adenine in lucerne (VICKERY and LEAVENWORTH), i, 873.
nucleotide from blood (HOFFMAN), i, 711, 851.
Adenylic acid, salts of (IZUMI), i, 174.
brucine and strychnine salts (PEISER), i, 1477.
Adhatoda vasica, alkaloid from (SEN and GHOSH), i, 958.
Adipic acid, $\beta\gamma$-*di*hydroxy-, and its ethyl ester (PANKOKE), i, 358.
Adipic acids, *di*bromo-, optically active, and their salts (HOLMBERG and MÜLLER), i, 1236.
Adipocere (TSCHIRCH and GFELLER), i, 1203.
Adipyl chloride, action of triethylamine on (WEDEKIND, MÜLLER, and WEINAND), i, 510.
Adonis vernalis, extraction of (STEPPUHN and PEWSNER), i, 762.
Adrenaline (*suprarenine*; *epinephrine*), secretion of, during starvation (OGAWA), i, 1218.
effect of, on blood and tissues (DRESEL and WOLLHEIM), i, 616.
effect of, on lactic acid in blood and tissues (CORI), i, 753.
effect of, and its derivatives, on blood-sugar (DUBIN, CORBITT, and FREEDMANN), i, 1502.
effect of amino-acids on the action of (ABDERHALDEN and GELLHORN), i, 332.
antagonism of insulin and (GOTTSCHALK; ZONDEK and UCKO), i, 1513.
analysis of (ECHAVE), ii, 248.
detection and determination of, in suprarenal powders (BAILLY), ii, 248.
Adsorption (SCHELTE), ii, 286; (PAVLOV), ii, 287, 507, 958; (LIEPATOV), ii, 385, 957; (GHOSH and DHAR), ii, 386, 511.
theory of (FRENKEL), ii, 194.
chemical theory of (BHATNAGAR, PRASAD, and BAHL), ii, 1155.
electrical theory of (ILJIN), ii, 958, 1149.
Adsorption, hydrolytic, theory of (MUKHERJEE), ii, 1149.
Schulze's law of (WEISER), ii, 855.
at the critical temperature (PATRICK, PRESTON, and OWENS), ii, 508.
S-shaped curves of (FLÖROV; OSTWALD and SCHULZE), ii, 657.
and evolution of mixed gases from an adsorbant (LORENZ and WIEDBRAUCK), ii, 382.
and capillarity (PATRICK and EBERMAN), ii, 284.
and partition, theory of (FRUMKIN), ii, 856.
and surface energy at phase boundaries (ILJIN), ii, 856, 958.
relation between osmotic pressure and (PÓLÁNYI), ii, 290.
and heterogeneous catalysis (ALEKSEEVSKI), ii, 858.
and cataphoresis (FROMAGEOT), ii, 128.
of gases by graphite (LOWRY and MORGAN), ii, 1053.
in gels (TOMITA), ii, 202.
of ions (AUDUBERT and QUINTIN), ii, 384; (MUKHERJEE and RAY), ii, 385.
at liquid-gas interface (IREDALE), ii, 508.
at the surface between air and solutions of aliphatic compounds (FRUMKIN), ii, 109.
of organic acids and their salts (FROMAGEOT and WURMSER), ii, 384; (UNGERER), ii, 658.
from solutions (BERL and WACHENDORFF), ii, 507.
of vapours by metallic oxides (PEARCE and ALVARADO), ii, 381.
by aluminium oxide and hydroxide (MUNRO and JOHNSON), ii, 191; (MILLER), ii, 192.
by charcoal (URBAIN; KROETZ), ii, 191; (RUFF and HOHLFELD), ii, 192; (BAKR and MCBAIN), ii, 193; (RICHARDSON and ROBERTSON; KOLTHOFF), ii, 383.
from viscous media (WEISSENBERGER and WALDMANN), ii, 655.
by various powdered charcoals (KÖNIG), ii, 1054.
by activated sugar charcoal (MILLER), ii, 656.
by lipoid mixtures (SCHÄFER), ii, 1149.
by precipitates (WEISER), ii, 108.
by silica gels (RAY), ii, 191; (PATRICK and JONES), ii, 193; (PATRICK and OPDYCKE), ii, 656.
separation of organic compounds by means of (FODOR and ROSENBERG), ii, 1060.

Adsorption compounds (HALLER), ii, 287.
effect of, on infectious diseases (BERING), i, 858.
Adsorption isotherms, derivation of (GORBATSCHEV), ii, 959.
Aerobacter aerogenes. See *Bacillus lactis aerogenes*.
Ætioporphyrin, formation of, from mesoporphyrin (FISCHER and MÜLLER), i, 845.
Ætiourinoporphyrin (FISCHER and HILGER), i, 307.
Affinity (BILTZ and HOLVERSCHEIT), ii, 268; (DE DONDER), ii, 539; (BILTZ and KEUNECKE), ii, 986; (BILTZ, BRÖHAN, and WEIN; BILTZ and WEIN), ii, 1182; (BILTZ and MESSERKNECHT), ii, 1183; (BILTZ and MAU), ii, 1184; (BILTZ and RAHLFS), ii, 1191.
relation between atomic grouping and (FEIGL), i, 170.
chemical, and atomic structure (WILSDON), ii, 481.
electrical meaning of (BORN), ii, 482.
internal pressures produced by (RICHARDS), ii, 362.
compressibility and internal pressure (SAERENS), ii, 91.
residual, and co-ordination (MORGAN and YARSLEY), i, 378; (MORGAN and SMITH), i, 1457; (MORGAN, CARTER, and HARRISON), ii, 1042.
specific, calculation of (DE DONDER), ii, 790.
Affinity constants of amines (BOURGEAUD and DONDELINGER), ii, 117.
Afwillite (PARRY and WRIGHT), ii, 429.
Agar-agar, physical chemistry of (HARVEY), ii, 965.
absorptive power of (EFFRONT), ii, 201.
swelling of gels of, in water (CLARKE), ii, 868.
physical differences between sols and gels of (HATSCHEK and HUMPHRY), ii, 34.
electro-dialysis of (HARVEY), ii, 293; (HOFFMAN and GORTNER), ii, 1158.
hydration of, by ions (MACDOUGAL and CLARKE), ii, 1156.
Ageratum conyzoides, constituents of oil from (MOUDGILL), i, 945.
Agglutinin, behaviour of, when adsorbed, to its antigen (EISLER), i, 96.
Agmatine, relationship of arginine to (MÜLLER), i, 1496.
putrefaction of (REINWEIN and KOCHINKI), i, 747.
Air. See Alveolar air and Atmospheric air.
Akermanite, constitution of (GOSSNER), ii, 821.
d-**Alanine**, asymmetric cobalt salts of (LIFSCHITZ), i, 522.
dl-**Alanine**, relation between taste and concentration of solutions of (HEIDUSCHKA and KOMM), i, 1389.
d-**Alanyl**-*d*-**alanine anhydride**, action of alkalis on (LEVENE and PFALTZ), i, 795.
Alanylaspartic acid, and its methyl ester (HAVESTADT and FRICKE), i, 162.
Alanylglycine anhydride, diacetyl derivatives (ABDERHALDEN and KOMM), i, 175.
Alanylhistidine (HAVESTADT and FRICKE), i, 162.
Albite in Bengal limestone (SPENCER), ii, 1092.
Albumin, solutions of (KOLTHOFF), ii, 1055; (KRUYT), ii, 1056.
action of acids on (TRENDTEL), i, 91.
precipitation of (THOMAS and NORRIS), i, 603.
egg- (*ovalbumin*), molecular dimensions and weight of (DU NOÜY), ii, 939.
surface tension of (JOHLIN), ii, 857.
osmotic pressure of the chloride of (HAMMARSTEN), ii, 196.
separation of proteoses of (RUDD), i, 320, 321.
cataphoresis in sols of (SCOTT and SVEDBERG), ii, 204.
serum, peptic hydrolysis of (RONA and KLEINMANN), i, 1507.
Albumins, coagulation of (RAKUZIN and ROSENFELD), i, 708.
Alcohol, $C_5H_6OCl_2$, from dichloropropaldehyde, acetylene and magnesium ethyl bromide (LESPIEAU), i, 226.
$C_{32}H_{66}O$, and its derivatives, from American cotton wax (FARGHER and PROBERT), i, 879.
$C_{34}H_{70}O$, and its derivatives, from American cotton wax (FARGHER and PROBERT), i, 879.
Alcohols, synthesis of (TERENTIEV), i, 110.
infra-red absorption spectra of (LECOMTE), ii, 351.
electrolytic oxidation of (KOIDZUMI), ii, 808.
dehydration of, over alumina (ADKINS and PERKINS), i, 626.
catalytic dehydration of mixtures of phenols and (BRINER, PLÜSS, and PAILLARD), i, 248.
catalytic dehydrogenation of (PALMER and CONSTABLE; CONSTABLE), ii, 311.

Alcohols, catalytic dehydrogenation of, apparatus for (WILLIMOTT), ii, 151.
catalytic dehydrogenation and dehydration of, with zinc oxide catalyst (LAZIER and ADAMS), i, 878.
change of, into aldehydes (VERLEY), i, 783.
reactivity of hydroxyl-hydrogen atoms in (NORRIS and ASHDOWN), i, 626.
interchange of groups between ketones and (VERLEY), i, 1034.
from sugars, oxidation of (VOTOČEK and LUKES), i, 773.
acetylenic, preparation of (GUEST), i, 627.
aliphatic, velocity of reaction of substituted benzoic anhydrides with (RULE and PATERSON), i, 29.
aromatic, action of, on aromatic compounds in presence of aluminium chloride (HUSTON), i, 249.
optically active (HEWITT and KENYON), i, 914.
of the hydroaromatic and terpene series (KENYON and PRISTON), i, 941.
polyhydric, solution volumes and refraction constants of (RIIBER, SÖRENSEN, and THORKELSEN), i, 773.
primary, condensation of resorcinol and similar compounds with (SEN and SARKAR), i, 812.
optically active, preparation of (BECHERER), i, 664.
secondary and tertiary, local anæsthesia with (QUIGLEY and HIRSCHFELDER), i, 195.
tertiary, action of hydrobromic acid on (RAMART), i, 250.
asymmetric, preparation of (THOMS and AMBRUS), i, 789.

Aldehydes, synthesis of (STEPHEN), i, 1131.
Friedel and Crafts synthesis with (SCHAARSCHMIDT, HERMANN, and SZEMZÖ), i, 1278.
influence of alkyoxy groups on synthesis of (SONN and PATSCHKE), i, 1279.
absorption spectra of (LECOMTE; PURVIS), ii, 627.
mixed dismutation of (NAKAI), i, 360.
reduction of (MEERWEIN and SCHMIDT), i, 1239.
preparation of acetylenic hydrocarbons from (BOURGUEL), i, 364.
change of, into alcohols (VERLEY), i, 783.
addition of chloroform to (HOWARD), i, 557.

Aldehydes, condensation of, with diindone (RADULESCU and GEORGESCU), i, 1286.
with diketohydrindene (RADULESCU and GEORGESCU), i, 1285.
to esters, in presence of alkoxides (CHILD and ADKINS), i, 632.
with ethyl α-acetylhexoate (RYAN and SHANNON), i, 538.
with methyl ethyl ketone (RYAN and CAHILL), i, 558.
with α-phenyl-β-methyl-Δ^{α}-buten-γ-one (RYAN and LENNON), i, 1282.
action of, on Grignard reagents (MARSHALL), i, 1428.
action of *p*-aminophenylarsinic acid and pyruvic acid on (ADAMS and JOHNSON), i, 319.
in blood (FABRE), i, 324.
aliphatic, condensation of furfuraldehyde with (IVANOV), i, 421.
aromatic, catalytic reduction of (ROSENMUND and JORDAN), i, 257.
condensation of, with hydroxy- and methoxy-2-methylquinolines, and 2-hydroxylepidine (TRÖGER and DUNKER), i, 342.
action of phenanthraquinone on, in presence of ammonia (SIRCAR and RAY), i, 980
reaction of sodium with (BLICKE), i, 37.
determination of, by the action of sulphites on (ROMEO and D'AMICO), i, 1380.

Aldehydesulphoxylates as protective colloids (BINZ and BAUSCH), i, 991.

3-Aldehydo-5-methylindole-2-carboxylic acid, and its ethyl ester (ODDO), i, 298.

***n*-Aldehydo-octoic acid**, ethyl and methyl esters and dimethyl acetal of the latter (HELFERICH and SCHÄFER), i, 7.

***m*-Aldehydophenyl carbonate**, and ethyl carbonate, and 4-nitro- (MASON and JENKINSON), i, 931.

Aldimines, synthesis of (GRIGNARD and ESCOURROU), i, 931.

Aldoximes, action of picryl chloride and of 2:4-dinitrochlorobenzene on (BRADY and KLEIN), i, 674.

Aldoxime peroxides (CIUSA and PARISI), i, 1070.

Alfalfa. See Lucerne.
, calcium requirements of fungi and (LOEW), i, 1218.
nitrogen in (FRED and PETERSON), i, 1122.
unsaturated acids in (TSUJIMOTO), i, 778.

Algæ, marine, chlorophyll in (LUBIMENKO), i, 216.
Aliphatic compounds, adsorption at the surface between air and solutions of (FRUMKIN), ii, 109.
solid crystalline, atomic heats of (SALANT), ii, 1042.
photochlorination of, in carbon tetrachloride (PLOTNIKOV), ii, 220.
higher, synthesis of (G. M. and R. ROBINSON), i, 354.
Aliphatic-aromatic compounds (v. BRAUN and REICH), i, 1405; (v. BRAUN and KAISER), i, 1414.
behaviour of, in the animal organism (THIERFELDER and KLENK), i, 192.
Alizarin, nitro-, colloidal, action of electrolytes on (LIEPATOV), ii, 1059.
Alkali alkyls (HEIN, PETZCHNER, WAGLER, and SEGITZ), ii, 217.
amides, displacement of metals in (BERGSTROM), ii, 885.
ortho-arsenites (VANZETTI), ii, 421.
borates (AUGER), ii, 697.
bromates, chlorates, and nitrates, viscosities of (SIMON), ii, 512.
*poly*bromides and *poly*chlorides (HÜTTIG and SCHLIESSMANN), ii, 1181.
carbonates, action of arsenious anhydride on (VANZETTI), ii, 421.
chlorides, circulation of, in diaphragm electrolysers (GIORDANI), ii, 550, 551.
cyanides, reduction of metallic oxides by (HACKSPILL and GRANDADAM), ii, 419.
halides, coloration of, by Röntgen rays (BAYLEY), ii, 21.
reflection of Röntgen rays by crystals of (ARMSTRONG, DUANE, and HAVIGHURST; KULENKAMPFF), ii, 1033.
thermal expansion of (HENGLEIN), ii, 375, 935, 951.
heats of hydration and solution and lattice energies of (LANGE), ii, 847.
heats of solution of (WÜST and LANGE), ii, 38.
heats of solution and dilution of (WÜST and LANGE), ii, 791.
solid solutions of ammonium halides and (HAVIGHURST, MACK, and BLAKE), ii, 502.
crystal measurements of (HAVIGHURST, MACK, and BLAKE), ii, 17.
hydroxides, activity of hydroxyl ions in (FRICKE), ii, 539.
hypochlorites (DIETZEL and SCHLEMMER), ii, 892.
metals, spectra of (DE WISNIEWSKI), ii, 77.
Alkali metals, band spectra of mixtures of (BARRATT), ii, 19.
spark spectra of (MOHLER), ii, 615.
ultra-violet spectra of (SHAVER), ii, 451.
spectra of mixed vapours of magnesium and (BARRATT), ii, 927.
and their alloys, photo-electric properties of (IVES; IVES and JOHNSRUD), ii, 344.
photo-electric thresholds and thermionic work functions of (RICHARDSON and YOUNG), ii, 343.
potentials of (NEUMANN and RICHTER), ii, 797.
thermionic effects caused by vapours of (LANGMUIR and KINGDON), ii, 254.
reactions between molten alloys of, and their molten chlorides (JELLINEK and WOLFF), ii, 974; (JELLINEK), ii, 1160.
and their halides, value of $\sqrt{a}$ for (VAN LAAR), ii, 1141.
transition probabilities in atoms of (BARTELS), ii, 624.
explosions with (STAUDINGER), ii, 1181.
displacement of, by iron (HACKSPILL and GRANDADAM), ii, 233.
ammoniation of ions of, in aqueous solutions (LOŠAN), ii, 654.
electrolytic separation of alkaline earths and (SAXON), ii, 984.
double salts of rare earths with (ZAMBONINI and CAROBBI), ii, 222; (ZAMBONINI and CAGLIOTI), ii, 222, 315; (CAROBBI), ii, 315.
determination and separation of (SMITH), ii, 486; (SMITH and ROSS), ii, 437, 601.
*di*sulphides, action of, on organic halides (THOMAS and RIDING), i, 113.
*poly*sulphides (THOMAS and JONES), ii, 58.
Alkali-cellulose (VIEWEG; HEUSER), i, 119.
Alkaline earth amides, displacement of metals in (BERGSTROM), ii, 885.
chlorides, activity coefficients and transference numbers of (LUCASSE), ii, 399.
metals, spectra of (LANDÉ), ii, 249; (GREEN and PETERSEN), ii, 451; (RUSSELL and SAUNDERS), ii, 911.
spark spectra of (DORGELO), ii, 724.
potentials of (NEUMANN and RICHTER), ii, 797.

Alkaline earth metals, reactions between molten alloys of, and their molten chlorides (JELLINEK and WOLFF), ii, 974; (JELLINEK), ii, 1160.
equilibrium between sodium and, and their fused chlorides (JELLINEK and OZERWINSKI), ii, 123.
electrolytic separation of alkalis and (SAXON), ii, 984.
molybdates, isomorphism of, with rare earth molybdates (ZAMBONINI and LEVI), ii, 1133.
phosphors, rare earths in (TOMASCHEK), ii, 354.
salts, biochemistry of (HODEL), i, 1496.
Alkaloid, $C_{19}H_{24}ON_2$, and its derivatives, from *Chelidonium majus* (GADAMER and WINTERFELD), i, 288.
Alkaloids from aconite. See Aconite.
of the aporphine series, conversion of, into those of the chelidonine series (OSADA), i, 283.
from the calabar bean. See Calabar bean.
from calumba root (FEIST and DSCHU), i, 830; (SPÄTH and DUSCHINSKY), i, 1313.
from cinchona. See Cinchona.
of the hellebore group (KELLER), i, 830.
from hygrine. See Hygrine.
jaborandi (SPÄTH and KUNZ), i, 575.
from morphine. See Morphine.
from opium. See Opium.
in germinating seeds (SABALITSCHKA and JUNGERMANN), i, 1223.
from strychnos. See Strychnos.
of the tropan group, amine-oxides of (POLONOVSKI and POLONOVSKI), i, 828.
device for extraction of (PALKIN, MURRAY, and WATKINS), ii, 708.
extraction of, from organs (FABRE), i, 719.
hydroferri- and hydroferro-cyanides of (CUMMING and BROWN), i, 572.
determination of (NORTH and BEAL; MÜLLER), ii, 607.
determination of, volumetrically (RASMUSSEN and SCHON), ii, 247.
Alkatan, chemistry of (HEPBURN and STROH), i, 108.
Alkoxides, potential of concentrated solutions of (KONTNÍKOVÁ and SHIKATA), ii, 672.
magnesium, preparation of, and their use in syntheses (TERENTIEV), i, 110.
Alkyl ethers, hydroxy-, derivatives of (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 374.
Alkyl hypochlorites (BACKEBERG), i, 775.
phosphites, neutral, preparation of (JANCZAK), i, 1051.
sulphides, preparation of (WOOD), i, 1034.
Alkylbarbituric acids, preparation of soluble compounds of (HOFFMANN, LA ROCHE & Co.), i, 300.
Alkylglutaric acids, dianilides of (V. AUWERS), i, 892.
Alkylglyoxalines, amino- (GERNGROSS), i, 440.
1-Alkylcyclohexan-3-ones, preparation of (SEIFERT), i, 407.
Alkylindoles, 3-amino-, synthesis of (MAJIMA and HOSHINO), i, 1450.
Alkylmercuric hydroxides, reactions of (KOTEN and ADAMS), i, 236.
Alkyloxy-acids, salts, electrolysis of (FAIRWEATHER), i, 631.
Alkylresorcinols, preparation of (SHARP & DOHME), i, 809.
Alkylsulphonic acids, preparation of barium and calcium salts of (CHEMISCHE FABRIK VORM. SANDOZ), i, 1377.
Allantoin, determination of, in presence of uric acid, creatinine, and amino-acids (LANGFELDT and HOLMSEN), ii, 1010.
Allophanic acid, β-chloro- and β-iodoethyl esters (CHINOIN FABRIK CHEMISCH-PHARMAZEUTISCHER PRODUKTE), i, 13.
Allotropy and metastability (COHEN and HELDERMAN), ii, 23; (COHEN and MOESVELD), ii, 374, 950.
Alloys, structure of (WESTGREN and PHRAGMÉN), ii, 502.
structural composition of (POLUSHKIN), ii, 189.
Röntgen ray structure of (SACKLOVSKI), ii, 939; (WEISS), ii, 940.
preparation of, by the wet method (MAZZUCCHELLI and VERCILLO), ii, 582.
electrical conductivity of (BORELIUS), ii, 749.
effect of a magnetic field on the electrical resistance of (WILLIAMS), ii, 753.
chemical resistance of (GUERTLER and LIEPUS), ii, 1147.
hydrogen overvoltage for (FISCHER), ii, 44.
depression of freezing points of (HONDA and ISHIGAKI), ii, 1050.
change in volume of, during solidification (ENDO), ii, 281.
inverse segregation in (MASING), ii, 1146.
colloidal separations in (ANDREW and HAY), ii, 954.

Alloys, examination of, by radio-detector action (CZOCHRALSKI), ii, 642.
X-ray apparatus for examination of (LANGE), ii, 482.
molten, electrolysis of (KREMANN, KIENZL, and MARKE; KREMANN, MÜLLER, and KIENZL; KREMANN, MÜLLER, and ORTNER), ii, 132; (KREMANN, and GRUBER-REHENBURG), ii, 678; (KREMANN and BENDA; KREMANN and BAUKOVAC; KREMANN and DELLACHER), ii, 679.
ternary, equilibria of (IWASE), ii, 535.
Allyl compounds, synthesis of (BERT), i, 803, 1052.
Allyl bromide, 9-bromo-, derivatives of (v. BRAUN and KÜHN), i, 1374.
*βγ-di*bromo-, compounds formed by action of trimethylamine and of pyridine on (v. BRAUN and KÜHN), i, 1375.
chloride, γ-chloro-, compound from trimethylamine and (v. BRAUN and KÜHN), i, 1375.
halides, halogenated, use of, in synthetic reactions (v. BRAUN and KÜHN), i, 1374.
iodide, action of potassium pentasulphide on (THOMAS and RIDING), i, 4.
2-Allylamino-5-phenyl-1:3:4-thiodiazine, and its hydrobromide (BOSE), i, 1466.
Allylanisole, *p*-β-bromo- (v. BRAUN and KÜHN), i, 1375.
Allylbarbituric acid, *di*-β-bromo- (RIEDEL), i, 1454.
Allylbenzene, γ-bromo-, and γ-chloro- (v. BRAUN and KÜHN), i, 1375.
p-bromo-γ-chloro-, γ-chloro-, and their *di*bromides (BERT), i, 804.
Allyl*iso*butyrone (HALLER, BAUER, and RAMART), i, 261.
α-Allylbutyrophenone, and its oxime (HALLER, BAUER, and RAMART), i, 261.
3-Allyl-*p*-cresol (CLAISEN), i, 1410.
Allylcrotylbarbituric acid (TAUB, SCHÜTZ, and MEISENBURG), i, 435.
2-Allyl-*p*-cymene, γ-chloro-, and its dibromide (BERT), i, 804.
γ-Allyldextrose, and its di*iso*propylidene ether and osazone (FREUDENBERG, v. HOCHSTETTER, and ENGELS), i, 635.
2-Allyldiketohydrindene-2-carboxylic acid, ethyl ester, spiran from (RADULESCU), i, 1159.
2-Allyl*cyclo*hexanone, 2-cyano- (v. AUWERS, BAHR, and FRESE), i, 312.
Allylmalonic acid, β-bromo-, and *di*-β-bromo-, ethyl esters (RIEDEL), i, 1454.
Allylnaphthalene, 1-β-bromo (v. BRAUN and KÜHN), i, 1375.
4-Allyloxyphenylmalonamic acid, and its ethyl ester (AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION), i, 402.
α-Allylpropiophenone (HALLER, BAUER, and RAMART), i, 261.
Allyltoluenes, γ-chloro-, and their dibromides (BERT), i, 804.
4-Allylveratrole, 5-amino-, acetyl derivative, and 5-nitro- (LIONS, PERKIN, and ROBINSON), i, 832.
Altitudes, high, effect of, on alcohol concentration in blood and its excretion (BIEHLER), i, 1115.
Alumen, in Pliny's Natural History (BAILEY), ii, 591.
Alumina. See Aluminium oxide.
Aluminium, atomic weight of (KREPELKA and NIKOLIĆ), ii, 620.
spectrum of (MCQUARRIE), ii, 1013.
absorption spectrum of (MAJUMDER and SWE), ii, 338.
spark spectrum of (v. WISNIEWSKI), ii, 451.
spectral frequencies of (HOLWECK), ii, 336.
photographic action of H-particles from (BLAU), ii, 1111.
absorption of cathode rays by (TERRILL), ii, 79; (SCHONLAND), ii, 459.
transmission of electrons through (HARTIG), ii, 921.
conductivities of (SCHOFIELD), ii, 273.
critical potential of (HOLWECK), ii, 729.
current-potential curves for (LIEBREICH and WIEDERHOLT), ii, 404.
electromotive behaviour of (SMITS), ii, 130; (SMITS and GERDING), ii, 794.
sizes of electron-kernels of magnesium, silicon, sodium, and (TURNER), ii, 349.
and its alloys, thermal expansion of (HIDNERT), ii, 375.
distortion and fracture of crystals of (TAYLOR and ELAM), ii, 488.
recrystallisation of (RÖHRIG), ii, 282.
corrosion of (MAASS and WIEDERHOLT), ii, 560.
solution of, in hydrochloric acid (WACHÉ and CHAUDRON), ii, 687.
testing of, by density (PASCAL), ii, 646.
strained, Röntgen ray analysis of (ONO), ii, 746.
Aluminium alloys, conductivity of (MASUMOTO), ii, 503.
expansion coefficients for (HONDA and ÔKUBO), ii, 104.

Aluminium alloys, with cadmium and magnesium (VALENTIN and CHAUDRON), ii, 205.
with chromium (SISCO and WHITMORE), ii, 1051.
with copper (MASING and KOCH), ii, 787.
dilatation of (CHEVENARD), ii, 768.
with copper and zinc (HANSON and GAYLER), ii, 974.
with iron, temper colours of (TAMMANN and SIEBEL), ii, 1169.
with magnesium (DANIELS), ii, 103; (URAZOV), ii, 786.
with mercury, reduction of sugars by (NANJI and PATON), i, 117.
with molybdenum and nickel (PFAUTSCH), ii, 536.
with silicon, fusion of (PARRAVANO and SCORTECCI), ii, 281.
with tin, electrolysis of (KREMANN and DELLACHER), ii, 679.
with zinc (TANABE), ii, 204; (ISIHARA), ii, 293, 786.
tensile tests of (ELAM), ii, 954.
decomposition of (FRAENKEL and GOEZ), ii, 314.
Aluminium salts, effect of, on soil acidity (NIKLAS and HOCK), i, 1525.
in soils, and their relation to plant growth (MAGISTAD), i, 1371.
determination of acidity, basicity, and aluminium content of solutions of (FEIGL and KRAUSS), ii, 329.
Aluminium antimonide, atomic structure of (OWEN and PRESTON), ii, 93.
boride, formation of (FUNK), ii, 705.
bromide, decomposition potential of (TREADWELL and STERN), ii, 41.
thermal analysis of binary systems of halides with (ISBEKOV), ii, 417.
chloride, conductivity of carbonyl chloride solutions of (GERMANN), ii, 1066.
density of carbonyl chloride solutions of (GERMANN), ii, 288.
vapour pressure of solutions of, in carbonyl chloride (GERMANN and MCINTYRE), ii, 196.
syntheses and degradations by means of (SCHROETER, VAN HULLE, GLUSCHKE, STIER, and MÜLLER), i, 125.
action of, on heptanaphthene (ZELINSKI and SMIRNOV), i, 1125.
*di*chromate, basic (CALCAGNI), ii, 891.
hydroxide, adsorption by (MILLER), ii, 192.
Aluminium hydroxide, adsorption of arsenious acid by (YOE), ii, 107.
adsorption of dyes by (WOOD and WOOLLER), ii, 285.
sols, mixtures of ferric hydroxide and (KÜHNL and PAULI), ii, 776.
precipitated (SHIDEI), ii, 1185.
precipitation of, electrometrically (BRITTON), ii, 1203.
precipitation of magnesium hydroxide with (PARISELLE and LAUDE), ii, 903.
oxide (*alumina*), solubility of, in water (REMY and KUHLMANN), ii, 119.
effect of temperature on hygroscopicity of (AARNIO), ii, 1157.
adsorption of gases by (MUNRO and JOHNSON), ii, 191.
β-form, use of, as crystal in measurements of Röntgen rays (PAULING and BJÖRKESON), ii, 895.
equilibrium of cryolite and (ROUSH and MIYAKE), ii, 974.
dehydration of hydrates of (GUICHARD), ii, 558.
dehydration of alcohols over (ADKINS and PERKINS), i, 626.
catalytic action of (ROSENMUND and JOITHE), i, 1403.
effect of impurities on (CHARRIOU), ii, 216.
catalysis by, of the reaction between ethyl alcohol and ammonia (DORRELL), ii, 1174.
solid solutions of, in ferric oxide (FORESTIER and CHAUDRON), ii, 534.
interaction of sodium chloride and (CLEWS), ii, 577.
silicates (NEUMANN), ii, 849.
sodium silicate, crystalline forms of (BOWEN and GREIG), ii, 997.
hydrosilicates, natural, origin of (SCHWARZ and WALCKER), ii, 887.
sulphate, equilibria of, with copper sulphate and manganese sulphate (CAVEN and MITCHELL), ii, 396.
sulphide (BILTZ), ii, 986.
Chloroaluminates, compounds of carbonyl chloride and (GERMANN and TIMPANY), ii, 1085.
Aluminium organic compounds, action of acid chlorides with (LEONE), i, 937.
action of ketones with (LEONE and BRAICOVIC), i, 677.
alkyl and aryl halides, and their compounds with ammonia and amines (LEONE), i, 530.
benzoylcamphor, and its mutarotation (FAULKNER and LOWRY), ii, 632.
Aluminates, compounds of mannitol with (HERASYMENKO), i, 774.

Aluminium detection, determination, and separation :—
detection of (SCHANTL), ii, 440; (HAMMETT and SOTTERY), ii, 601.
determination of, in presence of free acids (SABALITSCHKA and REICHEL), ii, 602.
determination of, gravimetrically, and its separation from manganese (SOLAJÁ), ii, 602.
determination of sodium in (FAIRLIE and BROOK), ii, 241.
separation of calcium and (KOLLÓ and GEORGIAN), ii, 330.
separation of, from manganese and magnesium and from phosphoric acid (MOSER, BRUKL, and VÉN), ii, 329.
Alveolar air, carbon dioxide tension in (KNIPPING), i, 176.
carbon dioxide in arterial blood and (BOOK and FIELD), i, 93.
Alvite, analysis of (BEDE-CHAN), ii, 710.
Amalgams. See Mercury alloys.
Ambergris, constitution of (SUZUKI), i, 1348.
Ambrain (SUZUKI), i, 1349.
Amides, acid organic, action of sulphur monochloride on (NAIK and PATEL), i, 121.
Δ^{α}-unsaturated acid, hydrolysis of (YATHIRAJA and SUDBOROUGH), i, 1134.
Amidines, tautomerism of (FORSYTH and PYMAN), i, 699.
condensations of, with ethoxymethylene derivatives of β-ketonic esters, β-diketones and cyanoacetic esters (MITTER and PALIT), i, 1319.
Amidoanilidocitric acid, ethyl ester (NAU, BROWN, and BAILEY), i, 1379.
Amidopersulphuric acid. See Hydroxylamine*iso*sulphonic acid.
Amines (JOHNSON and DASCHAVSKY), i, 540.
infra-red absorption spectra of (BELL), ii, 928.
affinity constants of (BOURGEAUD and DONDELINGER), ii, 117.
velocity of benzylation of (PEACOCK), i, 1399.
molecular compounds of, with 4:4'-dipyridylium dialkyl halides (EMMERT and ROH), i, 587.
dissociation constants of compounds of trinitrobenzene and (LEY, GRAU, and EMMERICH), ii, 1159.
action of, on semicarbazones (WILSON and CRAWFORD), i, 317.
alicyclic primary, preparation of (MAZOUREVITCH), i, 1247.
Amines, aliphatic, additive compounds of quinol with (HARGER), i, 23.
separation of, from ammonia (LEONE), ii, 907.
primary, action of nitrous acid on (BEEK and HERMANS), i, 794.
aromatic, preparation of (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 132.
fluorescence spectra of (NUNAN and MARSH), ii, 353.
action of thiosemicarbazide on (MAZOUREVITSCH), i, 984.
halogen-alkylated (WOLFF), i, 428.
secondary, reactions of diazo compounds with (LEVI and FALDINO), i, 171.
primary, secondary, and tertiary, preparation of (KINDLER), i, 387.
secondary, preparation of (ROSENMUND and JORDAN), i, 245.
identification of (MARVEL, KINGSBURY, and SMITH), i, 244.
Aminoacetals, condensation of aminoaldehydes with (RÄTH), i, 437.
Amino-acid, $C_4H_{11}O_3N$, and its phenylcarbimide derivative, from proteins (GORTNER and HOFFMAN), i, 602.
Amino-acids (KARRER and WIDMER), i, 593.
optical properties of (KEENAN), ii, 94.
action of Grignard reagents on (THOMAS and BETTZIECHE), i, 250, 251, 257; (BETTZIECHE), i, 251, 1147.
conversion of, into tertiary aminoalcohols (MCKENZIE and WILLS), i, 395.
combination of, with acids and alkalis (HARRIS), i, 450.
aldehydic derivatives of (BERGMANN, EUSSLIN, and ZERVAS), i, 890.
dipeptides of (HAVESTADT and FRICKE), i, 162.
molecular compounds of (PFEIFFER and ANGERN), i, 794.
decomposition of, by microbes (WAKSMAN and LOMANITZ), i, 867.
in nutrition (SEUFFERT, ITO, and YOKOYAMA; SEUFFERT and MARKS), i, 730.
oxidation of, in germinating seeds (OPARIN), i, 1518.
synthesis of, in the organism (MCGINTY, LEWIS, and MARVEL), i, 100; (KNOOP and OESTERLIN), i, 1493.
acetylation of, in the animal body (KNOOP and BLANCO), i, 1208.
deamination and transformation of, in the organism (KOTAKE), i, 730.

Amino-acids, hydrolytic deamination of (BERGMANN, MIEKELEY, WEINMANN, and KANN), i, 795.
action of, in blood (ROSENBAUM), i, 464.
specific dynamic action of, in relation to their metabolism (SETH and LUCK), i, 1002.
from hydrolysis of proteins, determination of (CHERBULIEZ and WAHL), ii, 1211.
determination of, in tryptic digests (ELLINGHAUS), i, 865.
α-Amino-acids, constitution and taste of (HEIDUSCHKA and KOMM), i, 522, 1389.
anhydrides of *N*-carboxylic derivatives of (WESSELY), i, 1151.
Amino-alcohols, wandering of acyl groups in (BETTZIECHE), i, 1147.
action of nitrous acid on (BETTZIECHE), i, 251.
semipinacolic deamination of (ORÉKHOV and ROGER), i, 261.
tertiary, elimination of the amino group from (MCKENZIE and DENNLER), i, 26.
β-Amino-alcohols, primary (BILLON), i, 120.
Amino-aldehydes, condensation of amino-acetals with (RÄTH), i, 437.
Amino-compounds, aromatic, action of sulphites on (BUCHERER and STICHEL), i, 1338.
Amino-ketones, aromatic, halochromism of (PFEIFFER), i, 408.
molecular compounds of (PFEIFFER, GOEBEL, and ANGERN), i, 262.
Aminosulphonic acid, use of, as a standard in volumetric analysis (HERBOTH), ii, 155.
Ammines, lattice energy of (BILTZ and GRIMM), ii, 842.
Ammonia, formation of, in the oxy-hydrogen flame (TOMINAGA), ii, 48.
synthesis of, at high pressures (MOLDENHAUER), ii, 215.
absorption of light by (LANDSBERG and PREDVODITELEV), ii, 352.
infra-red absorption spectrum of (SCHIERKOLK), ii, 180.
gaseous, rotation spectrum of (SPENCE), ii, 350.
liquid, electrolysis in, and its physical constants (CADY and TAFT), ii, 1073.
ionisation of (WALDIE), ii, 1106.
liquid, potentials in (BERGSTROM), ii, 794.
vapour, superheated, specific heat of (OSBORNE, STIMSON, SLIGH, and CRAGOE), ii, 643.
Ammonia, specific heat of aqueous solutions of (VREVSKI and KAIGORODOV), ii, 125; (VREVSKI; VREVSKI and SAVARITZKI), ii, 126.
thermal decomposition of, on varying surfaces (HINSHELWOOD and BURK), ii, 691.
liquid, molecular weight determinations in (SCHMID and BECKER), i, 1386.
solid, crystal structure of (MARK), ii, 1130.
concentration of, in mixtures of hydrogen and nitrogen over liquid ammonia (LARSON and BLACK), ii, 501.
solubility of, in water (SHERWOOD), ii, 852.
absorption of, in water and in hydrochloric acid (WHITMAN and DAVIS), ii, 106.
sorption of, by glass (BANGHAM and BURT), ii, 284.
equilibria in solutions of (VREVSKI), ii, 102; (SCHEFFER and DE WIJS), ii, 783.
scrubber for distillates of (MURRAY), ii, 236.
combustion of, in oxygen (RASCHIG), ii, 224.
explosion of carbon monoxide and oxygen with (BEESON and PARTINGTON), ii, 682.
catalytic oxidation of (KASSNER), ii, 413; (PASCAL and DECARRIÈRE; DECARRIÈRE), ii, 565; (SCHLŒSING), ii, 566.
action of, on bisimmonium bromides (v. BRAUN and ZOBEL), i, 1455.
action of, on carbohydrates (SHMOOK), i, 577.
catalysis by alumina of the reaction between ethyl alcohol and (DORRELL), ii, 1174.
action of, on ferrous salts (WEITZ and MÜLLER), ii, 317.
action of, on phosphorus chlorides (PERPÉROT), ii, 1186.
hormonal action of (PRÁWDICZ-NEMINSKI), i, 481.
in blood (PARNAS and HELLER), i, 323, 454; (PARNAS), i, 454; (PARNAS and TAUBENHAUS), i, 1484.
excretion of, after administration of acid (FISKE and SOKHEY), i, 723.
determination of, in soils (MCLEAN and ROBINSON; HARPER), i, 224.
determination of, in urine (YOVANOVITCH), i, 1114, 1204.
determination of, colorimetrically, in urine (ORR), i, 184.

Ammonia, determination of, in blood and urine (MURRAY), i, 710.
separation of aliphatic amines from (LEONE), ii, 907.
Ammonification in soils (GIBBS, BATCHELOR, and MAGNUSON), i, 1030.
Ammonium bases, quaternary, activation of nitrogen in (WEDEKIND), i, 678.
Ammonium compounds, heats of formation of (TSCHELINCEV), ii, 480.
Ammonium salts, acid properties of, in liquid ammonia (BERGSTROM), ii, 315.
solubility of, in presence of ammonia (WEITZ), ii, 1147.
compounds of, with mercury salts (RAY and BANDOPADHYAY), ii, 813.
hæmolytic action of (JACOBS), i, 1345.
determination of, with hypobromite (POHORECKA-LELESZ), ii, 76.
Ammonium borate, double decomposition of sodium sulphate and (SBORGI and BOVALINI), ii, 206; (SBORGI, BOVALINI, and MEDICI; SBORGI), ii, 207.
chloride, deposition of crystals of (MULLALY), ii, 801.
equilibrium of potassium and mercuric chlorides, water, and (OSAKA and ANDO), ii, 123.
vapour, action of, on metals (HOFMANN, HARTMANN, and NAGEL), ii, 685.
adsorption of, by soils (PAVLOV), ii, 287.
chromate, equilibria of, with ammonium sulphate and water and with ammonium chromate and water (ARAKI), ii, 786.
magnesium chromate, optical properties of mixed crystals of, with ammonium magnesium sulphate and rubidium magnesium chromate (PORTER), ii, 945.
fluoaluminate, fluoferrate, and oxyfluomolybdate, crystal structure of (PAULING), ii, 185.
halides, crystal measurements of (HAVIGHURST, MACK, and BLAKE), ii, 17.
solid solutions of alkali halides and (HAVIGHURST, MACK, and BLAKE), ii, 502.
iodide, orientation of, on mica (ROYER), ii, 270.
orientation of, on the surface of muscovite (ROYER), ii, 110.
nitrate, specific heat of aqueous solutions of (COHEN, HELDERMAN, and MOESVELD), ii, 126.
solubility and heat of solution of, at the transition point (COHEN and BREDÉE), ii, 976.
Ammonium nitrate, velocity of transformation of (SIEVERTS), ii, 558.
dehydration of (DAVIS and ABRAMS), ii, 581.
equilibrium of copper nitrate, water, and (MEIJER; SCHREINEMAKERS, BERKHOFF, and POSTHUMUS), ii, 123.
utilisation of, by plants (PRIANISCHNIKOV), i, 757.
dihydrogen phosphate, crystal structure of (HASSEL), ii, 1130.
hexachlororuthenate (AOYAMA), ii, 816.
sulphate, equilibrium of ammonium chromate, water, and (ARAKI), ii, 786.
miscibility of iron sulphate and magnesium sulphate with (ZWEIGLÓWNA), ii, 189.
magnesium sulphate, optical properties of mixed crystals of ammonium magnesium chromate and (PORTER), ii, 945.
pyrosulphite, absorption spectrum of (DIETZEL and GALANOS), ii, 1115.
Amniotic fluid, constituents of (REINWEIN and HEINLEIN), i, 721.
Amphibolites from Austria (MARCHET), ii, 997.
Ampholytes, solubility of (v. EULER and RUDBERG), ii, 853.
Amygdalin, hydrolysis of (HATANO), i, 201.
Amyl alcohol, surface tension of aqueous solutions of (EDWARDS), ii, 387.
catalytic dehydrogenation of, and its mixtures with ethyl alcohol (CONSTABLE), ii, 881.
iso-**Amyl alcohol**, mutual solubilities of aqueous mixtures of (KABLUKOV and MALISCHEVA), ii, 768.
tert.-**Amyl alcohol**, detection of, colorimetrically (EKKERT), ii, 1006.
n-**Amylacetylacetone** semicarbazone (v. AUWERS and DANIEL), i, 1180.
iso-**Amylallylbarbituric acid** (VOLWILER), i, 1174.
n-**Amylamine**, salts of (MAZOUREVITCH), i, 1241.
δ-(ε-**Amylamino**)**butylamine** dihydrochloride, ε-chloro- (v. BRAUN and ZOBEL), i, 1456.
Amylase (SJÖBERG and ERIKSSON), i, 736.
mode of action of (KUHN), i, 11, 636.
effect of solvent for, on saccharification of starch (PETIT and RICHARD), i, 1504.
complement of (SJÖBERG), i, 1504.
excretion of, in urine (AMBARD and VAUCHER), i, 609.
malt (SABALITSCHKA and SCHULTZE), i, 1358.

Amylase, malt, purification of (LÜERS and SELLNER), i, 737.
malt and pancreatic, destruction of, by heat (COOK), i, 1358.
pancreatic, adsorption of (WILLSTÄTTER, WALDSCHMIDT-LEITZ, and HESSE), i, 736.
effect of tryptophan and amino-acids on (SHERMAN, CALDWELL, and NAYLOR), i, 1007.
Amylases (PRINGSHEIM and LEIBOWITZ), i, 1043.
Amylbenzenes, 2:4-*di*hydroxy- (SHARP & DOHME, and DOHME), i, 541.
*iso***Amylbenzoyloximidocarbonic acid**, ethyl ester (OESPER and COOK), i, 523.
Amyleoniine, ε-amino-, and its benzoyl derivative (v. BRAUN and ZOBEL), i, 1456.
Amyldihydro*iso***indole**, ε-amino-, and its derivatives (v. BRAUN and ZOBEL), i, 1457.
Amylodextrin, oxidation of (SYNIEWSKI), i, 369.
Amylodextrinic acid, and its salts and hydrazide (SYNIEWSKI), i, 369.
Amylohemicellulose, nature of (LING and NANJI), i, 517.
Amylopectin, constitution of (LING and NANJI), i, 516.
action of α-diastase on (SYNIEWSKI), i, 470.
Amylophosphates, hydrolysis of, by enzymes (SAMEC), i, 1504.
Amylose, polymerised, constitution of (LING and NANJI), i, 516.
Amylpiperidine, ε-amino- (v. BRAUN and ZOBEL), i, 1456.
N-**Amylpyrrolidine**, ε-amino-, and its salts (v. BRAUN and ZOBEL), i, 1456.
*iso***Amyl-***m***-toluidine**, 4:6-*di*nitro- (GIUA and PETRONIO), i, 1397.
β-**Amyrin** from Manila elemi resin (ROLLETT and SCHMIDT), i, 945.
Anacardol, and its picrate (NAIDU), i, 1224.
Anæmia, distribution of cholesterol and unsaturated fatty acids (BODANSKY), i, 724.
lipoids of plasma in (BLOOR), i, 609.
on whole milk diet (HART, STEENBOCK, ELVEHJEM, and WADDELL), i, 1354.
pernicious, and vitamin deficiency (DHAR), i, 1221.
Anæsthesia, acidosis in (KOEHLER), i, 195.
ethylene (OBERHELMAN and DYNIEWICZ; LEAKE), i, 862.
local, with secondary and tertiary alcohols (QUIGLEY and HIRSCHFELDER), i, 195.
Anæsthetics, osmosis, of, in gels (YUMIKURA), i, 735.
local (WEIL), i, 157.
constitution and physiological action of (GILMAN and PICKENS), i, 333.
Analysis, methods of (CONGDON, CRABTREE, COLES, SMITH, and VEHALGO), ii, 65; (CONGDON and VANDERHOOK), ii, 601; (CONGDON, GUSS, and WINTER), ii, 1002.
errors in (HAHN and SCHEIDERER), ii, 69; (HAHN and JAEGER), ii, 1199.
specifications for reagents used in (COLLINS, FAIR, ROSIN, SPENCER, and WICHERS), ii, 899.
preparation of standard solutions for (PREGL), ii, 998.
combustion, of gases (ŠVÉDA), ii, 154, 432.
of organic compounds (ŠVÉDA and PROČKE), ii, 719.
electrolytic, by means of graded potentials (LASSIEUR), ii, 711.
electrometric, with electrodes of platinum or its alloys (VAN NAME and FENWICK), ii, 594.
with three-electrode valves (TREADWELL and PAOLONI), ii, 595.
electro-volumetric, theory of (EASTMAN), ii, 594.
differential (COX), ii, 999.
elementary organic (VORTMANN), ii, 827.
determination of carbon and hydrogen in (LINDNER), ii, 901.
inorganic qualitative, spot tests on filter-paper in (FEIGL), ii, 509.
of metals in Groups I to III (TANANAEV), ii, 324.
of metals of Group III (JÄRVINEN), ii, 602.
separation of phosphoric acid in (KESCHAN), ii, 328.
iodometric, formation of cyanogen iodide in (LANG), ii, 597, 713.
microchemical qualitative (FEIGL), ii, 435.
quantitative, apparatus for (POLLAK), ii, 431.
micro-combustion, apparatus for (FUNK and KON), ii, 998.
organic qualitative, use of sodium hyposulphite in (CLARK), ii, 332.
quantitative, by means of Röntgen ray spectra (GÜNTHER and WILCKE), ii, 237; (COSTER and NISHINA), ii, 324; (DELAUNEY), ii, 822.
of mixtures of two salts (COMELLA), ii, 714.
in biochemistry, use of electrical conductivity in (DEMJANOVSKI), i, 1113.

Analysis, toxicological, putrefaction products in (VAN ITALLIE and STEENHAUER), i, 719.
volumetric, use of amalgams in (SOMEYA), ii, 904, 1201.
use of bromine in (MANCHOT and OBERHAUSER), ii, 161.
logarithm tables for (KRAUS), ii, 323.
Anatoxins (RAMON), i, 339.
Andalusite, crystal structure of (NORTON), ii, 1127.
formation of mullite from (GREIG), ii, 987.
Andropogon, oil from new species of (SIMONSEN), i, 1164.
Androsin, synthesis of (MAUTHNER), i, 950.
Anethole, electrochemical oxidation of (FICHTER and CHRISTEN), i, 813.
nitrosochloride, reduction of, by stannous chloride (SHOESMITH and SLATER), i, 908.
Anhydride, $C_6H_8O_2N_2$, and its derivatives, from alanylserine (BERGMANN, MIEKELEY, and KANN), i, 1134.
Anhydrite, hydration of (FARNSWORTH), ii, 980.
Anhydro-3-acetamido-2-methylcinchoninic acid (GULLAND and ROBINSON), i, 1187.
Anhydro-2′-aminodiphenylamine-6-carboxylic acid, derivatives of (LINNELL and PERKIN), i, 63.
Anhydrobisdi-indandionylmethane (RADULESCU and GEORGESCU), i, 1288.
Anhydrobromochelidonine (GADAMER and WINTERFELD), i, 285.
Anhydrocotarnine-methylamine, and its salts (HAWORTH and PERKIN), i, 969.
Anhydrocotarnine-6-nitro-4:5-dimethoxyphthalide (RÂY and ROBINSON), i, 1153.
Anhydrocyanilic acid (WIELAND), i, 1049.
Anhydro-7-demethylomethyl-ψ-corydaline, and its salts (HAWORTH and PERKIN), i, 972.
Anhydro-7-demethylomethylpapaverinol, and its *per*chlorate (HAWORTH and PERKIN), i, 971.
Anhydrodidehydrobromochelidonine (GADAMER and WINTERFELD), i, 285.
Anhydrodidehydrochelidonine (GADAMER and WINTERFELD), i, 285.
Anhydro-α-diphenylacetyl-α(or β)-carboxy-β(or α)-carbethoxyhydrazine-β-diphenylacetic acid (INGOLD and WEAVER), i, 581.
Anhydroepicatechin tetramethyl ether (FREUDENBERG, FIKENTSCHER, and HARDER), i, 419.
Anhydrohydroxybenzoic acids, and their salts and derivatives (ANSCHÜTZ, STOLTENHOFF, and VOELLER), i, 1273.
αδ-Anhydro*tetra*hydroxyadipic acids, stereoisomerism of (LEVENE and SIMMS), i, 782.
Anhydro-7:8-methylenedioxy-11-phenylindenoquinoline methohydroxide, and its salts (ARMIT and ROBINSON), i, 1171.
10:11-Anhydro-7:8-methylenedioxyquinindoline 10-methohydroxide (ARMIT and ROBINSON), i, 1172.
Anhydronium bases (ARMIT and ROBINSON), i, 1170.
Anils, reaction of ethyl malonate with (WAYNE and COHEN), i, 550.
Anilidocitroamic acid (NAU, BROWN, and BAILEY), i, 1379.
Aniline and its aqueous solutions, physical properties of (APPLEBEY and DAVIES), ii, 948.
and its alkyl derivatives, infra-red absorption spectra of (BELL), ii, 928.
equilibrium of acetic acid, water, and (ANGELESCU and MOTZOC), ii, 854.
reaction of calcium hypochlorite with (RASCHIG), i, 243.
action of ethylene oxide on (GABEL), i, 535.
effect of ammonia on the hypochlorite reaction for (WEST), ii, 163.
*tri*chloroacetates (DOUGHTY), i, 805.
hydroferricyanide (CUMMING), i, 122.
hydrogen malate, malonate, oxalate, succinate, and tartrate (RAMBECH), i, 385.
*p-di*sulphoxide, and its derivatives (BERE and SMILES), i, 21.
derivatives, partial bromination of (FRANCIS), i, 1399.
detection of, colorimetrically (MURRAY), ii, 163.
determination of, in aqueous solutions (CARSON), ii, 447.
Aniline, bromo- and chloro-, *m*-nitrobenzenesulphonamides (MARVEL, KINGSBURY, and SMITH), i, 245.
o-chloro-, compounds of mercuric acetate with (VECCHIOTTI and MICHETTI), i, 1058.
4-chloro-3:5-*di*nitro-, and its acetyl derivative (LINDEMANN and WESSEL), i, 1099.
o-nitro-, action of, on nitrosobenzene (CHARRIER and BERETTA), i, 21.
*oo′-di*thio-, action of lead monoxide on (HODGSON), i, 596.
Anilines, nitro-, mutual solubility of (KOHMAN), ii, 1052.
vapour pressure of (BERLINER and MAY), ii, 1045.
action of alkali sulphate in kjeldahlisation of (MARGOSCHES and SCHEINOST), ii, 1200.

Aniline-black, vapour pressure and adsorption power of (KASAKEVITSCH), ii, 287; (STADNIKOV), ii, 771.
Aniline-*p*-sulphonic acid (*sulphanilic acid*), solubility of, in water (YAJNIK, JAIN, and NATH), ii, 1147.
4-Anilinoacetanilide, 3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.
2-Anilino-3-acetanilido-1:4-naphthaquinone (FRIES and BILLIG), i, 939.
ω-Anilinoacetophenone, and *p*-chloro-, *o*-tolylhydrazones (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
Anilino-*p*-aminoanilino-1:4-naphthaquinone (FRIES and BILLIG), i, 940.
2-Anilino-3-*p*-anisidino-1:4-naphthaquinone (FRIES and BILLIG), i, 940.
β-Anilinoanisylmalonic acid, ethyl ester (WAYNE and COHEN), i, 551.
9-Anilinoanthrone, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 819.
4-Anilinobenzazide, 3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.
4-Anilinobenzoic acid, 5-nitro-3-amino- (LINDEMANN and WESSEL), i, 1099.
4-Anilinobenzoyl chloride, 3:5-dinitro- (LINDEMANN and WESSEL), i, 1099.
5-Anilino-4-benzoyl-2-phenyl-1:3:4-thiodiazole (FROMM and TRUKA), i, 704.
β-Anilinobenzylmalonic acid, and *p*-bromo-, *p*-chloro-, and *m*-nitro-, esters of (WAYNE and COHEN), i, 550.
1-Anilinobenzthiazole, and its derivatives (HUNTER), i, 1335.
δ-Anilino-Δ$^{\alpha\gamma}$-butadienealdehydeanil, γ-iodo- (BAUMGARTEN), i, 1381.
β-Anilinobutaldehyde diethylacetal, and its picrate (MASON), i, 834.
Anilino-*m*-chlorophenylacetonitrile (HELLER and SPIELMEYER), i, 814.
1-Aniline-1-cyanocyclopentane (PLANT and FACER), i, 1271.
2-Anilino-4:6-di-*p*-hydroxynaphthyl-1:3:5-triazine (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 441.
2-Anilino-3:3′-diketo-6:7:6′:7′-dibenz-2:2′-dicoumaran (FRIES and PUSCH), i, 569.
2-Anilino-3:3′-diketo-4:6:4′:6′-tetramethyl-2:2′-dicoumaran (FRIES and BARTENS), i, 568.
4-Aniline-2:6-dimethylpyridine, 4-*o*-nitro- (SEKA), i, 587.
8-Anilino-3:7-diphenylphenosafranine, 2-amino- (KEHRMANN and STANOYÉVITCH), i, 1335.
Anilinodiphenylquinoxaline, amino- (KEHRMANN and STANOYÉVITCH), i, 1332.
2-Anilino-5-ethoxy-4-methyl-4:5-dihydrothiazole, and its picrate (BURTLES, PYMAN, and ROYLANCE), i, 697.
β-Anilinoethyl alcohol, *p*-bromo-. See Ethyl *p*-bromoaniline, *N*-hydroxy-.
4-α-Anilinoethylideneaminobenzoic acid, ethyl ester (WEIL), i, 157.
3-Anilinohydroxymethylindole hydrochloride, and its acetyl derivative (MAJIMA and KOTAKE), i, 1450.
2-Anilino-3-hydroxy-1:4-naphthaquinone (FRIES and BILLIG), i, 939.
3-Anilino-7-hydroxy*apo*safranone, 2-amino-, and its hydrochloride (KEHRMANN and SCHEDLER), i, 442.
3-Anilino-5-keto*iso*oxazole, *p*-chloro- and *p*-iodo- (WORRALL), i, 308.
4-Anilino-1-keto-3-oxindolidene-3:4-dihydronaphthalene, and 4-*p*-chloro- (FRIEDLÄNDER), i, 958.
3-Anilino-5-ketopyrazole, *m*-bromo-, *p*-chloro-, and *p*-iodo- (WORRALL), i, 308.
5-Anilino-6-methoxy-*m*-cresol, 2:4-*di*nitro- (KOHN and MARBERGER), i, 1265.
2-Anilino-6-methoxy-2-thiol-3-ketocoumaran, and 2-*p*-amino- (FRIES and SAFTIEN), i, 571.
4-Anilino-1-methyl-2-methylene-1:2-dihydroquinoline picrate (FISCHER, DIEPOLDER, and WÖLFEL), i, 439.
3-Anilino-2-methyl-4-quinazolone, 3-*p*-acetyl derivative (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1323.
4-Anilino-2-methylquinoline, and its derivatives (FISCHER, DIEPOLDER, and WÖLFEL), i, 438.
1-Anilinonaphthalene-8-sulphonic acid, amino and nitro derivatives (FINZI), i, 654.
Anilino-1:4-naphthaquinones, amino-, and aminonitroso-, and their acetyl derivatives (FRIES and BILLIG), i, 939.
4-Anilino-α-naphthol, and 4-*p*-chloro-, and their *O*-methyl ethers (FRIEDLÄNDER), i, 957.
1-Anilino-β-naphthol-4-sulphonic acid (LANTZ and WAHL), i, 910.
Anilino-*m*-nitrophenylacetonitriles, isomeric, and their derivatives (HELLER and SPIELMEYER), i, 814.
Anilino-*o*′-nitrotoluene-*p*′-sulpho-*p*-phenetidide, 2-nitro-, and 3:5-*di*nitro- (REVERDIN), i, 1409.
Anilino-oximinopinacolin (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
Anilino-*P*-oxodihydrobenzodiazphospholium (AUTENRIETH and BÖLLI), i, 1469.
Anilino-*P*-oxotetrahydrodiazphospholium (AUTENRIETH and BÖLLI), i, 1469.
1-Anilino*cyclo*pentane-1-carboxylic acid, and its derivatives (PLANT and FACER), i, 1271.

11-Anilinophenanthraphenazine, 10-amino- (KEHRMANN and STANOYÉVITCH), i, 1332.

Anilinophenylacetonitrile (CHRISTIAEN), i, 28.
action of ethyl ethylidenemalonate with (HIGGINBOTHAM, LAPWORTH, and SIMPSON), i, 35.

2-*p*-Anilinophenylbenztriazole, and *p'*-amino- (ELBS), i, 164.

3-Anilino-5-phenylfluorindine, 2-amino-, and its nitrate (KEHRMANN and SCHEDLER), i, 443.

2-Anilino-5-phenyl-1:3:4-thiodiazine, and its hydrobromide and acetyl derivative (BOSE), i, 1465.

δ-Anilinosemicarbazide, and its derivatives (SUTHERLAND and WILSON), i, 42.

2-Anilino-2-thiol-3-ketocoumaran (FRIES and SAFTIEN), i, 571.

β-Anilino-*p*-tolylmalonic acid, ethyl ester (WAYNE and COHEN), i, 551.

Anilino-3:4:5-trimethoxyphenylcarbinol, and its hydrochloride (SONN and MEYER), i, 932.

Anilodimethylterephthalonic acid, aniline salt (PERKIN and TAPLEY), i, 42.

Animals, fasting and poisoned with phosphorus, lipin and fat metabolism of (SACCHETTO), i, 1357.
marine, shell-growth of (ORTON), i, 1002.
warm-blooded, synthesis of carbohydrates in muscle of (JANSSON and JOST), i, 1354.

Animal tissues, staining of (GICKLHORN and KELLER), i, 468.
argon in (PICTET, SCHERRER, and HELFER), i, 1202.
fixation of calcium by (BREHME and GYÖRGY), i, 717; (BUDDE), i, 718.
cobalt in (BERTRAND and MÂCHEBŒUF), i, 996.
occurrence of metals in (MCHARGUE), i, 1023.
plant nucleotides in (JONES and PERKINS), i, 182.
determination of arsenic in (LAWSON and SCOTT), i, 996.
determination of chlorides in (VLĂDESCU), i, 1113.
determination of lead in (BERNHARDT), ii, 1003; (NAKASEKO and NAKANO), ii, 1205.
determination of nucleic acid phosphorus in (JAVILLIER and ALLAIRE), i, 996.
determination of water in (THOENES), i, 718.

Anisaldehyde, preparation of (BRINER v. TSCHARNER, and PAILLARD), i, 1069.
compound of aminomalononitrile with (GRISCHKEVITSCH-TROCHIMOVSKI and SEMENCOV), i, 1069.

Anisaldehydediphenylene-4:4'-dihydrazone (CHATTAWAY, IRELAND, and WALKER), i, 1195.

Anisaldoxime, *N*-aryl ethers of (BAMBERGER), i, 142.

***o*-Anisidine** hydroferricyanide (CUMMING), i, 122.

***o*-Anisidine,** 3:5-*di*bromo-, diazotisation and nitration of (ELION and JANSSEN), i, 389.

***m*-Anisidine,** 5-bromo-, and its benzoyl derivative (GRIFFITH and HOPE), i, 827.
4-chloro-6-nitro-, preparation of (WHISTON), i, 136.

ω-*o*- and -*p*-Anisidinoacetophenone-*o*-tolylhydrazones (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.

β-*o*-and-*p*-Anisidinobenzylmalonic acids, ethyl esters (WAYNE and COHEN), i, 551.

3-Anisidino-5-keto*iso*oxazoles (WORRALL), i, 308.

3-Anisidino-5-ketopyrazoles (WORRALL), i, 308.

2-*p*-Anisidino-1:4-naphthaquinone, 3 chloro-2-*N*-nitroso- (FRIES and BILLIG), i, 939.

***p*-Anisidino-3:4:5-trimethoxyphenylcarbinol,** and its hydrochloride (SONN and MEYER), i, 932.

Anisilic acid, action of, on thiophenol (BISTRZYCKI and RISI), i, 1426.

Anisole (*phenyl methyl ether*), *tetra-* and *penta*-bromo- (KOHN and FINK), i, 134.
*tri*bromohydroxy- and *di*bromonitrohydroxy- (KOHN and GRÜN), i, 1265.
bromonitro derivatives (KOHN and STRASSMANN), i, 1264.
2:6-*di*bromo-4-nitro-3-hydroxy-, and its salts (KOHN and LÖFF), i, 1264.
2:4:5-*tri*chloro- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 1145.
2:3:5:6-*tetra*chloro-*p*-nitro- (BERCKMANS and HOLLEMAN), i, 1136.
*tri*nitro-, and *tri*nitrophenetole, alcoholysis of (BRADY and HORTON), i, 1409.
3:4:5-*tri*nitro-2-hydroxy-, salts of (KOHN and LÖFF), i, 1265.

***p*-Anisolesulphonylacetone,** and its derivatives (TRÖGER and BROHM), i, 1453.

3-*o*- and -*p*-Anisolesulphonyl-2-methylquinolines, and their salts and derivatives (TRÖGER and BROHM), i, 1453.
Anisotropy of molecules (RAMANATHAN), ii, 478.
streaming (FREUNDLICH, STAPELFELDT, and ZOCHER), ii, 199.
β-Anisoxypropionic acid (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.
p-Anisyl groups, migration of phenyl and (TIFFENEAU and ORÉKHOV), i, 679.
p-Anisyl aminostyryl ketones, and their salts (PFEIFFER), i, 410.
β-Anisylbutan-γ-one, and its semicarbazone (TIFFENEAU, ORÉKHOV, and LÉVY), i, 544.
p-Anisylcamphene (LEDUC), i, 821.
p-Anisyl *p*-dimethylaminostyryl ketone, and its salts (PFEIFFER), i, 410.
4-*p*-Anisyl-2:6-dimethyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester, ψ-cyanide (MUMM), i, 965.
4-*p*-Anisyl-1:6-dimethylmethylenedihydropyridine, and its derivatives (MUMM), i, 967.
Anisylideneacetohexoic acid (RYAN and SHANNON), i, 558.
Anisylidene-*p*-aminobenzoic acid (WAYNE and COHEN), i, 551.
Anisylidene-*p*-aminocinnamic acid, ethyl ester (FRIEDEL), i, 664.
p-Anisylidene-*m*-aminocinnamylideneacetone, and its salts (PFEIFFER, PRAHL, FITZ, and STOLL), i, 681.
p-Anisylidene-*p*-anisidine (COGHILL), i, 583.
Anisylideneazine hydrochloride, compounds of stannic chloride and (SHOESMITH and SLATER), i, 908.
p-Anisylideneazophenylpyrroles (PLANCHER and GHIGI), i, 598.
Anisylidene-2-methylquinoline, salts of (PFEIFFER, PRAHL, FITZ, and STOLL), i, 681.
Anisylidene-4-methylthiosemicarbazone (BOSE), i, 1466.
p-Anisylidene-*m*-nitrocinnamylideneacetone (PFEIFFER, PRAHL, FITZ, and STOLL), i, 681.
Anisylidene-4-phenylthiosemicarbazide (BOSE), i, 1465.
Anisyl α-methoxy-β-hydroxyvinyl ketone, and its copper salt (MALKIN and ROBINSON), i, 827.
p-Anisyl *p*-methoxystyryl ketone, derivatives of (STRAUS and HEYN), i, 1430.
4-Anisyl-1-methylhydantoin (HAHN and RENFREW), i, 581.
4-Anisyl-1-methylhydantoin-3-acetic acid, ethyl ester (HAHN and RENFREW), i, 581.
α-Anisyl-α-methylpropaldehyde, and its semicarbazone (TIFFENEAU, ORÉKHOV, and LÉVY), i, 544.
α-Anisyl-β-methylpropylene oxide (TIFFENEAU, ORÉKHOV, and LÉVY), i, 544.
2-Anisyl-4-methylpyrimidine-5-carboxylic acid, and its ethyl ester (MITTER and PALIT), i, 1320.
Anisyl nitrocinnamylidenemethyl ketones (PFEIFFER), i, 409.
β-Anisylpropionic acid, α-cyano- (BAKER and LAPWORTH), i, 30.
Anisyl *iso*propyl ketone, and its semicarbazone (TIFFENEAU, ORÉKHOV, and LÉVY), i, 544.
2-*p*-Anisylquinoline, and its salts (PFEIFFER, PRAHL, FITZ, and STOLL), i, 681.
3-Anisylrhodanylidene-Δ$^{5:3'}$-oxindoles (HANN), i, 987.
p-Anisylsuccinic acid (CHRZASZCZEWSKA), i, 956.
and its anhydride (BAKER and LAPWORTH), i, 671.
3-*p*-Anisylthiophen (CHRZASZCZEWSKA), i, 956.
p-Anisyl-*p*-tolylsulphone (GILMAN, BEABER, and MYERS), i, 1057.
4-Anisyl-1:2:6-trimethyl-1:2:3:6-tetrahydropyridine-3:5-dicarboxylic acid, ethyl ester (MUMM), i, 966.
Anodes, economic (LASSIEUR), ii, 154.
apparatus for processes at (STSCHERBAKOV), ii, 979.
carbon, disintegration of, in nitric acid (CREIGHTON and OGDEN), ii, 1068.
Anode effect in electrolysis (TAYLOR), ii, 548.
Anorthoclase from Mt. Kenya (MOUNTAIN), ii, 819.
Anthocyanidins, synthesis of (WILLSTÄTTER and SCHMIDT), i, 54.
Anthocyanins, reaction for (NIKIFOROVSKI), i, 1224.
Anthorine, and its sulphate (GORIS and MÉTIN), i, 761, 762.
ψ-Anthorine, and its sulphate (GORIS and MÉTIN), i, 761, 762.
Anthracene, boiling point of (FINCK and WILHELM), ii, 759.
hydrogenation of (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 127.
action of aluminium chloride on (SCHAARSCHMIDT, MAYER-BUGSTRÖM, and SEVON), i, 242.
derivatives, action of nitrogen dioxide on (BARNETT), i, 1258.

Anthracene, determination of, by the Höchst test (RHODES, NICHOLS, and MORSE), ii, 1005.
determination of, in anthraquinone (LEWIS), ii, 74.
Anthracene, 9:10-*di*bromo-, action of sodium hydrosulphide on (COOKE, HEILBRON, and WALKER), i, 1410.
chloro-derivatives, *di*bromides, and chloronitro-derivatives (BARNETT and MATTHEWS), i, 18.
1:5:9-*tri*chloro-, *di*chloride, reactions of (BARNETT, COOK, and MATTHEWS), i, 1398.
1:5:9:10-*tetra*chloro-, and 1:5:9-*tri*chloro-9-bromo- (BARNETT, COOK, and MATTHEWS), i, 1398.
1-chloro-9(or 10)-nitro-, and 1:5-*di*chloro-9:10-*di*nitro- (BARNETT), i, 1259.
*meso*thio-, derivatives of (COOKE, HEILBRON, and WALKER), i, 1410.
2:3-Anthraceneoxythionaphthen, and its acetyl derivative (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1312.
Anthracenesulphonic acids, metallic salts, and their solubilities (EPHRAIM and PFISTER), i, 897.
Anthracene-2-thioglycol-3-carboxylic acid (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1150.
2:3:9:10-Anthradiquinone. See Hystazarindiquinone.
Anthragallol 2-methyl ether, and its diacetyl derivative (KUBOTA and PERKIN), i, 1159.
Anthranil, constitution of (LEUCHS), i, 1335.
cyanoformyl derivative (KARRER, DIECHMANN, and HAEBLER), i, 243.
Anthranilic acid, 4- and 5-hydroxy-, 2-acetyl and -benzoyl derivatives of (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 400.
Anthranilorhodamine (SEN and SIRCAR), i, 554.
Anthranol, 1:8-*di*hydroxy- (*cignolin*), detection of, colorimetrically (TORTI), ii, 905.
Anthranyl acetate and ethers, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 818.
alkyl and aryl ethers, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 901.
Anthranylaniline, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
Anthranyl-*m*-nitroaniline, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
Anthranylpyridinium bromide, 1:5-*di*chloro- (BARNETT and MATTHEWS), i, 18.
1:5-*di*chloro-9-hydroxy-, and its 9-acetyl derivative (BARNETT, COOK, and MATTHEWS), i, 819.
chloride, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
salts, 1:5:9-*tri*chloro- (BARNETT, COOK, and MATTHEWS), i, 1399.
Anthranyltoluidines, *di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
Anthraquinone, decomposition of, by heat (LEWIS and SHAFFER), i, 45.
influence of mercury on the sulphonation of (COPPENS), i, 1432.
nitrogen derivatives of (BADISCHE ANILIN- & SODA-FABRIK), i, 414.
azides (BRASS and ZIEGLER), i, 685.
mercurichlorides (COPPENS), i, 1433.
Anthraquinone, 2-amino-, preparation of (PHILLIPS), i, 1076.
*tri*amino-, and its benzoyl derivative and *di*nitro-1-amino- (BECKETT, THOMAS, and SCOTTISH DYES), i, 685.
1:4-*di*bromo-2-hydroxy- (DE DIESBACH and STREBEL), i, 1435.
1-nitro-, effect of administration of (JOHN), i, 465.
Anthraquinones, aminohydroxy-, and their derivatives (BRASS and ZIEGLER), i, 686.
bromo-, reduction of (BARNETT and COOK), i, 940.
chloro*di*nitroamino-, benzoyl derivatives (BARNETT), i, 1288.
hydroxy-, reduction products of (PERKIN and YODA), i, 1160.
Anthraquinone colouring matters (BRITISH DYESTUFFS CORPORATION, LTD., BADDILEY and TATUM), i, 145, 414.
Anthraquinone-2-aldehyde, 5:6:7:8-*tetra*chloro-, 5:6:7:8-*tetra*chloro-1-nitro-, and 1-nitro-, and their derivatives (RUGGLI and BRUNNER), i, 561.
Anthraquinone-2-aldehydeindogenide, and 5-nitro- (MACBETH and CRAIK), i, 1315.
Anthraquinoneanil (SANDER), i, 982.
Anthraquinone-2-carboxylic acid, 3-bromo- (DE DIESBACH and STREBEL), i, 1435.
Anthraquinone-3-carboxylic acid, 2-bromo- (HELLER and MÜLLER-BARDORFF), i, 546.
Anthraquinone 2-diazonium sulphates, nitro- (TANAKA), i, 1434.
α- and **β-Anthraquinonehydrazines**, acyl derivatives of (BATTEGAY and AMUAT), i, 169.

2:3-Anthraquinoneoxythionaphthen, and its acetyl derivative (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1312.
Anthraquinonequinonediazides (TANAKA), i, 1106, 1434.
Anthraquinonesulphonic acids, methyl esters of (COPPENS), i, 1432.
Anthraquinonyl-3-hydrazine, 2-hydroxy- (TANAKA), i, 1434.
Anthraquinyl diacetate, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 819.
Anthrax in the intestines (SANARELLI), i, 477.
Anthrone, 2:3:9-*tri*bromo-9-nitro- (BARNETT), i, 1259.
3-chloro- (MAYER and FISCHBACH), i, 1076.
1:5-*di*chloro-9-bromo- and -9-nitro- (BARNETT, COOK, and MATTHEWS), i, 818.
1:5-*di*chloro-9-hydroxy- (BARNETT and MATTHEWS), i, 18.
Anthrone series (MAYER and FISCHBACH), i, 1076.
Anthronitrile, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1141.
Anthronyl acetate, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 818.
ethyl ether, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1398.
Anthropodeoxycholic acid, constitution of (WIELAND and JACOBI), i, 1488.
and its diformyl derivative (WIELAND and REVEREY), i, 181.
Anthroxanic acid, constitution of, and its salts (LEUCHS), i, 1335.
Antigens, composition of (MUELLER, WAYMAN, and ZINSSER), i, 1016.
Wassermann, colloidal properties of (KERMACK and MACCALLUM), i, 197.
Antiglyoxalase (FOSTER), i, 1495.
Antimonoxalic acid, potassium salt (HOLMES and TURNER), i, 1130.
Antimony, atomic weight of (WEATHERILL), ii, 23.
absorption spectrum of the vapour of (NARAYAN and RAO), ii, 927.
electro-deposition of (BAYERLE), ii, 675.
electro-analytical precipitation of (SCHLEICHER and TOUSSAINT), ii, 1004.
Antimony alloys with bismuth (OTANI), ii, 533.
with copper (KURNAKOV and BELOGLAZOV), ii, 787.
with lead and zinc (TAMMANN and DAHL), ii, 535.
Antimony *tri*chloride, distillation of (RÖHRE), ii, 157.
complex salts of (MIYAKE), ii, 815.
halides, reactions of, with benzanilide and with benzylaniline (VANSTONE), i, 662.
hydride (*stibine*), preparation of, electrolytically (WEEKS), ii, 415, 882.
solid (DRUCE; WEEKS and DRUCE), ii, 700.
Antimonates, alkali (JANDER and BRANDT), ii, 988.
Antimony selenide (MOSER and ATYNSKI), ii, 584.
*tri*sulphide, velocity of coagulation of (JABŁCZYŃSKI and PRZEZDZIECKA-JEDRZEJOWSKA), ii, 665, 1060.
sols, adsorption of anions in coagulation of (GHOSH and DHAR), ii, 336.
telluride (BRUKL), ii, 895.
Antimony organic compounds (MATSUMIYA), i, 1472.
monoaryl and diaryl (CHEMISCHE FABRIK VON HEYDEN), i, 86, 87.
secondary and tertiary aromatic (CHEMISCHE FABRIK VON HEYDEN), i, 86.
Antimonyl tartrates of amines (CHRISTIANSEN and NORTON), i, 654.
Antimony determination and separation:—
determination of (AUGER), ii, 604.
determination of, electrometrically (FLEYSHER), ii, 243.
determination of, in the pentasulphide and in stibnite (RUPP, SIEBLER, and BRACHMANN), ii, 244.
separation of arsenic and (HAHN and WOLF), ii, 68.
separation of copper, lead, tin, and (LASSIEUR), ii, 328.
separation of lead and (LASSIEUR), ii, 159.
separation of tin and (SACCARDI), ii, 159.
Anti-oxygens (MOUREU, DUFRAISSE, and BADOCHE), i, 117, 362, 363; (MOUREU and DUFRAISSE), i, 362; (MOUREU, DUFRAISSE, and LOTTE), ii, 561.
Antipyrine (1-*phenyl*-2:3-*dimethyl*-5-*pyrazolone*) methiodide, compound of iodoform with, and its *di*iodide (STEINKOPF and BESSARITSCH), i, 495.
Antipyrine, 4-amino-, glycyl derivative, and its picronolate (KARRER, DIECHMANN, and HAEBLER), i, 243.

Antirachitic properties of irradiated compounds (HESS, WEINSTOCK, and HELMAN; HESS and WEINSTOCK), i, 750.
substances, production of ultra-violet light by (DRUMMOND and WEBSTER), ii, 630.
Apigeninidin *per*chlorate (PRATT and ROBINSON), i, 825.
Aporphine, synthesis of, and its salts and derivatives (GADAMER, OBERLIN, and SCHOELER), i, 576.
Apples, constituents of the skins and leaves of (RIVIÈRE and PICHARD), i, 345.
nitrogen and carbohydrates in the flowers and fruits of (HOWLETT), i, 1121.
pectin content of the leaves of (TUTIN), i, 1028.
pectose and pectin in (CARRÉ), i, 758.
quercetin in peel of (SANDS), i, 216.
sorbitol from (TUTIN), i, 1028.
physiology of (HAYNES; ARCHBOLD), i, 345.
Apple trees, effect of pruning on (HOOKER), i, 1367.
decay of xylem of, from *Polystictus versicolor* (SMITH), i, 1226.
rôle of carbohydrates and nitrogen in the growth of (HARVEY), i, 1367.
Aquopentamminecobaltic dichromate. See under Cobalt.
Aquopentammineferrous sulphate. See under Iron.
Arabinose, constitution of (HIRST and ROBERTSON), i, 364.
formation of starch from, by plants (POLONOVSKI and MORVILLEZ), i, 1222.
halogenacetyl derivatives, rotation of (HUDSON and PHELPS), i, 8.
γ-Arabinose, derivatives of (BAKER and HAWORTH), i, 365.
Arabinosemonodiphenylmethanedimethyldihydrazone (v. BRAUN and BAYER), i, 1383.
Arabonic acid, ethyl ester (SIMON and HASENFRATZ), i, 511.
l-Arabonolactone, derivatives of (SIMON and HASENFRATZ), i, 511.
Arachidic acid, synthesis of (ADAM and DYER), i, 354.
Arachidonic acid as a metabolic product of fatty acids (WESSON), i, 1353.
Arachis oil, lignoceric acid from (HEIDUSCHKA and PYRIKI), i, 229.
Aragonite, structure of (WYCKOFF), ii, 484; (TOMKEIEV), ii, 1035.
thermal properties of (BÄCKSTRÖM), ii, 1162.
Araucaria bidwilli, constituents of seeds of (MORRISON), i, 619.
Arbutia pustulosia, extractives of (HOLTZ and THIELMANN), i, 720.
Arbutin hydrolysis of, by emulsin (JOSEPHSON), i, 1359.
Argemone oil (IYER, SUDBOROUGH, and AYYAR), i, 1128.
Arginase (EDLBACHER and BONEM), i, 863; (EDLBACHER and RÖTHLER), i, 1505.
bacterial (KOSSEL and CURTIUS), i, 1505.
distribution of, in fishes and other animals (HUNTER and DAUPHINEE), i, 104.
detection and determination of (HUNTER and DAUPHINEE), i, 104.
determination of (HUNTER and DAUPHINEE), ii, 247.
Arginine in *Lupinus luteus*, enzymic decomposition of (WALTER), i, 1358.
in the animal organism (STEWART), i, 730.
relationship of agmatine to (MÜLLER), i, 1496.
relation of, to creatine and purine metabolism (ROSE and COOK), i, 1003.
Argon, spectrum of (LOWE and ROSE), ii, 452.
ultra-violet spectrum of (LYMAN and SAUNDERS), ii, 911.
spectral frequencies of (HOLWECK), ii, 336.
critical potential of (HOLWECK), ii, 729.
ionisation of (BARTON), ii, 459.
mobility of ions of, in air (ERIKSON), ii, 1107.
positive ions in (BARTON), ii, 6.
isotherms of (HOLBORN and OTTO), ii, 851.
in gases from fermentation of sugars (PICTET, SCHERRER, and HELFER), i, 865.
in living cells (PICTET, SCHERRER, and HELFER), i, 1202.
Aromatic compounds, constitution of, and their chemical and physical properties (PASTAK), i, 531; ii, 759.
emission band spectra of (MARSH), ii, 470, 675.
ereoisomerism of (KUHN and JACOB), i, 1260, 1404.
substitution in the nucleus in (BARNETT and MATTHEWS; PRINS), i, 18; (BARNETT and COOK), i, 123; (BARNETT, COOK, and MATTHEWS), i, 648, 1140, 1398.

Aromatic compounds, directive influence of nitrogen and oxygen atoms in substitution in (HOLMES and INGOLD), i, 1142.
catalytic hydrogenation of, with nickel and hydrogen (FELDMANN), i, 1263.
nuclear hydrogenation of, with colloidal platinum (SKITA), i, 140.
action of aromatic alcohols on, in presence of aluminium chloride (HUSTON), i, 249.
reaction of bromonitromethane on, in presence of aluminium chloride (SHERRILL), i, 237.
mercuration of (COFFEY), i, 844.
polynuclear heterocyclic (ARMIT and ROBINSON), i, 1170.
in plants (RETI), i, 418.
Arsenic in Cornwall (RUSSELL and HARWOOD), ii, 429.
electro-deposition of (BAYERLE), ii, 675.
colloidal, preparation of (DEDE and WALTHER), ii, 197.
in blood, milk, and cerebrospinal fluid after injection of salvarsan and its derivatives (FORDYCE, ROSEN, and MYERS), i, 189.
Arsenic *tri*chloride, distillation of (RÖHRE), ii, 157.
hydride, solid (DRUCE), ii, 700.
*di*iodide, preparation of (KARANTASSIS), ii, 994.
*tri*oxide (*arsenious oxide*), action of, on alkali carbonates (VANZETTI), ii, 421.
reaction of chlorine with (CAMBI and VOLTOLIN), ii, 148.
action of Grignard reagents on (MATSUMIYA and NAKAL), i, 1339.
reduction of permanganic acid by (TRAVERS), ii, 585.
Arsenious acid, adsorption of, by hydrated aluminium oxide (YOE), ii, 107.
reduction of permanganates by (GELOSO), ii, 661.
Arsenites, catalytic oxidation of (REINDERS and VLÈS), ii, 303.
Ortho-arsenites (VANZETTI), ii, 421.
Arsenic acid, adsorption of, by oxides (KOZAKEVITSCH), ii, 855.
Arsenic selenides (MOSER and ATYNSKI), ii, 584.
Arsenic *tri*sulphide, equilibrium of thallous sulphide and (CANNERI and FERNANDES), ii, 887.
colloidal (BOUTARIC and VUILLAUME), ii, 112.
Arsenic *tri*sulphide sols, stability of, and velocity of their falling particles (DUMANSKI), ii, 290.
adsorption of anions in coagulation of (GHOSH and DHAR), ii, 386.
cataphoresis of, in organic solvents (BIKERMAN), ii, 522.
protective action of soaps on (PAPACONSTANTINOU), ii, 393.
coagulation of, by barium chloride (RABINOVITSCH), ii, 778.
action of silver sols on (FREUNDLICH and MOOR), ii, 198.
Arsenic organic compounds (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319; (MARGULIES), i, 447, 448; (HAMILTON and SLY), i, 600; (LEWIS and STIEGLER), i, 1470; (CASSELLA & Co.), i, 1470, 1471; (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471; (MATSUMIYA and NAKAL; MATSUMIYA; ROBERTS and TURNER), i, 1339.
ter- and quinque-valent toxicity of (SCHUMACHER), i, 733.
quinquevalent asymmetric (AESCHLIMANN), i, 706.
inhibition of the toxicity of, in mammals (VOEGTLIN, DYER, and LEONARD), i, 861.
Arsenious oxide, alkaloid compounds of, with tartaric acid (DEBUCQUET), i, 1090.
Arsenic determination and separation:—
determination of, and its occurrence in urine and in fish (COX), ii, 157.
determination of, electrolytically (MOIR and JAMIESON), ii, 1094.
determination of, in organic compounds (NEWBERY), ii, 901.
determination of, in salvarsan (KIRCHER and v. RUPPERT), ii, 240.
determination of, in animal organs (PRIBYL), i, 1500.
determination of, in tissues (LAWSON and SCOTT), i, 996.
separation of antimony and (HAHN and WOLF), ii, 68.
Arsenic-antimony organic compounds (CHEMISCHE FABRIK VON HEYDEN), i, 85, 86.
Arsenic cathodes. See Cathodes.
Arsenobenzene, *o*-, *m*-, and *p*-*di*amino-, and their *N*:*N*′-dimethylenesulphonates (KASHIMA), i, 1195.
3:3′-*di*amino-4:4′-*di*hydroxy-, diglycyl derivative, and its hydrochloride (KARRER, DIECHMANN, and HAEBLER), i, 243.

Arsenobenzenes, detection of (PATTA), i, 1195.
Arseno-metallic compounds (BINZ, BAUSCH, and URBSCHAT), i, 1195.
Arsenostibinobenzene, 3:3′-*di*amino-4-hydroxy-,and3:4′-*di*amino-4-hydroxy-, 4′-acetyl derivative, and 4′-chloro-3:3′-*di*amino-4-hydroxy-, and its hydrochloride (CHEMISCHE FABRIK VON HEYDEN), i, 85.
Arsinic acids, preparation of (BURTON and GIBSON), i, 84.
aliphatic hydroxylated, preparation of (LES ÉTABLISSEMENTS POULENC FRÈRES and OECHSLIN), i, 122.
o-**4-Arsinobenzeneazo*di*bromofluorescein** (CHRISTIANSEN), i, 1193.
o-**4-Arsinobenzeneazofluorescein** (CHRISTIANSEN), i, 1193.
o-**4-Arsinobenzeneazophenol*tetra*chlorophthalein** (CHRISTIANSEN), i, 1193.
o-**4-Arsinobenzeneazophenolphthalein** (CHRISTIANSEN), i, 1192.
5-Arsinobenzenesulphamic acid, 2-hydroxy-, barium salt (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471.
5-Arsinobenzenesulphonic acid, 3-amino-2-hydroxy- (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471.
Arsonium compounds, effect of, on the nervous system (HUNT and RENSHAW), i, 861.
Arsphenamine. See Salvarsan.
Artemisic acid, formation of (BERTOLO), i, 546, 921.
Arthritis, lactic acid in (CAJORI, CROUTER, and PEMBERTON), i, 328.
Artichokes, inulin in (COLIN), i, 620.
Aryl sulphonates, reaction of magnesium organic halides with (GILMAN, BEABER, and MYERS), i, 1057.
***s*-Arylalkylcarbamides**, nitration of (KNIPHORST), i, 905.
Arylaminopropanes, hydroxy-, preparation of alkyl derivatives of (MERCK, WOLFES, and DÜTZMANN), i, 393.
Arylazides (BAMBERGER), i, 843.
Arylazo-β-naphthylamines, oxidation of, by hydrogen peroxide (CHARRIER and CRIPPA), i, 589.
Aryldithiazolylmethanes (BOGERT and CHERTCOFF), i, 80.
Arylhydroxylamines, chemistry of (BAMBERGER), i, 388.
Aryl 4-hydroxynaphthyl ketones, preparation of (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 558.
Arylidenecyanoacetic acids (BAKER and LAPWORTH), i, 30.
Arylmercuric hydroxides, reactions of (KOTEN and ADAMS), i, 236.
1-Arylpyrazolones, halogen-substituted (CHATTAWAY and STROUTS), i, 71.
Ascaris lumbricoides, metabolism of (SLATER), i, 1208.
Ascelpias syriaca (milkweed), constituents of the hairs of (SCHORGER), i, 872.
Asparagine, formation of, in plants (PRIANISCHNIKOV), i, 213.
preparation of (PIUTTI), i, 758.
rotatory power of solutions of (LIQUIER), ii, 743.
formation of rings from, and its formyl derivative (CHERBULIEZ and CHAMBERS), i, 1046.
enzymic deamination of (CLEMENTI and CANTAMESSA), i, 200.
Aspartic acid, deamination of (AHLGREN), i, 235.
Aspergillus niger (*Sterigmatocystis niger*), acid formation by (BERNHAUER), i, 205.
effect of the culture media on growth and formation of acids by (MOLLIARD), i, 480.
phosphorus metabolism of (SCHNÜCKE), i, 204.
polysaccharide produced by (SCHMIDT), i, 868.
Asperula odorata (woodruff), chemical composition of (HÉRISSEY), i, 1165.
glucosides of (HERBOTH), i, 760; (HÉRISSEY), i, 1369.
Asperuligenol (HÉRISSEY), i, 1165, 1369.
Asperuloside (HÉRISSEY), i, 1165, 1369.
Asthma, analysis of blood in (RAMIREZ, ST. GEORGE, and MOSES), i, 999.
Asymmetric compounds, calculation of rotation of (DE MALLEMANN), ii, 935.
Atmospheric air, refractive index of (PÉRARD), ii, 1137.
action of light on, saturated with halogen vapours (JONES), ii, 984.
radioactive content of (BONGARDS), ii, 621.
ionisation of (ERIKSON), ii, 6; (ANSLOW), ii, 459; (LEHMANN and OSGOOD), ii, 832.
potential differences between liquids and (FRUMKIN), ii, 544.
isotherms of (HOLBORN and OTTO), ii, 851.
specific heats of hydrogen and of (BRINKWORTH), ii, 373.
effect of curvature of surface on solubility of, in water (BAYLIS), ii, 980.
rare gases in (JEFFREYS), ii, 83.
iodine in (v. FELLENBERG), ii, 316.
origin of free oxygen in (TAMMANN), ii, 100.

Atmospheric air, altitude of ozone in (CABANNES and DUFAY), ii, 968.
absorption of radiation by ozone in (FABRY), ii, 627.
constant mixtures of carbon dioxide and (JOHNSTON and WALKER), ii, 851.
combustion of gases with (WHITE), ii, 48.
propagation of flame in mixtures of inflammable gases with (WHITE), ii, 408.
ignition of mixtures of paraffins and (WHEELER), ii, 408.
influence of organic vapours on the inflammability of mixtures of gases and (JORISSEN and MEUWISSEN), ii, 53, 307; (JORISSEN and VAN DER VALK), ii, 874; (JORISSEN and ONGKIEHONG), ii, 875.
ignition of mixtures of carbon monoxide and (CROWE and NEWEY), ii, 875.
apparatus for determination of carbon dioxide and oxygen in (PLANTEFOL), ii, 902.
Atoms, structure of (BEDREAG), ii, 363; (JOOS), ii, 736; (JORDAN), ii, 926; (CABRERA), ii, 1107.
and chemical affinity (WILSDON), ii, 481.
Bohr's theory of (TOLMAN), ii, 466; (MILLIKAN and BOWEN), ii, 467, 733; (FOOTE), ii, 624; (THOMSON), ii, 733.
Bohr's model of (EPSTEIN), ii, 1.
theory of emission from (PALACIOS), ii, 835.
vibrations radiated from (CHATURVEDI), ii, 926.
and the quantum theory (SOMMERFELD), ii, 835.
Whittaker's model of (ELDRIDGE), ii, 1112.
influence of arrangement of, on refractive index (BRAGG), ii, 92.
of the same electron structure, spectra of (HARTREE), ii, 2; (BOWEN and MILLIKAN), ii, 916.
polarisability of the core of, in relation to spectra (SCHRÖDINGER), ii. 722.
magnetic properties of (GERLACH), ii, 258; (SEMENOV), ii, 618; (WILSDON), ii, 641.
paramagnetism and electron configuration of (JACKSON), ii, 732.
space quantisation of, in a magnetic field (RUARK and BREIT), ii, 477.
absorption of radiation by the emitting (DE BROGLIE and THIBAUD), ii, 165.
Atoms, distribution of electrons in (STONER), ii, 85; (PAULI), ii, 339; (SMITH), ii, 1023.
transformation of, into radiation (STERN), ii, 1021.
equilibria between electrons, radiation and (DIRAC), ii, 6.
grouping of, and specific affinity (FEIGL), i, 170.
size of, in relation to optical rotation (BRAUNS), ii, 633.
radii of, from magnetic susceptibility (CABRERA), ii, 624.
law of force within (GREEN), ii, 466.
attraction and repulsion in (KORN), ii, 1112.
collisions between (FRANCK), ii, 836; (BOHR), ii, 1022.
disintegration of (RUTHERFORD), ii, 348; (PETTERSSON and KIRSCH), ii, 623.
by α-particles (KIRSCH), ii, 923.
calculation of transition probabilities in (SLATER), ii, 734.
mass variations in (HAM), ii, 734.
chemical properties of (KRAMERS), ii, 835.
Atomic constants in relation to additive properties (SWARTS), ii, 744.
number, relation between crystal structure and (SCOTT), ii, 369.
and optical separations (MENZIES), ii, 2.
and quantum numbers (HARTREE), ii, 467.
force fields (BRACKETT), ii, 2.
Atomic weight of aluminium (KŘEPELKA and NIKOLIĆ), ii, 620.
of antimony (WEATHERILL), ii, 23.
of bismuth (CLASSEN and SCHAPOSCHNIKOW), ii, 175.
of boron (BRISCOE and ROBINSON), ii, 346; (BRISCOE, ROBINSON, and STEPHENSON), ii, 619.
of bromine (MOLES), ii, 346; (ROBINSON and BRISCOE), ii, 620.
of carbon and silver (DEAN), ii, 255.
of chlorine (GLEDITSCH), ii, 174; (MOLES), ii, 346; (HARKINS and STONE), ii, 921, 1108; (MENZIES), ii, 1109.
of copper (RUER and BODE), ii, 620.
of gold obtained from mercury (HÖNIGSCHMID and ZINTL), ii, 924.
of hafnium (HÖNIGSCHMID and ZINTL), ii, 255, 347; (HEVESY), ii, 255.
of holmium (DRIGGS and HOPKINS), ii, 463.
of hydrogen (MOLES), ii, 346.
of lead isotopes (GLEDITSCH, DORENFELDT, and BERG), ii, 732.

Atomic weight of selenium (BRUYLANTS, LAFORTUNE, and VERBRUGGEN), ii, 174.
of silicon (HÖNIGSCHMID and STEINHEIL), ii, 174.
of silver (MOLES), ii, 346.
of zirconium (HÖNIGSCHMID, ZINTL, and GONZÁLEZ), ii, 174; (HEVESY), ii, 255.
Atomic weights, fundamental (MOLES), ii, 346, 1021.
Atriplex, absorption of water and chlorine ions by leaves of (WOOD), i, 1024.
Atrolactinic acid, synthesis of glycols from (ROGER), i, 659.
Atromentin, and its salts and derivatives (KÖGL and POSTOWSKY), i, 50, 1439.
Atropine, action of, on the intestines (JENDRASSIK and TANGL), i, 1502.
n- and *apo*-**Atropine** *N*-oxides, and their derivatives (POLONOVSKI and POLONOVSKI), i, 829.
Aurin, and its derivatives (GOMBERG and SNOW), i, 660.
Aurora, spectrum of (VEGARD, ONNES, and KEESOM), ii, 474; (VEGARD), ii, 630.
green line in spectrum of (MCLENNAN), ii, 249, 339; (MCLENNAN and SHRUM), ii, 723.
Auto-catalysis (QUARTAROLI), ii, 53.
Autohæmolysin, artificial production of (NANBA), i, 1344.
Autolysis (HERTZMAN and BRADLEY), i, 102; (RONA, MISLOWITZER, and SEIDENBERG), i, 335; (STEPPUHN and UTKIN-LJUBOVZOV), i, 864.
Autoxidation (MOUREU, DUFRAISSE, and BADOCHE), i, 117, 362, 363; (MOUREU and DUFRAISSE), i, 362; (TSCHIRCH), i, 356; (MOUREU, DUFRAISSE, and LOTTE), ii, 561; (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 933.
and dehydrogenation (MANCHOT and GALL), i, 561.
of organic compounds (STAUDINGER), i, 897, 898.
Auxoureases (HOSOKAWA), i, 104; (KOCHMANN), i, 200.
combination of, with enzymes (ROSENFELD), i, 336.
Avitaminosis, biochemistry of (PALLADIN and KUDRJAVZEVA; PALLADIN and NORMARK; PALLADIN and SAVRON), i, 461; (PALLADIN and KRATINOVA), i, 1514.
effect of, on gastric digestion (GROEBBELS and SPERFELD), i, 1514.
metabolism in (SHINODA), i, 610.
respiration in (ROCHE), i, 462.
Avogadro's constant, determination of (ALEXANDER), ii, 364.
Azides, action of toluquinone with (CHATTAWAY and PARKES), i, 985.
Azido-carbon *di*sulphide (WILCOXON, MCKINNEY, and BROWNE), i, 1051.
Azido compounds, action of sodium arsenite on (GUTMANN), i, 84.
3-Azidophenanthraphenazine (BRASS and NICKEL), i, 447.
3-Azidophenanthraquinone (BRASS and NICKEL), i, 447.
Azines, preparation of (AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION), i, 304.
hydrogenation of, with aluminium amalgam (MAZOUREVITCH), i, 1240.
Azines, amino-, from naphthalene derivatives (KEHRMANN and SAFAR), i, 1331.
Azine colouring matters from oxalyldibenzyl ketone (CHAKRAVARTI), i, 1330.
Azoanilinesulphonic acids, formation of (LEWCOCK), i, 597.
Azobenzene, binary systems of, with phenols (KREMANN, ZECHNER, and WEBER), ii, 650.
reduction of, by organo-magnesium halides (GILMAN and PICKENS), i, 1336.
Azobenzene, *p*-hydroxy. See Benzeneazophenol.
*pp'-di*hydroxy-, salts and green modification of (VORLÄNDER and KUNZE), i, 1106.
p-oximinoamino-, acetyl derivative (KARRER, DIECHMANN, and HAEBLER), i, 243.
Azobenzenes, nitro- (CHARRIER and BERETTA), i, 316.
Azobenzene-4:4'-dicarboxylic acid, 3:3'-*di*bromo-, and its silver salt and glycol ester (FREJKA and VITHA), i, 663.
and its ethylene ester (FREJKA and VITHA), i, 1416.
o-**Azobenzylaniline** (ELBS and GAUMER), i, 167.
o-**Azobenzyl**-*o*- and -*p*-**toluidines** (ELBS and GAUMER), i, 168.
Azo-colouring matters (WHEELER and MORSE), i, 22; (ROWE and TARBETT), i, 317; (FARBENFABRIKEN VORM. F. BAYER & CO.; FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 598; (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 598, 989.
constitution and fastness of (JOHN), i, 1336.

Azo-colouring matters, stereoisomeric (MORGAN and SKINNER), i, 1191.
influence of methyl and sulphonic acid groups on the colour of (WANNER), i, 841.
from ipecacuanha alkaloids (PALKIN and WALES), i, 1087.
mercury derivatives of (PROSKOURIAKOFF and RAIZISS), i, 1107.
action of phenylhydrazine and sodium hydrogen sulphite on (BUCHERER and STICHEL), i, 1338.
Azo-compounds, halochromism of (BRAND, STALLMANN, GROEBE, and STEIN), i, 397.
cuprohalide compounds of (DIELS and KOLL), i, 988.
addition of, to ethylenes (INGOLD and WEAVER), i, 580.
Azodicarboxylic acid, esters, reactions of, with aromatic hydrocarbons (STOLLÉ and ADAM), i, 1469.
Azodiethylacetonitrile (DOX), i, 797.
Azo-5:5′-di-2-phenyl-1:2:3:4-tetrazole, and the corresponding hydrazo compound (STOLLÉ and ORTH), i, 1464.
Azoimide (*hydrazoic acid; nitrogen hydride*), oxidation of (RASCHIG), ii, 223.
reduction of (RASCHIG), ii, 223.
reactions of, with azido-carbon disulphide and with thiocyanogen (WILCOXON, MCKINNEY, and BROWNE), i, 1051.
additive compounds of (OLIVERI-MANDALÀ), ii, 815.
Azomethane cuprochloride (DIELS and KOLL), i, 988.
Azomethylethylacetonitrile (DOX), i, 796.
2:3-*endo*Azo-7-methyl-4:5:6:7-tetrahydroindazole (v. AUWERS, BAHR, and FRESE), i, 313.
3:3′-Azo-7-methyltetrahydroindazole (v. AUWERS, BAHR, and FRESE), i, 313.
Azo*iso*propane cuprochloride (DIELS and KOLL), i, 988.
Azotobacter, fixation of nitrogen by (LIPMAN and TEAKLE), i, 491.
Azotobacter agile, fixation of nitrogen by (KOSTYTSCHEV and RYSKALTCHOUK), i, 1014.
Azotobacter chroococcum, fixation of nitrogen by mixed cultures of (LIPMAN and TEAKLE), i, 748.
***p*-Azoxyanisole**, diamagnetism of (FOEX and ROYER), ii, 755.
Azoxybenzenebisazodimethylaniline (ELBS), i, 164.
***o*-Azoxybenzylaniline** (ELBS and GAUMER), i, 167.
***o*-Azoxybenzyl-*o*- and -*p*-toluidines** (ELBS and GAUMER), i, 168.
Azoxyphenols, action of nitrous acid on (BIGIAVI and ANGELI), i, 316.
Azoxytetraphenylmethane (GOLDSCHMIDT and CHRISTMANN), i, 649.
Azoxy-2:4:5-triphenyloxazole (TRÖGER and PHILIPPSON), i, 986.

B.

Bacilli, acetone-producing (FOWLER and SUBRAMANYAN), i, 1216.
producing red pigment in acetone-butyl alcohol fermentation (FRED, PETERSON, and CARROLL), i, 1013.
tubercle, nutrition of (KONDO), i, 206.
metabolism of (KONDO), i, 477.
amino-acids of, and their metabolism (CAMPBELL), i, 1511.
distribution of nitrogen in the protein fraction of (JOHNSON and COGHILL), i, 748.
detection of tryptophan in (MME. E. and E. WOLLMAN), i, 205.
Bacillus abortus, effect of, on the proteins of blood (HOWE and SANDERSON), i, 477.
Bacillus acetoethylicum, acetone formation from sugars by (SPEAKMAN), i, 1013.
Bacillus erithrycke, effect of carbohydrates on hydrogen sulphide production by (HEAP and CADNESS), i, 480.
Bacillus botulinus, metabolism of (WAGNER, MEYER, and DOZIER), i, 1510.
Bacillus coli communis, effect of hydrogen-ion concentration on growth of (BLOK), i, 615.
formation of hydrogen sulphide by (MULSOW and PAINE), i, 1510.
action of bismuth on (LEMAY and JALOUSTRE), i, 206.
decomposition of cholic acid by (KAZIRO), i, 1363.
decomposition of dextrose by (AUBEL and SALABARTAN), i, 747.
Bacillus coli aerogenes, Voges-Proskauer reaction for (LINTON), i, 867.
Bacillus diphtheriæ, energy for culture of (ABT), i, 1014.
hydrogen-ion concentration in cultures of (ABT and LOISEAU), i, 479.
Bacillus lactis aerogenes, destruction of uric acid by (ECKER and MORRIS), i, 1118.
Bacillus macerans, fermentation of carbohydrates by (MOSKOVITS), i, 1511.

Bacillus pyocyaneus, blue pigment of (WREDE and STRACK), i, 174, 844.
assimilation and transformation of aromatic compounds by (SUPNIEWSKI), i, 340.
decomposition of carnosine by (HEFTER), i, 1362.
Bacillus tuberculosis, action of chemicals on growth of (KARWACKI), i, 1015.
Bacillus welchii, formation of acraldehyde from glycerol by (HUMPHREYS), i, 340.
Bacteria, conductivity changes for (PARSONS and STURGES), i, 1509.
changes in hydrogen-ion concentration of cultures of (SIERAKOVSKI), i, 204.
anaërobic growth of (QUASTEL and STEPHENSON), i, 1217.
acid agglutination of cells of (WEBSTER), i, 749.
action of water and salt solutions on (PANISSET, VERGE, and CARNEIRO), i, 339.
autolysis of (LEMOIGNE), i, 478.
chemical mechanism of reactions of (E. W. and A. E. STEARN), i, 339.
action of, on bile acids (LICHT), i, 478.
carbon dioxide in cultures of (SIERAKOVSKI and ZAJDEL), i, 338.
effect of dyes on growth of (BURNET), i, 1117.
effect of hydrogen peroxide on (BURNET), i, 1117; (PETROVANU), i, 1362.
production of hydrogen peroxide by (MCLEOD and GORDON), i, 1362.
utilisation of quinic acid by (BUTKEVITSCH), i, 1511.
decomposition of starch by (SIEDICH), , 1510.
decomposition of uric acid by (MORRIS and ECKER), i, 478.
vitamins promoting growth of (DAVIDSOHN), i, 108.
effect of, on buffering and amino-nitrogen increase in nutrient media (BLEYER), i, 746.
fermentation by (DE GRAAFF and LE FÈVRE), i, 478.
isolation of cultures of, and their oxydase activity (FELTON), i, 1509.
symbiosis of seeds and (FOWLER and CHRISTIE), i, 344.
chemical differentiation of (E. W. and A. E. STEARN), i, 1013.
acid-fast, metabolism of (KONDO), i, 206.
producing ethyl butyrate (BIDAULT and BLAIGNAN), i, 1216.
Bacteria, lactic acid, from cereals (FRED, PETERSON, and STILES), i, 1014.
respiration of (KOSTYTSCHEV and AFANASIEVA), i, 1118.
formation of acetylmethylcarbinol and 2:3-butyleneglycol by (KLUYVER and DONKER), i, 1215.
living, hydrogen-ion concentration of (BÁLINT), i, 338.
mannitol-producing, fermentation products of (STILES, PETERSON, and FRED), i, 1216, 1510.
nitrogen-fixing, effect of radioactive substances on (KAYSER and DELAVAL), i, 1116.
action of (GAARDER and HAGEM), i, 480.
activity of, in soils (TRUFFAUT and BEZSSONOFF), i, 1227.
resting, dehydrogenation by (QUASTEL and WHETHAM), i, 1015, 1217; (QUASTEL and WOOLDRIDGE), i, 1217.
reactions of (QUASTEL, STEPHENSON, and WHETHAM), i, 747.
soil, conversion of thiosulphates into sulphates by (GUITTONNEAU), i, 1218.
in moor soils (ARND), i, 490.
sulphur (BAAS-BECKING), i, 1217.
nitroprusside reaction of (CALLOW and ROBINSON), i, 478.
detection of the reducing power of (FELTON), i, 1509.
determination of indole and skatole in (FELLERS and CLOUGH), i, 1015.
Bactericidal action and chemical constitution (ISHIWARA), i, 750.
Baillonia spicata, glucoside from (HÉRISSEY), i, 147.
Balance, ultra. See Ultrabalance.
Balbiano's acid, structure of (ROTHSTEIN, STEVENSON, and THORPE), i, 884.
Balmer law as an equation of motion (PAGE), ii, 468.
Bamboo, growth of shoots of (KOMATSU and TANAKA), i, 1369.
Barbituric acid derivatives (VOORHEES and SKINNER), i, 887.
preparation of (RIEDEL), i, 1453.
narcotic effect of (REDONNET), i, 862.
alkyl derivatives, distinction between (ZAMPARO), ii, 907.
distribution of, in the organism (FREDET and FABRE), i, 467.
*iso*Barbituric acid, oxidation of (DAVIDSON and BAUDISCH), i, 1189.
Barbituric acids, alkylated, localisation and excretion of (FABRE and FREDET), i, 1504.

Barite. See Barytes.
Barium, structure of (COLLINS), ii, 623.
pure, preparation of (DANNER), ii, 62.
pole-effect in spectrum of (MOHR), ii, 612.
equilibrium between lithium and, and their fused chlorides (JELLINEK and CZERWINSKI), ii, 124.
Barium alloys with mercury, electrodes of. See Electrodes.
Barium aluminate, hydrated, effect of heating on (MALQUORI), ii, 813.
uranyl carbonate (HEDVALL), ii, 991.
chloride, conductivity of solutions of, and its mixtures with cobalt chloride (MAZZETTI), ii, 210.
heats of solution of, in aqueous alcohol (DE KOLOSOVSKI), ii, 540.
energy of dilution and activity of ions in aqueous solutions of (PEARCE and GELBACH), ii, 867.
nitrate, periodic crystallisation of (HEDGES and MYERS), ii, 1168.
oxide, action of, on silicates at high temperatures (TAMMANN and GREVEMEYER), ii, 580.
*per*oxide, new (CARLTON), ii, 1183.
selenide, crystal structure of (SLATTERY), ii, 369.
sulphate, solubility and size of grain of crystals of (BALAREFF), ii, 853.
apparatus for precipitation of (MURRAY), ii, 236.
co-precipitation of radium sulphate and (DOERNER and HOSKINS), ii, 381.
Barium detection:—
detection of (KOLTHOFF), ii, 1095.
detection of, in presence of strontium (FEIGL), ii, 435.
Barley, nutrients for culture of (JONES and PEMBER), i, 1080.
culture of, with nitrogen, phosphorus and potassium (PEMBER and MCLEAN), i, 1121.
effect of ethyl and methyl alcohols on growth of (PURI), i, 217.
Barytes, reflection of Röntgen rays by (ALLISON), ii, 18.
crystal structure of (PAULING and EMMETT; WYCKOFF and MERWIN), ii, 485.
Base, $C_6H_{14}O_3N_2$ and its derivatives, from hydrolysis of proteins (SCHRYVER, BUSTON, and MUKHERJEE), i, 794.
$C_7H_{14}O_2N_2$ from *Geodia gigas* (ACKERMANN, HOLTZ, and REINWEIN), i, 720.
$C_{10}H_{15}N$, and its salts, from 5-ethyl-2-vinylpyridine methiodide (KOENIGS and HOFFMANN), i, 299.
Base, $C_{11}H_{15}O_3N_5S$, from yeast (SUZUKI, ODAKE, and MORI), i, 338.
$C_{13}H_{30}O_4N_2$, from amniotic fluid (REINWEIN and HEINLEIN), i, 721.
$C_{14}H_{15}ON$, from *m*-phenoxymethylbenzylamine (v. BRAUN and REICH), i, 1406.
$C_{14}H_{25}ON$, and its methiodide, from *o*-phenoxymethylbenzylamine (v. BRAUN and REICH), i, 1406.
$C_{14}H_{33}ON$, from *p*-phenoxymethylbenzylamine and fuming hydrochloric acid (v. BRAUN and REICH), i, 1405.
$C_{18}H_{17}N$ and its salts, from distillation of chelerythrine and sanguinarine (GADAMER and STICHEL), i, 287.
$C_{22}H_{17}N$, and its hydrochloride, from $C_{28}H_{25}N_3$ and hydrochloric acid (LEUCHS and WINZER), i, 1282.
Bases, action of haemoglobin with (ADAIR), i, 850.
inactive, and inactive acids, mutual resolution of (INGERSOLL), i, 814.
metallo-organic (HEIN and MEININGER), ii, 842.
organic, electrolysis of (PODROUŽEK), ii, 677.
adsorption and basic exchange of salts of (UNGERER), ii, 658.
hydroferri- and hydroferro-cyanides of (CUMMING), i, 122.
preparation of iodomercurates of, from their iodoantimonates (CAILLE and VIEL), i, 68.
weak, indicator for determination of (CHABOT), ii, 899.
weak organic, detection of (ROBINSON), ii, 606.
determination of, volumetrically (HARRIS), ii, 155.
Basedow's disease, fat and cholesterol in blood in (BING and HECKSCHER), i, 999.
Bassia longifolia, variations in constituents of (FOWLER and DINANATH), i, 346.
Bauxite, effect of heating on (HOULDSWORTH and COBB), ii, 671.
Beans, effect of light on etiolated leaves of (PALLADIN), i, 1517.
calabar. See Calabar bean.
French and soya, oxidising enzymes in (NITZESCU and COSMA), i, 471.
jack. See *Canavalia ensiformis.*
kidney, hexamethylenetetramine as a nutrient for (E. and G. NICOLAS), i, 623.
soja. See Soja beans.
Bearing metal, lead-base, microstructure of (ELLIS), ii, 282.

Beckmann transformation (v. AUWERS and JORDAN), i, 264; (v. AUWERS, LECHNER, and BUNDESMANN), i, 265; (LACHMANN), i, 678; (KOMATSU and HIRAIDZUMI), i, 934; (MEISENHEIMER, LANGE, and LAMPARTER), i, 1073; (YAMAGUCHI), i, 1278.
Becquerel effect on copper oxide electrodes (VAN DIJCK), ii, 1083.
Becquerelite, structure and analysis of (SCHOEP), ii, 235.
Beech wood, pectic substance from (O'DWYER), i, 1225.
Beer, bitter principles in (KLEIN), ii, 248.
effect of fermentation of wort of, on water-soluble vitamins (SOUTHGATE), i, 209.
Beet, sugar, phosphatides from the root of (GRAFE and HORVAT), i, 1522.
Behenic acid, bromoiodo-, and iodohydroxy- (HOLDE and GORGAS), i, 883.
Benzaldehyde, preparation of (MANN and PAULSON), ii, 556.
catalytic reduction of (CAROTHERS and ADAMS), ii, 693.
compound of aminomalononitrile and (GRISCHKEVITSCH-TROCHIMOVSKI and SEMENCOV), i, 1069.
and chloro-, chlorophenylhydrazones of (HUMPHRIES, HUMBLE, and EVANS), i, 989.
phenylhydrazone, action of bromine on (CHATTAWAY and WALKER), i, 929.
p-toluenesulphonylhydrazone (FREUDENBERG and BLÜMMEL), i, 52.
determination of chlorine in (BUKSCHNEWSKI; FAUST and SPÄNGLER), ii, 1000.
p-amino-, benzoyl derivative (PFEIFFER), i, 410.
and its derivatives (PFEIFFER, KALCKBRENNER, and BEHR), i, 549.
ω- and *p*-bromo-, *ω*-chloro- and *ω*-cyano-, 2:4-dibromophenylhydrazones (CHATTAWAY and WALKER), i, 929.
bromonitro-, chloronitro-, and nitro-, bromo- and chloro-phenylhydrazones of, and their acetyl derivatives (CHATTAWAY and WALKER), i, 1194.
m-hydroxy-, bromo and nitro derivatives, and their derivatives (HODGSON and BEARD), i, 674.
iodo derivatives, phenylhydrazones of (FICHTER and LOTTER), i, 1055.
o- and *m*-nitro-, condensation of 8-methoxy-2-methylquinoline with (TRÖGER and DANEHL), i, 974.
Benzaldehyde, *m*- and *p*-nitro-, bromo- and chloro-phenylhydrazidines (CHATTAWAY and WALKER), i, 1194.
2:6-*di*nitro-, hydrazones of (v. AUWERS and FRESE), i, 1102.
6-nitro-3-hydroxy-, derivatives of (MASON and JENKINSON), i, 931.
Benzaldehyde-*p*-arsinic acid, hydrazones and semicarbazone of (MARGULIES), i, 448.
Benzaldehyde-2:4-*di*bromophenylhydrazidine (CHATTAWAY and WALKER), i, 930.
Benzaldehyde-2-chloro-5-pyridylhydrazone (PIERONI and HAUPT), i, 1316.
Benzaldehydediphenylene-4:4'-dihydrazone, and *o*-, *m*-, and *p*-nitro- (CHATTAWAY, IRELAND, and WALKER), i, 1195.
Benzaldehydephenylcitronellylhydrazone (RUPE and RINDERKNECHT), i, 658.
Benzaldimine (GRIGNARD and ESCOURROU), i, 931.
Benzaldoxime, and *p*-hydroxy-, *m*- and *p*-nitro-, aryl ethers of (BAMBERGER), i, 142.
Benzaldoxime, *p*-nitro-, benzoyl derivative (NEBER, HARTUNG, and RUOPP), i, 1072.
Benzaldoximes, catalysis of, with reduced copper (YAMAGUCHI), i, 1278.
Benzaldoximes, 2-chloro-5-nitro- (BRADY and BISHOP), i, 930.
Benzamide, solubility of, in mixed solvents (PLEUGER), ii, 283.
Benzamide, 4-chloro-3:5-*di*nitro-, and 3:5-*di*nitro-4-amino- (LINDEMANN and WESSEL), i, 1099.
Benzanilide, reactions of antimony halides with (VANSTONE), i, 662.
p-disulphoxide (BERE and SMILES), i, 22.
1:2-Benzanthracene, 9-(or 10)-nitro- (BARNETT and MATTHEWS), i, 821.
1:2-Benzanthraquinone, reduction of (BARNETT and MATTHEWS), i, 820.
1:2-Benzanthrones, and their benzoates (BARNETT and MATTHEWS), i, 821.
Benzazide, 4-chloro-3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.
Benzazimide, acetyl and benzoyl derivatives (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1325.
Benzazimide, 3-amino-, and its derivatives (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1322.
Benzazimidecarboxylic acid, ethyl ester (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1325.

Benz-*o*-chloromethylbenzylamide (v. BRAUN and REICH), i, 1407.
6:7-Benzcoumarandiol-2-anil, 5-bromo- (FRIES and PUSCH), i, 570.
4:5-Benzcoumaran-3-one, bromo derivatives and 2-*aci*nitro-, sodium salt (FRIES and PUSCH), i, 569.
6:7-Benzcoumaran-3-one, 2:2:5-*tri*bromo- (FRIES and PUSCH), i, 570.
Benzcoumaran-3-one-2-anils (FRIES and PUSCH), i, 569.
4:5-Benzcoumarophenazine (FRIES and PUSCH), i, 569.
Benz-*m*- and -*p*-cyanomethylbenzylamides (v. BRAUN and REICH), i, 1406.
Benz-β-*o*-cyanomethylphenylethylamide (v. BRAUN and REICH), i, 1407.
***meso*-Benzdianthrone**, 4:5:8:4′:5′:8′-*hexa*-chloro- (ECKERT), i, 414.
Benzeins, preparation of (SEN and SARKAR), i, 812.
Benzene, structure of (VAN LAAR), i, 799, 894; (SCHOORL; PRINS), i, 894; (RAMANATHAN), i, 1255.
molecular structure of (BECKENKAMP), ii, 90.
formula of (BECKENKAMP), ii, 358.
triangular formula for (RICHARD), i, 1054.
nucleus, structure of (DOMINIKIEWICZ), i, 15.
and substitution (GIUA and PETRONIO), i, 1396.
substitution in (PRINS), i, 879; (FRANCIS, HILL, and JOHNSTON), i, 1141; (VORLÄNDER), i, 1255; (FRANCIS), i, 1261, 1399; (SONN and PATSCHKE), i, 1279; (FRANCIS and HILL), ii, 163.
model of (SCHROER), i, 879.
synthesis of, from acetylene (KOVACHE and TRICOT), i, 799.
spectra of (MARSH), ii, 625.
absorption spectrum of (DREISCH), ii, 178.
absorption spectrum of aqueous solutions of (VLÈS and GEX), ii, 1115.
infra-red absorption spectra of (DREISCH), ii, 627.
Tesla-luminescence spectrum of (MCVICKER, MARSH, and STEWART), ii, 86.
fluorescence of the vapour of (PRINGSHEIM and REIMANN), ii, 181.
latent heat of fusion of (STRATTON and PARTINGTON), ii, 25; (MAASS and WALDBAUER), ii, 492.
boiling-points of mixtures of ethyl alcohol, water, and (BARRATT), ii, 766.
Benzene, interfacial tension between potassium and sodium amalgams and (BHATNAGAR, PRASAD, and MUKERJI), ii, 194.
surface tension of (ALI), ii, 763.
and its mixtures with *cyclo*hexanols (WEISSENBERGER and SCHUSTER), ii, 648.
cryoscopy with (JONES and BURY), ii, 1040.
catalytic hydrogenation of, in presence of copper (PEASE and PURDUM), i, 798.
effect of thiophen on catalytic nickel in reduction of (KUBOTA and YOSHIKAWA), ii, 805.
action of benzoyl peroxide on (GELISSEN and HERMANS), i, 545.
action of iodine on (COSTEANU), i, 238.
behaviour of, in the body (THIERFELDER and KLENK), i, 193.
as indicator in iodometry (KANÔ), ii, 1010.
derivatives, ultra-violet absorption spectra of (KLINGSTEDT), ii, 929.
melting points of (PASTAK), ii, 759.
substitution in (SKRAUP and POLLER), i, 143.
ring closure in the meta-position in (v. BRAUN and ENGEL), i, 382.
determination of *m*-isomerides in (FRANCIS and HILL), ii, 163.
vicinal trisubstituted, substitution in (RUBENSTEIN), i, 1428.
Benzene, bromo-, compound of aluminium chloride, nitrogen peroxide, and (SCHAARSCHMIDT, BALZERKIEWICZ, and GANTE), i, 532.
*p-di*chloro-, freezing point of (COOPER), i, 800.
1-chloro-2-bromo-4:6-*di*nitro-, and 1:3-*di*chloro-*di*nitro- (SANÉ and JOSHI), i, 134.
chloronitro derivatives, physical properties of (DESVERGNES), ii, 490.
reactions of, with sodium sulphides (HODGSON and WILSON), i, 532.
m-chloronitro-, nitration of (HODGSON), i, 1397.
chlorothiol- (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.
and its homologues, fluoro derivatives, rotation of (RIZZI), ii, 357.
hydroxy derivatives, surface tensions of aqueous solutions of (HARKINS and GRAFTON), ii, 658.
iodo-, electrolytic oxidation of (FICHTER and LOTTER), i, 1055.

Benzene, *di*iodo derivatives, compounds of magnesium with (THOMAS), i, 1053.
p-iodoxynitro-, action of alkali hydroxides (VORLÄNDER and BÜCHNER), i, 1055.
nitro-, electrolysis of, with the mercury dropping cathode (SHIKATA), ii, 304.
cryoscopy with (BROWN and BURY), ii, 32; (SIDGWICK and EWBANK), ii, 38; (BROWN), ii, 296.
colloidal solutions of dehydrating agents in (BROWN and BURY), ii, 1055.
action of, on lead in acetic acid solution (PRINS), ii, 1169.
m-*di*nitro-, melting point of (PUSHIN), ii, 277.
*tri*nitro-, dissociation constants of compounds of amines with (LEY, GRAU, and EMMERICH), ii, 1159.
nitroso-, polarisation of (ROBINSON), i, 801.
action of, on *o*-nitroaniline (CHARRIER and BERETTA), i, 21.
Benzenes, chloronitro-, mutual solubility of (KOHMAN), ii, 1052.
o- and *p*-chloronitro-, separation of (MOLINARI), i, 380.
*tetra*chloronitro-, and their reactions with sodium methoxide (BERCKMANS and HOLLEMAN), i, 1136.
*di*nitro-, mutual solubility of (ANDREWS), ii, 1052.
Benzeneazo-*p*-acetamidophenol, *o*-nitro- (ELBS), i, 164.
Benzeneazo-4-amino-β-naphthol, 1-amino- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 989.
Benzeneazo-2-amino-4-phenylthiazole, *p*-nitro- (BOGERT and CHERTCOFF), i, 315.
Benzeneazoaniline, *o*-nitro- (ELBS), i, 164.
Benzeneazobenzylformaldoxime, and its derivatives (WALKER), i, 1193.
Benzeneazodimethylaniline, *o*-amino-, and *o*-nitro-, hydrochloride (ELBS), i, 164.
2-Benzeneazo-4:5-dimethylglyoxaline, 2-*p*-bromo-, and its hydrochloride (BURTLES and PYMAN), i, 1326.
Benzeneazodiphenylamine, *o*-nitro-, and its derivatives (ELBS), i, 164.
5-Benzeneazo-6-hydroxy-2-methylnaphthalene, and its 4′-sulphonic acid and 4′-nitro- (DZIEWOŃSKI, SCHOENÓWNA, and WALDMANN), i, 1057.
1-Benzeneazo-2:4-*di*hydroxynaphthalene, *p*-amino-, and its 8-sulphonic acid (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i,
3-Benzeneazo-2:6-lutidine, 3-*p*-hydroxy-, and its derivatives (GULLAND and ROBINSON), i, 1186.
Benzeneazomethylglyoxalines, *p*-bromo- (BURTLES and PYMAN), i, 1326.
4-Benzeneazo-1-naphthol, 4-*o*-nitro- (ELBS), i, 165.
Benzeneazo-α-naphthylamine, *o*-nitro- (ELBS), i, 165.
γ-Benzeneaze-Δαβ-pentenoic acid (MACBETH and TRAILL), i, 782.
Benzeneazophenol, oxidation of (BIGIAVI and KINDT), i, 597.
Benzeneazophenylpyrroles (PLANCHER and GHIGI), i, 597.
β-Benzeneazopropane (GOODWIN and BAILEY), i, 843.
Benzeneazoresorcinol, *o*-nitro- (ELBS), i, 164.
Benzenebisazoresorcinol, *o*-nitro- (ELBS), i, 164.
Benzene-*p*-disulphonic acid, electrochemical oxidation of (FICHTER and STOCKER), i, 239.
Benzenepersulphonic acid (FICHTER and STOCKER), i, 240.
Benzenesulphendimethylamide. See Dimethylaminothiolbenzene.
Benzenesulphenic acid, derivatives of (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.
Benzenesulphinic acid, hydroxylamine salt (WHALEN and JONES), i, 802.
Benzenesulphobulbocapnine methyl ether (OSADA), i, 283.
Benzenesulphocorydine, and its methyl ether (OSADA), i, 284.
3-Benzenesulphonamido-*p*-cresol, 5-chloro-, and its derivatives (RAIFORD and LANKELMA), i, 810.
Benzenesulphonic acid, electrochemical oxidation of (FICHTER and STOCKER), i, 239.
metallic salts, and their solubilities (EPHRAIM and PFISTER), i, 896.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
arylamine salts (KEYWORTH), i, 124.
Benzenesulphonic acid, *p*-amino-. See Aniline-*p*-sulphonic acid.
4-bromo-3:5-*di*nitro-, and 4-chloro-3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1098.
p-hydroxy-, solubility of, in water (YAJNIK, JAIN, and NATH), ii, 1147.
Benzenesulphonyl iodide, 2:5-*di*chloro- (GIBSON, MILLER, and SMILES), i, 1137.
***p*-Benzene-*p*-sulphonylazo-2-amino-4-phenylthiazole** (BOGERT and CHERTCOFF), i, 315.

Benzenethiolsulphonic acid, bromo, chloro, and nitro derivatives, substituted phenyl esters of (MILLER and SMILES), i, 392.
2:5-*di*chloro-, and 3-nitro-, 4-tolyl esters (GIBSON, MILLER, and SMILES), i, 1137.
Benzhydrazide, *o*-amino-, acetyl and benzoyl derivatives (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1322.
Benzhydrazideacetophenone, *o*-amino-, acetyl derivatives (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1323.
Benzhydrol (*diphenylcarbinol*), binary systems of, with amines and phenols (KREMANN and DRAZIL), ii, 649.
Benzhydryl-lactic acid, and its barium salt (SOMMELET), i, 247.
***o*-Benzhydrylphenol** (CLAISEN), i, 1410.
Benzhydryltrimethylammonium bromide (SOMMELET), i, 247.
Benzidine (4:4′-*diaminodiphenyl*), action of acid anhydrides on (SHIMOMURA), i, 981.
action of carbon disulphide on (ROSSI and CECCHETTI), i, 701.
compound of pyridinium methiodide and (EMMERT, ROH, and KOBERNE), i, 588.
Benzil (*dibenzoyl*), conversion of, into benzilic acid (SCHEUING), i, 44.
semicarbazones of (HOPPER), i, 895.
Benzil, 2:4-*di*- and 2:4:6-*tri*-hydroxy-, and their acetyl derivatives (MARSH and STEPHEN), i, 1158.
Benzilam (TRÖGER and PHILIPPSON), i, 986.
Benzilam-azo-β-naphthol (TRÖGER and PHILIPPSON), i, 986.
β-Benzildioxime, electrolytic reduction of (ISHIBASHI), i, 1431.
Benzilic acid (*diphenylglycollic acid*; *hydroxydiphenylacetic acid*), formation of, from benzil (SCHEUING), i, 44.
action of, on thiophenol (BISTRZYCKI and RISI), i, 1426.
Benzilic acid transformation (SCHÖNBERG), i, 254.
Benzilide (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 934.
Benziminazole-2-naphthyl-8′-carboxylic acid (CHAKRAVARTI), i, 162.
Benziminazole-2-trimethyl*cyclo*pentane-carboxylic acids (CHAKRAVARTI and GUPTA), i, 980.
5:6-Benzobenzthiopyrone, 3-bromo- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
Benzotrichloride, 2:4:6-*tri*nitro- (GANGULY), i, 647.
4:5-Benzocoumarandione-3-anil (SAFTIEN), i, 1318.
Benzoic acid, ultra-violet absorption by phenol and (KEPIANKA and MARCHLEWSKI), ii, 179.
heat of combustion of (JAEGER and STEINWEHR), ii, 127.
solubility of, in benzene and in toluene (CHIPMAN), ii, 30.
partition coefficient of, between carbon tetrachloride and sodium hydroxide (KLEIN), ii, 802.
electrolytic reduction of, at the boiling point (DECANS and DUFOUR), i, 1272.
and its salts, elimination of, from the body (BORDAS, FRANÇOIS-DAINVILLE, and ROUSSEL), i, 1206.
Benzoic acid, salts, diffusion potentials and ionic mobilities of (PRIDEAUX and CROOKS), ii, 42.
and *p*-chloro-, *p*-hydroxy-, and *p*-nitro-, metallic salts of (EPHRAIM and PFISTER), i, 1148.
lead salt, solubilities of (AUERBACH and WEBER), i, 1130.
sodium salt, effect of, on blood and urine (SWANSON), i, 465.
theophylline salt (KNOLL & Co.), i, 828.
Benzoic acid, *o*-cyanobenzyl ester (BARKENBUS and HOLTZCLAW), i, 1148.
and *p*-amino-, β-hydroxyethyl esters, and their derivatives (CRETCHER and PITTENGER), i, 1415.
phenyl ester, reaction of sodium with (BLICKE), i, 662.
Benzoic acid, amino-, bromo-, chloro-, and nitro-, hydroxylamine salts (OESPER and BALLARD), i, 1233.
amino-, and nitro-, γ-dimethylamino-α-β-dimethylpropyl esters, and their hydrochlorides (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 1419.
p-amino-, *n*-butyl ester, picrate (THAYER), i, 467.
2:6-*di*bromo-, electrolytic reduction of (OLIVIER), i, 30.
2-bromo-*p*-amino-, and 2-bromo-*p*-nitro-, salts and esters of (FREJKA and VITHA), i, 663, 1416.
4:5-*di*bromo-2-amino- and 3 nitro-2-amino-, acetyl derivatives (CHAPMAN and STEPHEN), i, 1151.
2-chloro-3:5-*di*nitro-, derivatives of (BARNETT), i, 1288.
hydroxy-derivatives, action of keten on (VAN ALPHEN), i, 1149.
o-hydroxy-. See Salicylic acid.

Benzoic acid, nitro-derivatives, solubilities of, in water (YAJNIK, JAIN, and NATH), ii, 1147.
p-nitro-, use of, as a standard in acidimetry (THORNTON and GETZ), ii, 597.
ethylene ester (CRETCHER and PITTENGER), i, 1416.
trinitro-, metallic salts (KRAUZ and TUREK), i, 647.
2:4:6-*trinitro*-, methylmercuric, and phenylmercuric salts (KHARASCH and GRAFFLIN), i, 1107.
ethyl- and *p*-tolyl-mercuric derivatives (KOTEN and ADAMS), i, 237.
o-thiol-, mercury compounds of (SACHS and BLESSL), i, 1274.
p-thiol-, synthesis of (THOMPSON), i, 815.
Benzoic anhydrides, *o*-, *m*-, and *p*-chloro-, and their reactions with aliphatic alcohols (RULE and PATERSON), i, 29.
o-**Benzoicsulphinide** (*saccharin*), constitution of (TÄUFEL and WAGNER), i, 841.
Benzoin, semicarbazones of (HOPPER), i, 895.
Siam (REINITZER), i, 945.
Benzonitrile, action of organo-magnesium compounds on (ECTORS), i, 138.
Benzonitrile, *p*-nitro- (NEBER, HARTUNG, and RUOPP), i, 1072.
Benzophenone, boiling point of (FINCK and WILHELM), ii, 759.
liquid and solid, vapour pressure of (VOLMER and KIRCHOFF), ii, 494.
adsorption of, at the surface of mercury (VOLMER and MAHNERT), ii, 508.
derivatives, absorption spectra of (TASAKI), ii, 838.
action of nitric acid on (ELION), i, 262.
δ-anilinosemicarbazone (SUTHERLAND and WILSON), i, 42.
2:4-*di*- and 2:4:6-*tri*-chlorophenylhydrazones (HUMPHRIES, HUMBLE, and EVANS), i, 989.
4-*p*-tolylsemicarbazone (WHEELER and BOST), i, 318.
Benzophenone, 2:4:2′:4′-*tetra*amino- (GULLAND and ROBINSON), i, 1187.
2:4-*di*hydroxy- (SHARP & DOHME, and DOHME), i, 541.
Benzophenoneoxime chlorostannate (SONN and MEYER), i, 932.
Benzophenoneoximes, *p*-nitro-, isomeric, and their derivatives (BRADY and MEHTA), i, 43.
Benzopinacol, dissociation of derivatives of (BLICKE), i, 811.
Benzopiperidone (v. BRAUN and REICH), i, 1407.
Benzopyrans (*chromans*), preparation of (CLAISEN), i, 277.
Benzopyrone, 3-bromo- (ARNDT), i, 1309.
7-hydroxy-, acetyl derivative (PFEIFFER, OBERLIN, and KONERMANN), i, 1303.
3:3′-*di*thio- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.
Benzopyrones (*chromones*), synthesis of (ALLAN and ROBINSON), i, 148.
Benzopyrylium salts, 3-hydroxy, preparation of (RIDGWAY and ROBINSON), i, 54.
o-**Benzoquinone**, 4-amino-, acetyl derivative (KEHRMANN and HOEHN), i, 560.
4:5-*di*amino- (HOEHN), i, 938.
p-**Benzoquinone**, preparation of (CRAVEN and DUNCAN), i, 938.
transformation of, in solution (MEUNIER and QUEROIX), i, 412.
velocity of addition of hydrogen chloride to, in methyl alcohol (EBERT), ii, 408, 556.
4-*p*-tolylsemicarbazone (WHEELER and BOST), i, 318.
determination of (RZYMKOVSKI), ii, 907.
p-**Benzoquinone**, 2:3:6-*tri*bromo-5-nitro- (KOHN and STRASSMANN), i, 1264.
chloro-, preparation of (VAN ERP), i, 685.
o-**Benzoquinone-2-chloroimine**, 4:6-*di*nitro- (BLASZKOVSKA), ii, 1043.
p-**Benzoquinone-4-oxime**, 3-bromo-, and 3-iodo- (HODGSON and MOORE), i, 1408.
4:5-Benzothionaphthen-2-aldehyde, 3-hydroxy- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
2:3-Benzoxazine, 1-hydroxy- (GRIFFITHS and INGOLD), i, 1190.
Benzoxy-. See Benzoyloxy-.
Benzoyl chloride, influence of phosphorus oxychloride on the catalytic reduction of (ZETZSCHE and ARND), i, 1415.
action of, on phenylthiosemicarbazides (FROMM and TRUKA), i, 703.
Benzoyl chloride, 2-bromo-4-nitro- (FREJKA and VITHA), i, 1416.
4-chloro-3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.
m-hydroxy-, and its derivatives (ANSCHÜTZ and KRONE), i, 668.
Benzoyl groups, replacement of, by nitro groups (ELION), i, 44.

Benzoyl *per*oxide (DIETRICH), i, 544.
action of secondary amines on (GAMBARJAN), i, 1260.
action of, with benzene and toluene (GÉLISSEN and HERMANS), i, 545.
action of, on boiling benzene, and *p*-chloro- (GÉLISSEN and HERMANS), i, 379.
action of, on chloroform and on carbon tetrachloride (BOËSEKEN and GÉLISSEN), i, 30.
action of, on diphenyl, on alcohols and on acetic acid (GÉLISSEN and HERMANS), i, 663, 664.
Benzoylacetaldehyde dioxime (v. AUWERS and OTTENS), i, 1460.
phenylhydrazone (v. AUWERS and SCHMIDT), i, 585.
semicarbazones, and oximino- (v. AUWERS and OTTENS), i, 1460.
Benzoylacetone, *O*-alkyl ethers of (WEYGAND and FRIELING), i, 1288.
β-Benzoylacrylic acid, formation of Pechmann dyes from (BOGERT and RITTER), i, 36, 255.
β-Benzoylacrylic acid, β-*p*-hydroxy- and **β-*m*-nitro-** (BOGERT and RITTER), i, 816.
***iso*-β-Benzoylacrylic acid *di*bromide.** See β-Benzoylpropionic acid, **αβ-*di*bromo-**.
Benzoylalanylglycine (GOLDSCHMIDT and STEIGERWALD), i, 1109.
Benzoylallylecgonine, and its salts, and their anæsthetic action (POULSSON and WEIDEMANN), i, 466.
o*-Benzoylbenzoic acid**, 2′:6-di*nitro-** (QUAYLE and REID), i, 1289.
Benzoylbenzylecgonine, and its hydrochloride, and their anæsthetic action (POULSSON and WEIDEMANN), i, 466.
β-Benzoyl-*p*-bromophenylhydrazine, **β-*m*-** and **-*p*-nitro-**, **α-acetyl** derivatives (CHATTAWAY and WALKER), i, 1194.
β-Benzoyl-α-2:4-*di*bromophenylhydrazine (CHATTAWAY and WALKER), i, 930.
β-Benzoyl-2:4-*di*bromophenylhydrazine, **β-*m*-** and **-*p*-nitro-**, and their **α-acetyl** derivatives (CHATTAWAY and WALKER), i, 1194.
β-Benzoyl-2:4:6-*tri*bromophenylhydrazine, **β-*m*-nitro-**, **α-acetyl** derivative (CHATTAWAY and WALKER), i, 1194.
β-Benzoylbutyric acid, and its semicarbazone (HIGGINBOTHAM, LAPWORTH, and SIMPSON), i, 35.
Benzoylchlorodiphenylamines (CHAPMAN), i, 1400.
β-Benzoyl-*p*-chlorophenylhydrazine, **β-*p*-nitro-**, **α-acetyl** derivative (CHATTAWAY and WALKER), i, 1194.
β-Benzoyl-2:4-*di*chlorophenylhydrazine, **β-*m*-** and **-*p*-nitro-**, and their **α-acetyl** derivatives (CHATTAWAY and WALKER), i, 1194.
β-Benzoyl-2:4:6-*tri*chlorophenylhydrazine, **β-*m*-** and **-*p*-nitro-**, and their **α-acetyl** derivatives (CHATTAWAY and WALKER), i, 1194.
***O*-Benzoyldi*iso*butylhydroxylamine**, and its hydrogen sulphate (GAMBARJAN), i, 1260.
***O*-Benzoyldiethylhydroxylamine** hydrogen sulphate (GAMBARJAN), i, 1260.
5-Benzoyl-5:10-dihydrophenarsazine, 10-chloro- (BURTON and GIBSON), i, 85.
Benzoyldi-*p*-tolylamine (CHAPMAN), i, 1401.
Benzoyl-*l*-ecgonine, esters and their derivatives (WELLCOME FOUNDATION, LTD., GRAY and HENRY), i, 1446.
aromatic esters of, and their salts (GRAY), i, 829.
Benzoylenecarbamide, salts and derivatives of (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1325.
Benzoylethanol, chloro-*o*-bromo-*p*-amino- (FREJKA and VITHA), i, 1416.
Benzoylformhydroxamic acids, oximes of, and their derivatives (GASTALDI and REPOSSI), i, 987.
Benzoylformic acid, and its methyl ester xylylhydrazones (BUSCH and v. BEUST), i, 400.
Benzoylgalactosylamine, and its phenylhydrazone (FREUDENBERG and DOSER), i, 367.
Benzoylhydroperoxide. See Perbenzoic acid.
Benzoylmethylnitrolic acid, benzoyl derivative (RUGGERI), i, 79.
8-Benzoyl-α-naphthoic acid, preparation and properties of, and its derivatives (MASON), i, 33.
γ-Benzoyl-α-*p*-nitrophenylbutyronitriles, α-bromo- (ALLEN), i, 964.
2-Benzoyloxybenzaldehyde, *p*-nitro-, and its phenylhydrazone (ZETZSCHE, SILBERMANN, and VIRLI), i, 1411.
3-Benzoyloxybenzoic acid, *m*-hydroxy- (m-*diplosal*), and its derivatives (ANSCHÜTZ and KRONE), i, 668.
4-Benzoyloxybenzoyl chloride, *p*-hydroxy-, acetyl derivative, and its derivative (ANSCHÜTZ and ZERBE), i, 668.

δ-Benzoyloxy-Δ$^{\alpha\gamma}$-butadienealdehydes, γ-bromo-, γ-chloro-, and γ-iodo-, and their derivatives (BAUMGARTEN), i, 1381.

β-Benzoyloxybutyric acid, γ-amino-, picrate and ethyl ester (BERGMANN, MIEKELEY, WEINMANN, and KANN), i, 795.

2-Benzoyloxy-7-diphenylcarbamyloxynaphthalene (LESSER, KRANEPUHL, and SAD), i, 1426.

ζ-Benzoyloxy-*n*-heptan-γ-ol (HELFERICH and FRIES), i, 1039.

Benzoyloxymethyleneacetone semicarbazone (v. AUWERS and DANIEL), i, 1181.

***d*- and *l*-α-Benzoyloxypropionic acids**, ethyl esters (KENYON, PHILLIPS, and TURLEY), i, 507.

Benzoylphenylbenzylcarbinol. See Benzylbenzoin.

3-Benzoyl-5-phenylhydrazino-1:2:4-oxadiazole (RUGGERI), i, 79.

Benzoylphenylhydrazinoglyoxime (RUGGERI), i, 79.

γ-Benzoyl-β-phenyl-α-*p*-nitrophenylbutyronitrile (ALLEN), i, 964.

3-Benzoyl-2-phenyl-1-*p*-nitrophenyl-*cyclo*propanes, 1-cyano- (ALLEN), i, 964.

α-Benzoyl-γ-phenylpropionic acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.

1-Benzoyl-3-phenyl*iso*quinoline, 4-hydroxy-, and its acetyl derivative (WEISS and SONNENSCHEIN), i, 938.

β-Benzoylpropionic acid, α**β**-*di*bromo- (BOGERT and RITTER), i, 816.

Benzoylpyridines, nitro derivatives (TSCHITSCHIBABIN, KIUNDSHI, and BENEVOLENSKAJA), i, 1316.

2-Benzoylpyrrole, 3:4-*di*- and 3:4:5-*tri*-iodo- (TERENTIEV and TSCHELINCEV), i, 295.

***O*-Benzoylserine**, methyl ester (BERGMANN, MIEKELEY, WEINMANN, and KANN), i, 795.

Benzoyl-*p*-toluidide, *p*-hydroxy-, and its acetyl derivative (ANSCHÜTZ and ZERBE), i, 667.

1-Benzoyl-1:2:2-trimethyl-3-cyanomethyl*cyclo*pentane (HALLER and LEGAGNEUR), i, 683.

1-Benzoyl-1:2:2-trimethyl*cyclo*pentane-3-carboxylic acid, and its amide (HALLER and LEGAGNEUR), i, 683.

1-Benzoyl-1:2:2-trimethyl-3-phenacyl-*cyclo*pentane (HALLER and LEGAGNEUR), i, 683.

δ-Benzoylvaleric acid, *o*-amino-, acetyl and benzoyl derivatives (PATERSON and PLANT), i, 1147.

Benzoylveratroylacetic acid, ethyl ester (GULLAND and ROBINSON), i, 1188.

Benzoylveratroylmethane, and its copper salt (GULLAND and ROBINSON), i, 1188.

Benzthiazole, chloro-, *di*bromide (HUNTER), i, 987.

Benz*iso*thiazole, and its derivatives, and 2-amino- and 2-hydroxy- (STOLLÉ, GIESEL, and BADSTÜBNER), i, 1466.

Benzthiazoles, amino- (HUNTER), i, 1335.

Benzthiazole series (CLARK), i, 841.

Benz*iso*thiazole-2-carboxylic acid, and its derivatives (STOLLÉ, GIESEL, and BADSTÜBNER), i, 1466.

Benzthiopyrans, spectrochemistry of (KROLLPFEIFFER), ii, 1028.

Benzthiopyrone (*thiocoumarin*), and *mono*- and *di*-bromo-, and their derivatives (ARNDT), i, 1309.

Benzthiopyrone, 6-chloro- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.

1:2:3-Benztriazole-2:5′-salicylic acid, and its salts and acetyl derivative (ELBS), i, 163.

1:2:3-Benztriazone-3-phenyl-*p*-arsinic acid (KING and MURCH), i, 320.

Benzyl alcohol, condensation of phenol and (HUSTON), i, 249.

oxidation of, and its esters, in the organism (SNAPPER, GRÜNBAUM, and STURKOP), i, 467.

detection of, as oxalate (PFAU), ii, 905.

Benzyl alcohol, 2:6-*di*bromo-*p*-hydroxy- (KOHN and WEISSBERG), i, 655.

o:*p*-*di*hydroxy- (SEN and SARKAR), i, 812.

Benzyl chloride, *o*-hydroxy-, acetyl derivative (WELLCOME FOUNDATION, LTD., GRAY, and HENRY), i, 1446.

2:3:4-*tri*chloro-6-nitro-, and 2:4:6-*tri*nitro- (GANGULY), i, 647.

ethers, conversion of, into carbinols (SCHORIGIN), i, 1404.

chloro- and β-hydroxy-ethyl ethers (BENNETT), i, 883.

esters, substituted (BARKENBUS and HOLTZCLAW), i, 1148.

iodide, 2:4-*di*nitro- (CONANT, KIRNER, and HUSSEY), i, 494.

β-hydroxyethyl sulphide (FROMM and JÖRG), i, 352.

γ-Benzylacetylacetone (MORGAN and TAYLOR), i, 634.

α-Benzylacrylic acid (v. BRAUN and KÜHN), i, 1375.

Benzylallylbutyrophenone (HALLER, BAUER, and RAMART), i, 261.

Benzylallylpropiophenone (HALLER, BAUER, and RAMART), i, 261.
Benzylamine, salts of (MAZOUREVITCH), i, 1241.
hydroferricyanide (CUMMING), i, 122.
Benzylamines, nitro-, and their salts (HOLMES and INGOLD), i, 1142.
Benzylaniline, preparation of (NOLAN and CLAPHAM), i, 805.
reactions of antimony halides with (VANSTONE), i, 662.
Benzylanilines, nitro-, electrochemical reduction of (ELBS and GAUMER), i, 167.
Benzyl-*o*-benzoic acid, 2':6-*di*nitro- (QUAYLE and REID), i, 1289.
Benzylbenzoin (VILA and CEREZO), i, 557.
urethane of (SCHEUING and HENSLE), i, 27.
Benzylbenzoylacetone (TROTMAN), i, 383.
Benzylbenzoyl-*d*-ψ-ecgonine, and its salts (GRAY), i, 830.
Benzyl-β-benzoyloxyethylsulphone (FROMM and JÖRG), i, 352.
Benzyl-*p*-bromoaniline, *o*-hydroxy- (BAMBERGER), i, 142.
Benzylcarbamide, α-hydroxy-, and its salts (WOOD and LILLEY), i, 401.
β-Benzylcellobioside (HESS and SALZMANN), i, 1383.
Benzyl chloromethyl ketone, acetate of (LEWIS, NIERENSTEIN, and RICH), i, 936.
4-Benzylcoumarin, 7-hydroxy- (BAKER and ROBINSON), i, 1300.
Benzylcreatinines, and their picrates (GREENWALD), i, 840.
6-Benzyl-*o*-cresol (SCHORIGIN), i, 1404.
2-Benzyl-*p*-cresol, and its phenylcarbamate (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.
3-Benzyl-*p*-cresol (CLAISEN), i, 1410.
Benzyldeoxybenzoin, β-bromo- (PASCUAL VILA), i, 144.
γ-Benzyldextrose, and its di*iso*propylidene ether and osazone (FREUDENBERG, v. HOCHSTETTER, and ENGELS), i, 635.
α-Benzyl-α-diethylaminomethylacetoacetic acid, ethyl ester (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1249.
Benzyl-1:2-dihydrocoumarones, *penta*hydroxy-, and their acetyl derivatives (DEAN and NIERENSTEIN), i, 282.
2-Benzyl-1:5-dimethylpyrazolium iodide, 3-chloro- (v. AUWERS and NIEMEYER), i, 1178.
Benzyldimethyltetrahydroindazoles (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.
Benzyl-β-ethoxyethylsulphone (FROMM and JÖRG), i, 352.
Benzylethyldi-*m*-propylarsonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 496.
Benzyl-Δ¹-hexahydroanthracenes (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
2-Benzyl*cyclo*hexanone, 2-cyano-, and its semicarbazone (v. AUWERS, BAHR, and FREESE), i, 312.
***iso*Benzylhistamine**. See 4-Ethyl-1-benzylglyoxaline, 4-β-amino-.
Benzylhydrohydrastinine, and its hydrochloride (HAWORTH, PERKIN, and PINK), i, 1170.
Benzyl-*o*-hydroxybenzoyl-*l*-ecgonine, and its picrate (GRAY), i, 830.
Benzyl-β-hydroxyethylsulphone (FROMM and JÖRG), i, 352.
Benzylhydroxymethylbenzoyl-*l*-ecgonines (GRAY), i, 830.
Benzylideneacetohexoic acid (RYAN and SHANNON), i, 553.
Benzylideneacetone. See Styryl methyl ketone.
Benzylideneaminoacetic acid, and *o*-hydroxy-, salts of (BERGMANN, EUSSLIN, and ZERVAS), i, 891.
α-Benzylideneaminoglutaric acid, *o*-hydroxy-, barium and brucine salts (BERGMANN, EUSSLIN, and ZERVAS), i, 891.
5-Benzylideneaminophenanthraquinone (SIRCAR and GUPTA), i, 984.
7-Benzylideneaminophenanthraquinone, 2-amino-7-*o*-*mono*- and -7-*o*:*p*-*di*hydroxy- and -7-*m*-nitro-, and 2- and 4-*m*-nitro- (SIRCAR and GUPTA) i, 984.
***dl*-α-Benzylideneamino-β-phenylpropionic acid**, *o*-hydroxy-, barium salt (BERGMANN, EUSSLIN, and ZERVAS), i, 891.
Benzylideneaminosuccinic acid, *o*-hydroxy- and *p*-nitro-, salts of (BERGMANN, EUSSLIN, and ZERVAS), i, 891.
Benzylideneaniline, reaction of carbon disulphide with (BIGELOW) i, 242.
Benzylideneaniline, *o*-hydroxy-, copper salt (ZETZSCHE, SILBERMANN, and VIELI), i, 1411.
Benzylideneanisylidene-β-methyl*cyclo*hexanone, *p*-hydroxy-, and its salts (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 268.
Benzylidenebenzylamine *di*bromide (BERG), i, 817.

Benzylidenebenzylpyridines, and their salts (KOENIGS, KÖHLER, and BLINDOW), i, 834.
Benzylidene*iso*butylamine *di*bromide (BERG), i, 817.
Benzylidenecoumaranone, 2′-chloro-, and its dibromide (RÖTHLISBERGER), i, 572.
Benzylidenecreatinine, picrate and acetyl derivative of (GREENWALD), i, 840.
***iso*Benzylidenedeoxybenzoin**, preparation of (PASCUAL VILA), i, 144.
Benzylidenedibutyl ethers (ADAMS and ADKINS), i, 785.
Benzylidenedicarbamic acid, methyl ester (DATTA and CHATTERJEE), i, 892.
Benzylidenediethylene *tetra*sulphide, compounds of gold chloride with (RÂY), ii, 184.
Benzylidenedi-indone (RADULESCU and GEORGESCU), i, 1287.
Benzylideneglycylaminoacetic acid, and *o*-hydroxy-, barium salts (BERGMANN, EUSSLIN, and ZERVAS), i, 891.
Benzylidene*cyclo*hexanones, 2:6-*di*amino-, and their derivatives (PFEIFFER), i, 411.
2:6-*di*nitro- (PFEIFFER), i, 409.
α-Benzylidenehydrazino-β-aminoethane oxalate, and *α-o*-hydroxy- (SOMMER, SCHULZ, and NASSAU), ii, 990.
Benzylideneimine chlorostannate (SONN and MEYER), i, 932.
Benzylidenemalonic acid, menthyl ester (WAYNE and COHEN), i, 551.
Benzylidenemalonic acid, *p*-hydroxy-, ethyl ester (CHRZASZCZEWSKA), i, 956.
2-Benzylidene-1-methyldihydropyridine, 2-*di*nitro- (TSCHITSCHIBABIN, KUINDSHI, and BENEVOLENSKAJA), i, 1317.
Benzylidene-1-methyldihydropyridines, *p*-nitro- (KOENIGS, KÖHLER, and BLINDOW), i, 833.
Benzylidene-β-phenylethylamine, and its methiodide (OSADA), i, 284.
α-Benzylidene-α′(β-phenylethyl)succinic acid (BOUGAULT), i, 1152.
Benzylidene-*p*-toluidine, *o*-nitro- (HELLER and SPIELMEYER), i, 838.
β-Benzylideneundecane (THOMS and AMBRUS), i, 790.
2-Benzylindazole, *o*- and *p*-chloro-, and their picrates (v. AUWERS and PFUHL), i, 1101.
4-nitro- (v. AUWERS and FRESE), i, 1102.
1-Benzylindole-2-carboxylic acid (BODFORSS), i, 699.
α-Benzylmandelic acid (MALKIN and ROBINSON), i, 559.
1-Benzyl-3-methyl-2-allylpyrazolium iodide (v. AUWERS and DANIEL), i, 1180.
Benzylmethylamine, α-hydroxy-, and its derivatives (WOOD and LILLEY), i, 401.
Benzylmethylamines, nitro-, and their salts (HOLMES and INGOLD), i, 1143.
Benzylmethyl-β-bromoallylamine, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1401.
1-Benzyl-2-methyl-1:2-dihydro*iso*quinoline, 1-*o*-nitro- (GADAMER, OBERLIN, and SCHOELER), i, 576.
Benzylmethylindazoles, and their picrates (v. AUWERS and LOHR), i, 74.
Benzyl methyl ketone, 2:4-*di*nitro-, derivatives of (NEBER, HARTUNG, and RUOPP), i, 1073.
Benzyl methyl ketoximes, *o*-nitro-, isomeric, and their derivatives (NEBER, HARTUNG, and RUOPP), i, 1072.
Benzylmethylnonylcarbinol (THOMS and AMBRUS), i, 790.
Benzylmethylpropargylamine, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.
1-Benzyl-3-methylpyrazole, 4-bromo-5-chloro-, and 5-chloro-, and its hydrochloride (v. AUWERS and NIEMEYER), i, 1178.
1-Benzyl-5-methyl-3-pyrazolone (v. AUWERS and NIEMEYER), i, 1178.
4-Benzyl-3-methyl-5-pyrazolone (HIRST, MACBETH, and TRAILL), i, 1251.
Benzylmethyltetrahydroindazoles, and their picrates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.
1-Benzyl-2-methyltetrahydro*iso*quinoline, 1-*o*-amino-, salts of (GADAMER, OBERLIN, and SCHOELER), i, 576.
5-Benzyl-7-methylxanthen, 3:5-*o*:*p*-*tri*hydroxy- (SEN and SARKAR), i, 813.
Benzylnorhydrohydrastinine, and its salts (HAWORTH, PERKIN, and PINK), i, 1170.
Benzyl-*s*-octahydroanthracenes, and bromo- and hydroxy- (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
3-Benzyloxyanisole (SONN and PATSCHKE), i, 1280.
***p*-Benzyloxybenzoic acid**, ethyl ester (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 1473.
***o*-Benzyloxyphenyldi-α-naphthylcarbinol** (GOMBERG and MCGILL), i, 1270.
***o*-Benzyloxyphenyldi-α-naphthylfluorene** (GOMBERG and MCGILL), i, 1270.

o-**Benzylphenol**, and its phenylurethane (CLAISEN), i, 1410.
6-Benzylphenthiazine (DESAI), i, 388.
1-Benzyl-5-β-phenylethyl-5-ethylbarbituric acid (DOX), i, 301.
Benzyl-β-phenylethylsuccinic acids (BOUGAULT), i, 921, 1152.
Benzylpyridines, and *p*-nitro-, and their salts (KOENIGS, KÖHLER, and BLINDOW), i, 833.
Benzylpyridines, amino, hydroxy, and nitro derivatives, and their derivatives (TSCHITSCHIBABIN, KUINDSHI, and BENEVOLENSKAJA), i, 1316.
2-Benzyl pyrryl ketone, and its derivatives (ODDO), i, 296.
Benzylresorcinol (HIRZEL), i, 393.
N-**Benzylsuccinimide** (CHERBULIEZ and SULZER), i, 1252.
4-Benzyl*cyclo*telluropentane-3:5-dione, and its dioxime (MORGAN and TAYLOR), i, 634.
1-Benzyl-5:6:7:8-tetrahydroanthracene (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
1-Benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (FORSYTH, KELLY, and PYMAN), i, 1167.
3-Benzylthioldiphenyl-1:2:4-triazoles (FROMM and TRUKA), i, 704.
Benzyl-*p*-toluidine, *o*-nitro- (ELBS and GAUMER), i, 168.
Benzyltriethylammonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 495.
Benzyltriethylphosphonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 496.
Benzyltropyl-*l*-ecgonine, and its salts (GRAY), i, 829.
Benzylxanthone (CONANT and SLOAN), i, 955.
Benzylxanthyl *per*chlorate (CONANT and SLOAN), i, 955.
Berberine, imino-, and its hydrochloride (HAWORTH, PERKIN, and PINK), i, 1170.
Beryllium, preparation of (STOCK, PRAETORIUS, and PRIESS), ii, 1090.
Beryllium compounds, isomorphism of magnesium compounds and (ZAMBONINI and CAROBBI), ii, 144.
Beryllium halides, densities of (MESSERKNECHT and BILTZ), ii, 1141.
ammoniates of (BILTZ and MESSERKNECHT), ii, 1183.
hydroxide, adsorption by (KLEEBERG), ii, 956.
precipitation of, electrometrically (BRITTON), ii, 1203.
oxide, various states of (COPAUX and MATIGNON), ii, 1192.
Beryllium oxide, solubility of, in water (REMY and KAUFMANN), ii, 119.
oxide and sulphate, heats of formation and solution of (MARCHAL), ii, 370.
sulphate and its hydrates (KRAUSS and GERLACH), ii, 314.
Beryllates, complex (ROSENHEIM and LEHMANN), ii, 220.
Beryllium organic compounds:—
Beryllium benzoylcamphor, mutarotation of, and its compound with chloroform (BURGESS and LOWRY), i, 46.
chloride, complex compounds of, with organic compounds (FRICKE and RUSCHHAUPT; FRICKE and HAVESTADT), ii, 886.
***iso*Betelphenol**. See 4-Methoxypropenylbenzene, 3-hydroxy-.
Bile, effect of salts of, on substances adsorbed by blood proteins (ROSENTHAL), i, 1203.
action of, on pancreatic digestion of proteins (ROSENOV), i, 1507.
calcium in (DITTRICH; DRURY), i, 325.
excretion of phthaleins in (ROSENTHAL and WHITE), i, 101.
goat's, and a calculus therefrom (SCHENK), i, 854.
human and ox, constituents of (WIELAND and JACOBI), i, 1488.
sheep's, choleic acid in (SCHENCK), i, 1488.
Bile acids (WIELAND and REVEREY), i, 181; (WINDAUS, BOHNE, and SCHWARZKOPF), i, 405; (SCHENK), i, 854, 1488; (WIELAND), i, 1065; (WIELAND and JACOBI), i, 1488.
structure of, in relation to their depressant action (MACHT, GROLLMAN, and HYNDMAN), i, 1355.
action of bacteria on (LICHT), i, 478.
and their salts, compounds of lecithin with (BOEHRINGER SOHN), i, 824.
determination of (HERZFELD and HAEMMERLI), i, 722.
Bile pigments (KÜSTER, HAAS, and MAURER), i, 307; (KÜSTER and HAAS), i, 722; (FISCHER and NIEMANN), i, 1198.
formation of, in surviving organs (ERNST and SZAPPANYOS; ERNST; ERNST and FÖRSTER), i, 732.
formation of hæmoglobin from (RICH), i, 711.
Bile salts, action of, on gelatin (STUCKERT), ii, 392.
determination of, in blood (SZILÁRD), i, 1485.
Bilirubin, formation of, from hæmoglobin (RICH and BUMSTEAD), i, 1482.

Bilirubin, preparation of (KÜSTER and HAAS), i, 722.
identity of hæmatoidin and (RICH and BUMSTEAD), i, 1475.
fluorescent oxidation products of (ADLER), i, 328.
detection of (BARRENSCHEEN and WELTMANN), i, 187.
detection of, in fæces (ADLERSBERG and PORGES), i, 98.
Binary systems, effect of substitution on equilibria in (KREMANN and DRAZIL), ii, 649; (KREMANN, ZECHNER, and WEBER; KREMANN, ZECHNER, and DRAZIL), ii, 650.
investigation of, by addition of a third component (FREETH), ii, 669.
crystallisation in (RUER), ii, 125.
organic, equilibria in (KITRAN), ii, 533.
Bioelectric cells. See under Cells.
Biological oxidation. See Oxidation.
Bios (TANNER), i, 617.
formation of, in infusions of barley and maize (EASTCOTT), i, 1017.
preparation and purification of (SIMS), i, 1017.
Bioses from lichenin, and their acetates (PRINGSHEIM, KNOLL, and KASTON), i, 1386.
Biosterin. See Vitamin-*A*.
Bisabolene, synthesis of (RUZICKA and CAPATO), i, 943.
Bisallylaminobenzoquinone (HARGER), i, 25.
Bis(aminomethyl)-benzenedicarboxylic acids, dilactams (DE DIESBACH and ZURBRIGGEN), i, 1427.
Bisamylaminobenzoquinone (HARGER), i, 25.
Bisazopyrrolenephthalide (ODDO and MINGOIA), i, 978.
Bisazopyrrolephthalein (ODDO and MINGOIA), i, 978.
1:1-Bisbenzthiazole *tetra*bromide (HUNTER), i, 987.
Bisbenzylaminobenzoquinone(HARGER), i, 25.
Bis(bromomethyl)benzenedicarboxylic acids, and their derivatives (DE DIESBACH and ZURBRIGGEN), i, 1427.
Bis(*di*bromomethyl)benzenedicarboxylic acids, and their derivatives (DE DIESBACH and ZURBRIGGEN), i, 1427.
Bis-*iso*- and -*sec.*-butylaminobenzoquinones (HARGER), i, 25.
Bis-(carbethoxy-2:3-dimethylpyrryl)-methanes (FISCHER and BELLER), i, 1334.
Bis-(4-carbethoxy-2:3-dimethylpyrryl)-methene hydrochloride (FISCHER and BELLER), i, 1333.
Bis-1-*p*-chlorophenyl-3-methyl-5-pyrazolone (CHATTAWAY and STROUTS), i, 71.
α-2:3-Bisdeoxyglucose, derivatives of (BERGMANN), i, 887.
4:4′-Bis(dicarbomethoxyhydrazino)diphenyl (STOLLÉ and ADAM), i, 1469.
2:7-Bis(dicarbomethoxyhydrazino)fluorene (STOLLÉ and ADAM), i, 1469.
1:1′-Bisdihydronaphthyl, and its dibromide (SCHROETER, ZADEK, and HOFFMANN), i, 677.
Bisdi-indonylmethane (RADULESCU and GEORGESCU), i, 1287.
Bisdi-α-naphthafluorenyl (MAGIDSON), i, 384.
Bisdi-α-naphthafluorenylene, and *di*bromo- (MAGIDSON), i, 385.
Bis-α-ethoxy-α-ethylbutyrylcarbamide (NEWBERY), i, 376.
Bisethylaminobenzoquinone (HARGER), i, 25.
Bis(hydroxymethyl)benzenedicarboxylic acids, dilactones of (DE DIESBACH and ZURBRIGGEN), i, 1427.
Bis-3-hydroxy-β-naphthoyldianisidine (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 599.
Bis-3-hydroxy-β-naphthoyldiphenetidine (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 599.
9:9′-Bis-*p*-hydroxyphenyl-10-keto-9:10-dihydrophenanthrene (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
9:9′-Bis-*p*-hydroxy-*m*-tolyl-10-keto-9:10-dihydrophenanthrene (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
Bisimmonium bromides, action of ammonia on (v. BRAUN and ZOBEL), i, 1455.
Bismethylaminobenzoquinone (HARGER), i, 24.
2:3:10:11-Bismethylenedioxy-7:8-dihydroprotoberberine, and its picrate (BUCK, PERKIN, and STEVENS), i, 959.
6:7:3′:4′-Bismethylenedioxy-9-hydroxyprotopapaverine (BUCK, PERKIN, and STEVENS), i, 959.
6:7:3′:4′-Bismethylenedioxy-9-keto-3:4-dihydroprotopapaverine, and its derivatives (BUCK, PERKIN, and STEVENS), i, 959.
6:7:3′:4′-Bismethylenedioxy-9-ketoprotopapaverine, and its derivatives (BUCK, PERKIN, and STEVENS), i, 959.
2:3:10:11-Bismethylenedioxyoxyprotoberberine (BUCK, PERKIN, and STEVENS), i, 959.

2:3:10:11-Bismethylenedioxyproto-berberine, and its salts (BUCK, PERKIN, and STEVENS), i, 958.
6:7:3′:4′-Bismethylenedioxyproto-papaverine, synthesis of, and its picrate (BUCK, PERKIN, and STEVENS), i, 958.
6:7:3′:4′-Bismethylenedioxy-1:2:3:4-tetrahydroprotopapaverine, and its salts (BUCK, PERKIN, and STEVENS), i, 958.
Bismuth, atomic weight of (CLASSEN and STRAUCH), ii, 175.
absorption spectrum of the vapour of (NARAYAN and RAO), ii, 927.
absorption and fluorescence spectra of (RAO), ii, 473.
spectral lines of (JOOS), ii, 612.
electro-deposition of (BAYERLE), ii, 675.
thermal expansion of crystals of (ROBERTS), ii, 94.
single crystal rods of, thermo-electric force of (BRIDGMAN), ii, 1136.
effect of *X*-rays on crystallisation of (ADINOLFI), ii, 485.
colloidal (GUTBIER and KAUTTER), ii, 860.
chemistry and physiology of (KÜRTHY and MÜLLER), i, 100; (KÜRTHY), i, 101.
Bismuth alloys with antimony (OTANI), ii, 533.
with cadmium or tin and lead, hardness of (DI CAPUA), ii, 1051.
with mercury, electrolysis of (KREMANN, KAPAUN, and BUDAN), ii, 313.
Bismuth compounds, fixation of, in organs (LISSIEVICI-DRAGANESCO), i, 465.
physiological action of (FRITZ), i, 334.
action of, in syphilis (LEVADITI, NICOLAU, SALGUE, and SCHOEN), i, 463.
Bismuth salts, action of, on red blood corpuscles (SIMON), i, 1500.
action of, on *Staphylococcus*, *Streptococcus*, and *Bacillus coli* (LEMAY and JALOUSTRE), i, 206.
complex (MÜLLER and KÜRTHY), ii, 61.
Bismuth carbonate, physical condition of (JONES), ii, 994.
*di*hydride (WEEKS and DRUCE), ii, 988.
*tri*hydride (WEEKS and DRUCE), ii, 1188.
hydroxide, peptisation of (KUHN and PIESCH), ii, 525.
nitrates, effect of vacuum and of heat on (PICON), ii, 1188.
Bismuth oxychloride, equilibrium of water and (WARIS), ii, 786.
selenide (MOSER and ATYNSKI), ii, 584.
sulphide, reaction between hydrochloric acid and (RAMACHANDRAN), ii, 1208.
precipitation of, from acid solutions (RAMACHANDRAN), ii, 1005.
Bismuth organic compounds (MASCHMANN), i, 527; (SUPNIEWSKI), i, 1473.
with pyrocatechol (ROSENHEIM and BARUTTSCHISKY), i, 808.
cacodyl, existence of (GANASSINI and SANTI), i, 893.
tri- and tri-*m*-nitro-phenyl dinitrates (VORLÄNDER), i, 1255.
Bismuth detection, determination, and separation:—
detection of (FEIGL), ii, 435.
determination of (KÜRTHY and MÜLLER), ii, 73.
determination of, electrometrically (ZINTL and RAUCH), ii, 442.
determination of, electro-volumetrically (ZINTL and RAUCH), ii, 1004.
determination of, in blood, organs, and excreta (AUTENRIETH and MEYER), i, 182.
determination of, in urine (KÜRTHY and MÜLLER), i, 100.
determination and separation of (GIRARD and FOURNEAU), ii, 1207.
determination of, and separation from lead (FEIGL and ORDELT), ii, 442.
separation of lead and (LASSIEUR), ii, 159.
Bis-nitropyrocatecholboric acids, salts of (MEULENHOFF), i, 541.
Bis(1-phenyl-4-methylpyrazolyl)ethane (FISCHER and NIEMANN), i, 1198.
Bistrimethylstibine*di*chloropalladium (MORGAN and YARSLEY), i, 378.
Bistrimethylstibine*di*chloroplatinum (MORGAN and YARSLEY), i, 378.
Blackberry, acids of (NELSON), i, 618.
Blende, crystal structure of diamond and (BECKENKAMP), ii, 271.
Blood, effect of irradiation on (KROETZ), i, 178.
effect of Röntgen rays on (KONRICH and SCHELLER), i, 1356.
effect of Röntgen rays on the acid-base equilibrium in (PAGNIEZ, COSTE, and SOLOMON), i, 1201.
hydrogen-ion concentration in (GIGON), i, 1219; (BIGWOOD), i, 1342; (HOU), i, 1483.
of normal and cancer subjects (CORRAN and LEWIS), i, 188.

Blood, relation between reaction and ionic equilibrium of (GOLLWITZER-MEIER), i, 1482.
effect of ionic equilibria in, on the respiratory centre (GOLLWITZER-MEIER), i, 177.
effect of alkalinity of, on respiration (GOLLWITZER-MEIER), i, 177.
transport of oxidised carbon from tissues to (COLLINGWOOD), i, 451.
capillary exchange in (HENDERSON and MURRAY), i, 1483.
oxygen supply and exchange in (MURRAY and MORGAN), i, 1481.
fresh, putrefied, and frozen, gases in (KOHN-ABREST), i, 604.
eosinophile granule substance of (NEUMANN), i, 94.
ultra-filtration of (BLUM and DELAVILLE), i, 605.
sedimentation of red corpuscles in (BERCZELLER and WASTL), i, 452.
method for taking samples of (FRITZ and PAUL), i, 1486.
replacement of, by gum arabic solutions (UCKI), i, 177.
coagulation of (STUBER and LEE), i, 94; (STUBER and KUHN), i, 452; (WÖHLISCH), i, 452, 1486.
action of potassium salts on (OSAPÓ and v. KLOBUSITZKY), i, 717.
action of zinc salts on (LUMIÈRE and COUTURIER), i, 717.
in cold-blooded animals (ŠAHOVIĆ), i, 716.
anticoagulants for (LUMIÈRE), i, 606.
effect of sunlight on complement in (JACOBY and JACOBY), i, 178.
effect of anaphylactic shock on constituents of (BLUM, DELAVILLE, and CAULAERT), i, 188.
in tropical regions and in avitaminosis, constituents of (VAN BERKHOUT), i, 453.
constituents of, and serum in cancer (THEIS and BENEDICT), i, 724.
chemistry of, during excitation of the digestive glands (ONOHARA), i, 712.
chemistry of, during ingestion of food (ONOHARA), i, 322.
composition of, in labour (WILLIAMS), i, 713.
mineral composition of, in narcosis (BLANCHETIÈRE and CARDOT), i, 455.
mineral constituents of, in rickets (ACKERSON, BLISH, and MUSSEHL), i, 609.
chemistry of, during sleep (GOLLWITZER-MEIER and KROETZ), i, 322.
acetaldehyde in (FABRE), i, 852.
Blood, acetone substances in (HUBBARD and NOBACK), i, 712.
adenine nucleotide from (HOFFMAN), i, 711, 851.
aldehydes in (FABRE), i, 324.
behaviour of amino-acids in (ROSENBAUM), i, 464.
adsorption of amino-acids by (SBARSKY and MUCHAMEDOFF), i, 451.
ammonia in (PARNAS and HELLER), i, 323, 454; (PARNAS), i, 454; (PARNAS and TAUBENHAUS), i, 1484.
arsenic in, after injection of salvarsan (FORDYCE, ROSEN, and MYERS), i, 189.
calcium in (GYÖRGY; JANSEN), i, 324; (KYLIN and SILFVERSVÄRD), i, 852; (CAMERON and MOORHOUSE), i, 857.
effect of removal of endocrine glands on (LEITES), i, 95.
effect of hypnotic suggestion on (GLASER), i, 860.
normal and tuberculous (MATZ), i, 1492.
distribution of calcium and phosphate ions in (GYÖRGY), i, 322.
effect of hæmolysis on the calcium and phosphorus in (WANG and FELSHER), i, 995.
influence of vitamins on phosphates and calcium in (v. EULER and MYRBÄCK), i, 1515.
calcium, potassium, and sodium in, after ovariectomy (BLANCHETIÈRE), i, 1207.
carbon monoxide in (NICLOUX), i, 321.
distribution and exchange of chlorine in (BURGER), i, 710.
dextrose in, in health and in diabetes (LUNDSGAARD and HOLBØLL), i, 1206, 1207, 1494.
action of drugs on (ETS), i, 734.
fat and cholesterol in, in pathological conditions (HECKSCHER; BING and HECKSCHER), i, 999.
fats and lipoids in (IWATSURU), i, 1515.
increase of globulins in, in hæmolysis (REYMANN), i, 1345.
effect of injection of histamine on (HASHIMOTO), i, 1005.
effect of insulin on the composition of (MAZZOCCO and MORERA; SAVINO), i, 482.
iron in, in scurvy (MOURIGNAND, LEULIER, and MICHEL), i, 330.
lactic acid in, at high altitudes (LAQUER), i, 324.

Blood, lactic acid in, effect of adrenaline on (CORI), i, 753.
effect of insulin on (CORI), i, 753; (BEST and RIDOUT), i, 754; (COLLAZO and LEWICKI), i, 870.
effect of insulin on lactic acid and hydrogen-ion concentration in (KUHN, BAUR, and HECKSCHER), i, 343.
effect of aliphatic compounds on lactic acid and sugar in (KNOOP and JOST), i, 180.
effect of injection of urea on non-protein nitrogen of (SCHILL and KUNZE), i, 712.
changes in the phosphorus in (BIERRY and MOQUET), i, 454.
hydrolysis of the phosphoric esters of (MARTLAND), i, 454.
relation of phosphates in, to carbohydrate metabolism (BOLLIGER and HARTMAN), i, 1000.
variations in phosphoric acid during glycolysis in (PIAZZA), i, 1486.
new phosphoric acid derivative from (GREENWALD), i, 712.
propepsin in (GOTTLIEB), i, 742.
proteins of, and their determination (HUECK), i, 1484; (HOLM and TOMASSON), i, 1485.
changes in proteins of plasma in hydration of (PETERS, EISENMAN, and BULGER), i, 1490.
solubility of silver salts in (v. NEERGAARD), i, 1357.
sugar in (VISSCHER; SCOTT and BEST), i, 1343.
distribution of (HÖGLER and UEBERRACK), i, 453; (FOCK and HOLBØLL), i, 1486.
tables for (DREYFUSS), i, 94.
effect of dextrose administration on (ALBRITTON), i, 463.
effect of dihydroxyacetone on (RABINOVITSCH), i, 1352.
relations of, to glycogen (PRINGSHEIM), i, 605.
effect of injection of glucoses on (LIPMANN and PLANELLES), i, 179.
in presence of insulin (HÄUSLER and LOEWI), i, 753.
action of santonin on (STASICK), i, 1501.
after removal of the spleen (BIERRY, RATHERY, and LEVINA), i, 857.
non-protein sulphur of (KAHN and POSTMONTIER), i, 999.
influence of adrenaline on concentration of urea in (DUBOIS and POLONOVSKI), i, 481.
Blood, variations in urea in, due to deficiency of vitamin-*C* (RANDOIN and MICHAUX), i, 751.
urea in, after sarcoma inoculation and exposure to *X*-rays (DODDS, LAWSON, and MOTTRAM), i, 1492.
uric acid in (LENNOX and O'CONNOR), i, 711.
effect of fat diet on (HARDING, ALLIN, EAGLES, and VAN WYCK), i, 604.
influence of sodium chloride on (HARDING, ALLIN, and VAN WYCK), i, 94.
arterial, carbon dioxide in alveolar air and (BOCK and FIELD), i, 93.
and venous, oxygen and carbon dioxide in (STEWART), i, 451.
capillary, carbon dioxide content of (VERZÁR and VÁSÁRHELYI), i, 178.
of lactating cows, sugar in (WIDMARK and CARLENS), i, 608.
of children, calcium and phosphorus content of (ANDERSON), i, 188.
sugar content of (BROWN), i, 994.
dogs', constituents of (HADEN and ORR), i, 1484.
*iso*agglutinins in (MCENERY, IVY, and PECHOUS), i, 1344.
determination of urea in (VARTEJEANU), i, 1113.
of fish, sugar in (MCCORMICK and MACLEOD), i, 856.
goats', sugar in (SCHUHECKER), i, 715.
guinea-pigs', hydrogen carbonate and hydrogen ions in, in scurvy (LEPPER and ZILVA), i, 1208.
human, sugar and fat in (ARNOLDI and COLLAZO), i, 179.
infants', cholesterol in (BANU, NEGRESCO, and HERESCO), i, 452.
of infants and children, amino-acid content of (HOEFFEL and MORIARTY), i, 1484.
insects', hydrogen-ion concentration in (GLASER), i, 853.
of invertebrates, ionic reaction of (DUVAL), i, 325.
of ruminants, phosphorus content of (KAY), i, 994.
seal's (SUZUKI), i, 1345.
whale's (OKAHARA; MASUMIZU), i, 1349.
Blood detection and determination:—
analysis of (LATHAM), i, 1343.
analysis of the "primary ether extract" of (BING and HECKSCHER), i, 995.
analysis of, in asthma, hay fever, etc. (RAMIREZ, ST. GEORGE, and MOSES),

Blood detection and determination :—
detection of bromine in (BERNHARDT and UCKO), i, 454.
detection of poisonous gases in (KOHN-ABREST), i, 451.
determination of, in fæces (VAN ECK), i, 187.
determination of ammonia and urea in (MURRAY), i, 710.
determination of bile salts in (SZILÁRD), i, 1485.
determination of bismuth in (AUTENRIETH and MEYER), i, 182.
determination of calcium in (STANFORD and WHEATLEY), i, 1199.
determination of calcium in, and blood serum (BUDDE and FREUDENBERG; CLARK and COLLIP; SALVESEN), i, 713.
determination of calcium and phosphorus in (MYRBÄCK), i, 1485.
determination of carbon monoxide in (TERVAERT), i, 710.
determination of carbon dioxide in (HOLLÓ and WEISS), i, 95.
determination of chlorides in (BENGUEREL), i, 455; (RODILLON), i, 722; (MISLOWITZER and VOGT), i, 1485.
determination of cholesterol in (TOMINAGA), i, 453; (SACKETT), i, 995.
determination of cyanates in (MONTGOMERY), i, 455.
determination of dextrose in (MILROY), i, 1486.
determination of fat in (STEWART and WHITE), i, 1485.
determination of formic acid in (DE EDS), i, 713.
determination of hydrogen-ion concentration of, with cresol-red (HIRSCH), i, 606.
determination of hydrogen ions, carbon dioxide tension, and hydrogen carbonate in (HOLLÓ and WEISS), i, 709.
determination of lecithin in (GRIGAUT), i, 453.
determination of nitrogen in, by Folin's method (OSBORN), i, 323.
determination of oxygen and carbon dioxide in (BURWELL and ROBINSON), i, 604.
determination of organic substances in (BÁLINT and RUSZCZYNSKI), i, 323.
determination of phenol and cresol in (HAAS and SCHLESINGER), i, 334.
determination of phosphates in (MCCLUSKEY), i, 605.
Blood detection and determination :—
determination of phosphorus compounds in (STANFORD and WHEATLEY), i, 1200.
determination of lipoid phosphorus in (WHITEHORN), i, 95.
determination of reducing substances in (HILLER, LINDER, and VAN SLYKE), i, 1200.
determination of sodium in (HADEN), i, 1112.
determination of sugar in (BIERRY and MOQUET; GILBERT and BOCK; CALVERT), i, 179; (PATON), i, 180; (DINGEMANSE), i, 323; (DIAZ and CUENCA), i, 453; (DRESEL and ROTHMANN; CONDORELLI), i, 714; (LORBER), i, 852; (BENEDICT), i, 994; (TERVAERT), i, 1200.
determination of urea in (KARR), i, 323; (REHBERG; ROIG and HELMHOLTZ), i, 853; (ADDIS; VARTEJEANU), i, 1113; (PATTERSON), i, 1200.
determination of urea and sugar in (GRUSKIN), i, 1113.
determination of uric acid in (BULMER, EAGLES, and HUNTER; GARRY), i, 605; (BENEDICT), i, 995; (DELAVILLE and JONES), i, 1344.
Blood-corpuscles, viscosity of suspensions of (BERCZELLER and WASTL), i, 452.
effect of narcotics on the rate of sinking of (BAUMECKER), i, 321.
acidity of (DESGREZ, BIERRY, and LESCŒUR), i, 604.
sugar in (RICHTER-QUITTNER), i, 95.
mammalian, glutathione in (HOLDEN), i, 1484.
red, rate of sinking of (v. KLOBUSITZKY), i, 710.
valency of cations and anions on (OLIVER and BARNARD), i, 94.
action of bismuth on (SIMON), i, 1500.
naphthol reaction of (LOELE), i, 1342.
Blood pigments (KÜSTER and HEESS), i, 992; (SCHUMM), i, 1347.
constitution of (FRIEDLI), ii, 179.
acid scission products of (FISCHER and KLARER), i, 577.
oxido-reductions by (LIPSCHITZ), ii, 1070.
porphyrins from (PAPENDIECK and BONATH), i, 711.
Blood-plasma, physical properties of (ROFFO and CORREA), ii, 293.
development of (PICKERING and GLADSTONE), i, 1343.
mineral content of (RICHTER-QUITTNER), ii, 178.

Blood-plasma in renal disease, alkali salts in (RABINOVITCH), i, 462.
phosphorus and calcium in, during callus development of a fracture (SATANOVSKI), i, 1208.
determination of bicarbonates in (LEPPER and MARTIN), i, 1201.
determination of uric acid in (DELAVILLE and JONES), i, 1201.
Blood-serum, structure of (HANDOVSKY), i, 715.
refractive index and protein content of (BELTZ and KAUFMANN), i, 1200.
influence of alcohol on viscosity of (HAYASHI), ii, 663.
colloid constituents of (HANDOVSKY), i, 322.
concentration of inorganic constituents of, and cerebro-spinal fluid (HAMILTON), i, 1352.
distribution of ions in (RONA, PETOW, and WITTKOWER), i, 94; (RONA, HAUROWITZ, and PETOW), i, 95.
bone-forming elements in (PETERSON), i, 715.
effect of ultra-violet light on calcium in (MORITZ), i, 995.
porphyrins in (PAPENDIECK), i, 96.
proteins of (GROMELSKI), i, 95.
action of chloral hydrate on (NEŠKOVIĆ), i, 716.
action of formaldehyde on (HENLEY), i, 716.
influence of coagulation time of blood on toxicity of (LUMIÈRE and COURJON), i, 853.
determination of hydrogen ions in (CULLEN and BIILMANN), i, 1201.
determination of lipoids in (MINOVICI and ILIESCO), i, 452.
determination of potassium in (LEBERMANN), i, 96, 714.
determination of sodium in (LEBERMANN), i, 324.
Bodies, black, for use in calibration of pyrometers (ROBERTS), ii, 756.
Boiling, prevention of bumping while (REBBECK), ii, 996.
Boiling point, relation between melting point, critical temperature, and (PRUD'HOMME), ii, 99.
additive properties of (VAN ARKEL and DE BOER), ii, 758, 1141; (VAN LAAR), ii, 1141.
of fused salts (LORENZ and HERZ), ii, 276.
of organic compounds, influence of hydrogen and halogens on (VAN ARKEL and DE BOER), ii, 758.
of paraffin hydrocarbons, chart for (BAHLKE and WILSON), ii, 73.
Boletus granulatus, sterol from (MARSTON), i, 346.
Bomb, calorimetric. See Calorimeter, bomb.
Bone, chemistry of growth of (HAMMETT), i, 1001, 1208.
calcification of (HOLT, LA MER, and CHOWN; HOLT), i, 1209.
effect of excess of calcium on formation of (KORENCHEVSKI), i, 1355.
fixation of calcium and phosphorus in (TELFER), i, 859.
effect of calcium and sodium glycerophosphates and sodium dihydrogen phosphate on the formation of, in rachitic rats (KORENCHEVSKI and CARR), i, 464.
defective formation of, in rickets (ROBISON and SOAMES), i, 462.
hexosephosphoric esters in development of (MARTLAND and ROBISON), i, 201.
effect of yellow phosphorus on (BERNHARDT and RABL), i, 1357.
effect of callus formation in fracture of, on blood plasma (SATANOVSKI), i, 1208.
exhumed, protein in (KERNBACH), i, 326.
determination of calcium and phosphates in (v. EULER and JOHANSSON), i, 1489.
Borates. See under Boron.
Borax. See Sodium borate.
Boric acid. See under Boron.
Borneol, rotatory power of (LOWRY and CUTTER), ii, 356.
l-**Borneol** from spruce turpentine (WHEELER and HARRIS), i, 1437.
*iso***Borneol**, active, preparation of (VAVON and PEIGNIER), i, 1079.
β-**Borneolpropionic acid**, and its isomeride and lactone (RUPE and TSCHOPP), i, 1079.
γ-**Borneolpropyl alcohol**, and its derivatives (RUPE and TSCHOPP), i, 1079.
Bornyl esters, rotation of (KENYON and PRISTON), i, 942.
*iso***Bornylane**, and its derivatives (NAMETKIN), i, 47.
Bornylenecarboxylic acid, esters of (RUPE and VONAESCH), i, 499.
α-**Bornylene ethyl** and **methyl ketones**, and their derivative (RUPE and KOPP), i, 274.
*tert.-iso***Bornylol** (NAMETKIN, ABAKUMOVSKI, and SELIVANOV), i, 48.
*iso***Bornylone** (NAMETKIN, ABAKUMOVSKI, and SELIVANOV), i, 48.
Borodisalicylic acid, salts of (MEULENHOFF), i, 542.
strychnine salt (MEULENHOFF), i, 920.

Boron, atomic weight of (BRISCOE and ROBINSON), ii, 346; (BRISCOE, ROBINSON, and STEPHENSON), ii, 619.
structure and valency of (WAHL), ii, 937, 938.
valency of (RÂY), ii, 267.
and its *sub*oxide, preparation of (KAHLENBERG), ii, 425.
series spectra of (BOWEN and MILLIKAN), ii, 1013.
Boron compounds, valency in (MÜLLER), ii, 841.
Boron chlorides (STOCK, BRANDT, and FISCHER), ii, 571.
nitride, luminescence of (TIEDE and TOMASCHEK), ii, 931.
*mon*oxide, spectrum of (MULLIKEN), ii, 346.
*trio*xide, thermal expansion of (SAMSOEN), ii, 1051.
Boric acid, constitution and derivatives of (HERMANS), i, 500; ii, 697.
equilibrium of chromium trioxide, water, and (GILBERT), ii, 869.
solubility of mixtures of, with mannitol and with *cis*-tetrahydronaphthalene-1:2-diol (HERMANS), i, 501.
phosphors of (MICKWITZ), ii, 476.
osmosis of, through the skin (KAHLENBERG), i, 101.
determination of, with invert-sugar (GILMOUR), ii, 68.
determination of, volumetrically (CIKRTOVÁ and ŠANDERA), ii, 714.
determination of, in presence of aluminium iron or chromium (FUNK and WINTER), ii, 714.
Orthoboric acid, volatility of, in steam (ANSCHÜTZ and RIEPENKRÖGER), ii, 1084.
Borates, absorption spectra of beads of (SCHAUM and FUNCK), ii, 178.
of the alkali metals (AUGER), ii, 697.
complex (ROSENHEIM), i, 31.
Perborates, electrolytic preparation of (BODFORSS and ARSTAL), ii, 414.
Boron organic compounds:—
Boric acid, complex compounds of (MEULENHOFF), i, 541.
compounds of pyrocatechol and (WEIL and ADLER), i, 136; (BÖESEKEN and MIJS), i, 911.
Boron determination:—
determination of, in tungsten (BROPHY), ii, 901.
Boronia safrolifera, oil from (PENFOLD), i, 688.
Boswellia serrata, gum from (FOWLER and MALANDKAR), i, 1437; (MALANDKAR), i, 1438.
Brain, carbohydrate content of (TAKAHASHI), i, 1487.
carbohydrate metabolism of (B. E. and E. G. HOLMES), i, 1001, 1495.
hypoglycæmia and carbohydrate metabolism of (ASHER and TAKAHASHI), i, 331.
phosphatides of (THIERFELDER and KLENK), i, 997.
human, constituents of (LEMATTE and BEAUCHAMP), i, 1487.
hypocerebric acid from (FRÄNKEL and KARPFEN), i, 720.
rabbits', aminogenesis in, during hunger (PALLADIN and BJELJAEVA), i, 190.
determination of lipins in (GORODISSKY), i, 1487.
Brass, corrosion of, in sea-water (BENGOUGH and MAY), ii, 218.
influence of lead and tin on the brittle ranges of (BUNTING), ii, 282.
electrolytic, Röntgen ray analysis of (NAKAMURA), ii, 745.
Brazilin, constitution of, and its derivatives (PFEIFFER, OBERLIN, and KONERMANN), i, 1303.
Bread, brown and white, in the diet of rats (HARTWELL), i, 211.
Brilliant Congo R, preparation of (PALKIN and EVANS), i, 599.
Bromates. See under Bromine.
Bromine, atomic weight of (MOLES), ii, 346; (ROBINSON and BRISCOE), ii, 620.
chemical constants of (WOHL), ii, 98.
and its specific heat at low temperatures (SUHRMANN and V. LÜDE), ii, 96.
photochemical combination of hydrogen and (BODENSTEIN and LÜTKEMEYER), ii, 218.
photochemical combination of unsaturated hydrocarbons with (PLOTNIKOV), ii, 985.
photochemical reaction between tartaric acid and (GHOSH and MUKHERJEE), ii, 1179.
Budde effect in (LUDLAM), ii, 470.
viscosity of (STEACIE and JOHNSON), ii, 376.
reactions of, and its solutions (KAUFMANN and HANSEN-SCHMIDT), ii, 554.
reactions of, with aliphatic acids (WATSON), i, 1232.
action of, on azides (SPENCER), ii, 416.
effect of light on the reaction of potassium oxalate with (BERTHOUD and BELLENOT), ii, 141.

Bromine, use of, in volumetric analysis (MANCHOT and OBERHAUSER), ii, 161.
Hydrobromic acid, velocity of synthesis of (BRAMLEY), ii, 802.
and its sodium salt, conductivities of, in methyl and ethyl alcohols (GOLDSCHMIDT and DAHLL), ii, 128.
dielectric constant of (COMPTON and ZAHN), ii, 1118.
vapour pressure and composition of vapour phases in equilibrium with solutions of (VREVSKI, SAVARITZKI, and SCHARLOV), ii, 101; (VREVSKI), ii, 102.
constant-boiling aqueous solution of (EWING and SHADDUCK), ii, 859.
equilibria of, with ethylene and propylene (MAASS and WRIGHT), ii, 214.
action of, on tertiary alcohols (RAMART), i, 250.
Bromides, detection and determination of, in presence of cyanides (SCHULEK), ii, 432, 712.
determination of, with a mercury electrode (MÜLLER and AARFLOT), ii, 65.
determination of, iodometrically (LANG), ii, 597.
determination of, microchemically, with chlorine and iodine (STREBINGER and POLLAK), ii, 823.
Bromates, determination of, in the presence of hypobromites and iodates (SCHULEK), ii, 1197.
Hypobromites, determination of, in presence of hypoiodites (SCHULEK), ii, 1197.
Bromine detection:—
detection of (SCHERINGA), ii, 326; (LORENZ, GRAU, and BERGHEIMER), ii, 597.
detection of, in blood (BERNHARDT and UCKO), i, 454.
Bromination (FRANCIS), i, 1261, 1399.
of isomeric aromatic compounds (FRANCIS, HILL, and JOHNSTON), i, 1141.
Bromocresol-green, dissociation constant of (HOLMES and SNYDER), ii, 325.
Bromoform, density of, and its use in testing aluminium (PASCAL), ii, 646.
compounds of, with quaternary salts (STEINKOPF and BESSARITSCH), i, 495.
Bromophenol-blue, effect of alcohol and salts on dissociation of (RICHTER), ii, 237.
Brownian movement, theory of (ZEILINGER), ii, 389.
Bracine (LIONS, PERKIN, and ROBINSON), i, 831.
Brucinonic acid, hydrazone of, and its derivatives (LEUCHS and KANAO), i, 61.
Bryophyllum calycinum, diurnal changes in acidity of (GUSTAFSON), i, 1221.
Buccinum undatum (whelk), amphoteric chitins in radula of (PANTIN and ROGERS), i, 720.
Buchu-camphor (*diosphenol*), 8-hydroxy- (CUSMANO and MASSA), i, 686.
Buckthorn. See *Rhamnus cathartica*.
Buds, action of photocatalysers on the bursting of (NEITHAMMER), i, 1023.
Buffer mixtures (KOLTHOFF), ii, 396.
Bulbocapninecarboxylic acid, benzyl ester, methyl ether (OSADA), i, 283.
Bunya-bunya. See *Araucaria bidwilli*.
Burette, automatic, with flask for standard alkali solutions (McMILLAN), ii, 711.
micro- (REHBERG), i, 852.
Butadiene, *di*bromo- (LESPIEAU and PRÉVOST), i, 493.
Δαγ-Butadienealdehyde, γ-iodo-δ-hydroxy- (BAUMGARTEN), i, 1381.
***n*-Butaldehyde**, condensation of, with methyl ethyl ketone (POWELL), i, 7.
***n*-Butaldehyde**, *aaβ-tri*chloro-, phytochemical reduction of (ROSENFELD), i, 615.
γ-hydroxy- (HELFERICH and SCHÄFER), i, 7.
***iso*Butaldehyde**, acetals from (THOMS and KAHRE), i, 788.
Butane, adsorption of, by silica gels (PATRICK and LONG), ii, 382.
***d*-Butane**, β-thiol- (LEVENE and MIKESKA), i, 512.
***trans-cyclo*Butane-1:2-dicarboxylic acid**, resolution of, and its *l*-quinine salt and *d*-ethyl ester (GOLDSWORTHY), i, 33.
***d*-Butane-β-sulphonic acid** (LEVENE and MIKESKA), i, 512.
Butenonitriles, thermochemistry of (BRUYLANTS and CHRISTIAEN), i, 797.
Butesin. See Benzoic acid, *p*-amino-, *n*-butyl ester.
Δγ-Butinene, *aβ-di*hydroxy-, and its derivatives (LESPIEAU), i, 351.
Δβ-Butinen-α-ol, and its acetate (YVON), i, 514.
Butter, oxidation of vitamin-*A* in the preparation of (PLATON), i, 484.
rancidity of (STÄRKLE), i, 205.
murumuru (ANDRÉ and GUICHARD), i, 1124.
Butterfly, lemon. See *Gonypteryx rhamni*.
Buttgenbachite (SCHOEP), ii, 1196.
***n*-Butyl alcohol**, thermal properties of (PARKS), ii, 491.

n-**Butyl alcohol**, equilibrium of ethyl alcohol, water, and (DROUILLON), ii, 651.
*iso***Butyl alcohol**, miscibility of ethyl alcohol, water, and (BRUN), ii, 769.
tert.-**Butyl alcohol**, *tri*chloro-, preparation of, and its esters (TAFFE), i, 2.
Butylacetals (ADAMS and ADKINS), i, 784.
Butylallylbarbituric acids (VOLWILER), i, 1174.
ε-(δ-**Butylamino)amylamine**, δ-chloro-, salts of (v. BRAUN and ZOBEL), i, 1456.
Butylammonium tetrachloroferrate (REMY and KOTHE), ii, 1089.
n-**Butylaniline** *m*-nitrobenzenesulphonamide (MARVEL, KINGSBURY, and SMITH), i, 245.
*iso***Butylbenzene**, 2:4-*di*hydroxy- (SHARP & DOHME and DOHME), i, 541.
n-**Butylbenzoyloximidocarbonic acid**, ethyl ester (OESPER and COOK), i, 523.
4-*iso***Butyl-1:6-dimethylpyridine-3:5-dicarboxylic acid**, ethyl ester, methosulphate (MUMM), i, 964.
Butylene, dielectric constant of (SMITH and ZAHN), ii, 1118.
2:3-Butyleneglycol, formation of, in sugar fermentation (KLUYVER and DONKER), i, 1215.
α-**Butylhexoic acid** (HESS and BAPPERT), i, 349.
*o-iso***Butyl***cyclo***hexylamine**, and its salts and derivatives (v. BRAUN and BAYER), i, 429.
α-*n*-**Butylhydroxylamine**, and its hydrochloride (NEUFFER and HOFFMAN), i, 891.
α-*n*-**Butylhydroxyurethane** (NEUFFER and HOFFMAN), i, 891.
*iso***Butylidenediurethane** (THOMS and KAHRE), i, 789.
1-*n***-Butylindole**, and its picrate (v. BRAUN and BAYER), i, 429.
α-*iso***Butylindole** (VERLEY and BEDUWÉ), i, 578.
*cyclo***Butylmethyl** bromide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.
*cyclo***Butylmethylamine**, and its benzoyl derivative (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.
*cyclo***Butylmethyl-***n***-butylaniline**, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
*cyclo***Butylmethylmethylaniline**, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
*cyclo***Butylmethyltrimethylammonium** bromide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.
ε-**Butylnonane** (IVANOV), i, 503.
1-*n***-Butyloctahydroindole**, and its salts (v. BRAUN and BAYER), i, 429.
N-**Butylpiperidine**, δ-amino-, and its benzoyl derivative (v. BRAUN and ZOBEL), i, 1455.
n-**Butylvinylcarbinol**, resolution and rotation of, and its salts and esters (KENYON and SNELLGROVE), i, 771.
n-**Butylxanthydrol** (CONANT and SLOAN), i, 955.
n-**Butylxanthyl** *per*chlorate (CONANT and SLOAN), i, 955.
n-**Butyranilide**, γ-chloro- (LIPP and CASPERS), i, 963.
n-**Butyric acid**, molecular film of, between water and hexane (HARKINS and MCLAUGHLIN), ii, 771.
velocity of esterification of, in glycerol (KAILAN and OBOGI), ii, 49.
alkoxymethyl esters (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
ethyl ester, bacteria producing (BIDAULT and BLAIGNAN), i, 1216.
furfuryl ester (ZANETTI), i, 567.
Butyric acid, α-bromonitro-, and α-chloronitro-, ethyl esters (MACBETH and TRAILL), i, 629.
γγ-*di*chloro-, and its methyl ester (MELDRUM and ALIMCHANDANI), i, 1273.
*tri*chloro-, conductivity of, in methyl alcohol (GOLDSCHMIDT and AARFLOT), ii, 976.
β-hydroxy-, formation of, by bacteria (LEMOIGNE), i, 478, 867.
action of oxygenated yeast on (MARIAN), i, 105.
excretion of, after extirpation of the pancreas (BIERRY and RATHERY), i, 856.
and acetone in urine (LUBLIN), i, 459.
determination of, in urine (GOLDBLATT), i, 1204.
l-**Butyric acid**, β-hydroxy-, degradation of, and its amide (KARRER and KLARER), i, 1036.
*iso***Butyric acid**, hydroxylamine salt (OESPER and BALLARD), i, 1233.
furyl ester (NAKAI), i, 360.
*dl-iso***Butyric acid**, αβ-*di*hydroxy-, and its salts and derivatives (GLATTFELD and SHERMAN), i, 881.
Butyrin (WEATHERBY, MCILVAINE, and MATLIN), i, 1128.
Butyronitrile, β-hydroxy-, and its sodium derivative (DEWAEL), i, 14.
Butyrophenone-5-arsinic acid, 3-nitro-2-hydroxy- (MARGULIES), i, 447.
n-**Butyro-***p***-toluidide**, γ-chloro- (LIPP and CASPERS), i, 963.

β-*iso*Butyryl-*p*-bromophenylhydrazide (VAN ALPHEN), i, 82.
***l*-Butyrylhydrazide, β-hydroxy-** (LEVENE and HALLER), i, 1375.
Butyryl-leucine, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
β-*iso*Butyrylnitrophenylhydrazides (VAN ALPHEN), i, 82.
Butyryl-*N*-phenylaminoacetic acid, β-amino- (LEUCHS and SANDER), i, 1248.
β-*iso*Butyryltolylhydrazides (VAN ALPHEN), i, 82.

C.

Cacao fat, glycerides of (AMBERGER and BAUCH), i, 114.
Cadinylene sulphochloride, crystallography and optically active properties of (KARANDÉEV), i, 1164.
Cadmium, structure of (COLLINS), ii, 1112.
spectrum of (RUARK and CHENAULT), ii, 725.
shifting of lines in (FUKUDA), ii, 1101.
spectral lines of (JOOS), ii, 612.
absorption spectra of neutral and ionised atoms of (STÜCKLEN), ii, 338.
arc spectrum of (RUARK), ii, 1016.
atomic and band spectra of (HULTHÉN), ii, 1113.
infra-red line spectrum of (RANDALL and ST. PETER), ii, 1101.
spark spectrum of (v SALIS), ii, 334; (BROWN and BEAMS), ii, 913.
fluorescence of the vapour of (KAPUSCINSKI), ii, 838.
resonance radiation from vapour of (POWER), ii, 1113.
effect of gelatin on the electro-deposition of (MILLIAU), ii, 680.
polarisation of, in alkaline solution (JIRSA and LORIS), ii, 45.
expansion coefficient of (BORELIUS and JOHANSSON), ii, 27.
thermal expansion of (GRÜNEISEN and GOENS), ii, 488.
absorption coefficient of electrons in vapour of (BRODE), ii, 1020.
velocity of diffusion of, in mercury (COHEN and BRUINS), ii, 648.
physical properties of crystals of (GRÜNEISEN and GOENS), ii, 22.
single crystal rods of, thermo-electric force of (BRIDGMAN), ii, 1136.
Cadmium alloys with aluminium and magnesium (VALENTIN and CHAUDRON), ii, 205.
Cadmium alloys with bismuth and lead, hardness of (DI CAPUA), ii, 1051.
with gold (SALDAU), ii, 872.
with lead, electrolysis of (KREMANN, KIENZL, and MARKL), ii, 132.
with lead and thallium (DI CAPUA), ii, 787.
with mercury, electrolysis of (KREMANN, MÜLLER, and ORTNER), ii, 132.
with silver, electrodeposition of (ATEN and VAN PATTEN), ii, 1166.
Cadmium carbonate, thermal dissociation of (ANDRUSSOV), ii, 538.
chloride, equilibrium of pyridine and (MASON and MATHEWS), ii, 1063.
halides, ammoniates of (BILTZ and MAU), ii, 1184.
additive compounds of 3:5-dibromo-*o*-toluidine with (HANN and SPENCER), i, 653.
hydroxide, precipitation of, electrometrically (BRITTON), ii, 1204.
iodide, specific heat of solutions of (COHEN, HELDERMAN, and MOESVELD), ii, 126.
spectrographic study of complexes of (JOB), ii, 471.
complex compounds of stannous iodide and (AUGER and KARANTASSIS), ii, 1182.
double nitrates with metals of the cerium group (CAROBBI), ii, 222.
oxide, solubility of, in water (REMY and KUHLMANN), ii, 119.
selenide (MOSER and ATYNSKI), ii, 584.
silicates (DUBON), ii, 221.
Cadmium organic compounds:—
diphenylcarbazides (FEIGL and LEDERER), i, 170.
Cadmium determination and separation:—
determination of (LUFF), ii, 826.
determination of, electrolytically (BÜTTGENBACH), ii, 439.
separation of copper and (SACCARDI), ii, 159.
separation of zinc and (LUFF), ii, 159
Cæsium, optical constants of (NATHANSON), ii, 187.
spectrum of (OUDT), ii, 915.
flame spectrum of (BLEEKER and BONGERS), ii, 77.
spark spectrum of (SOMMER), ii, 4.
low-voltage arc in the vapour of (NEWMAN), ii, 829.
photo-electric ionisation of the vapour of (FOOTE and MOHLER), ii, 919.
quantum number of (LINDSAY), ii, 467.

Cæsium *di*bromoiodide and *tri*iodide, crystal structure of (BOZORTH and PAULING), ii, 748.
stannic iodide (AUGER and KARANTASSIS), ii, 814.
chloroplatinate, solubility of, in water (ARCHIBALD and HALLETT), ii, 652.
Cæsium detection :—
detection of (MURMANN), ii, 437.
Calabar beans, alkaloids of (POLONOVSKI and POLONOVSKI), i, 151, 959.
Calamine, optical properties of (SÈVE), ii, 18.
Calantas wood oil, constituents of (BROOKE), i, 418.
Calcification (HOLT, LA MER, and CHOWN; HOLT), i, 1209.
Calcio-ancylite from Russian Lapland (TSCHERNIK), ii, 322.
Calcite, index of refraction of (HATLEY), ii, 21.
luminescence of (HEADDEN), ii, 89.
electrical conductivity of (v. RAUTENFELD), ii, 639.
thermal properties of (BÄCKSTRÖM), ii, 1162.
density of (DEFOE and COMPTON), ii, 646.
rhombohedral angle of (BRAGG and CHAPMAN), ii, 92.
lattice constants of gypsum and (HJALMAR and SIEGBAHN), ii, 92.
Calcium, *K*-absorption spectrum of (ROBINSON), ii, 614.
spark spectra of (DORGELO), ii, 724.
electrolytic deposition of, and its normal potential (EILERT), ii, 547.
thermal ionisation of (SAHA), ii, 1161.
chromosphere, equilibrium of (MILNE), ii, 628.
precipitation of, as oxalate, in presence of ammonium citrate (JAKÓB), ii, 69.
in normal and tuberculous blood (MATZ), i, 1492.
ions, action of, on the heart (HOLZLÖHNER), i, 1500.
Calcium alloys with mercury, electrolysis of (KREMANN, MÜLLER, and ORTNER), ii, 132.
Calcium compounds, effect of heat on the solubility of, in milk (BELL), i, 998.
in the body (SHERMAN and MACLEOD), i, 1001.
fixation of, in bones (TELFER), i, 859.
Calcium salts, perfusion with emanation and (ZWAARDEMAKER, FEENSTRA, and STEYNS), i, 193.
action of, as auxoureases (KOCHMANN), i, 200.
Calcium salts, adsorption of nicotine by (CHAPIN), i, 697.
assimilation of, by animals (HART, STEENBOCK, and ELVEHJEM), i, 108.
fixation of, by animal tissues (BREHME and GYÖRGY), i, 717; (BUDDE), i, 718.
influence of piperidine on deposition of (ÉDERER), i, 869.
effect of, on cats (HEUBNER), i, 613.
in the mothers' diet, effect of, on the young (KORENCHEVSKI and CARR), i, 463.
in bile (DITTRICH; DRURY), i, 325.
in blood (GYÖRGY; JANSEN), i, 324; (KYLIN and SILFVERSVÄRD), i, 852.
effect of hypnotic suggestion on (GLASER), i, 860.
and cerebro-spinal fluid (CAMERON and MOORHOUSE), i, 857.
determination of, in blood (STANFORD and WHEATLEY), i, 1199.
Calcium carbonate, formation of, from calcium oxalate in tissues (LOEPER, SCHULMANN, and TOUNET), i, 1497.
heat of dissociation of (BÄCKSTRÖM), ii, 1140.
thermal dissociation of (ANDRUSSOV), ii, 803.
deposition of crystals of (KOHLSCHÜTTER and EGG), ii, 1036.
hydrates of (HUME), ii, 697.
effects of, in soils (RAMANN; BLANCK and LOHMANN), i, 223; (GEHRING and WEHRMANN), i, 1031.
Röntgen ray analysis of various forms of (ÔSAWA), ii, 745.
μ-Calcium carbonate and vaterite (GIBSON, WYCKOFF, and MERWIN), ii, 1183.
Calcium chloride, electrical conductivity of aqueous solutions of (CROWE), ii, 541.
toxicity and excretion of (BOWLER and WALTERS), i, 723.
fluoride, solubility of, in acetic acid (DUPARC, WENGER, and GRAZ), ii, 652.
solubility of, in hydrochloric acid (SABALITSCHKA and MOSES), ii, 417.
hydride, spectrum of (MULLIKEN), ii, 469.
action of, on methyl ethyl ketone (PORLEZZA and GATTI), i, 788.
reduction of nitro compounds by (DURAND and HOUGHTON), i, 646.

Calcium hypochlorite, heat of formation of (NEUMANN and MÜLLER), ii, 488.
reaction of aniline with (RASCHIG), i, 243.
oxide (*lime*), action of, on silicates at high temperatures (TAMMANN and GREVEMEYER), ii, 580.
requirements of, for soils (ARRHENIUS), i, 766.
effects of, in soils (RAMANN; BLANCK and LOHMANN), i, 223; (SCHEFFER), i, 624.
conversion of, into carbonate in soils (BLANCK and SCHEFFER), i, 491.
Tricalcium phosphate, precipitated, adsorption by (JOLIBOIS and MAZE-SENCIER), ii, 770.
Calcium phosphates, equilibria of, in calcification of bone (HOLT, LA MER, and GHOWN; HOLT), i, 1209.
metasilicate, equilibrium of sodium metasilicate, silica, and (MOREY and BOWEN), ii, 1161.
sulphate, velocity of crystallisation of (CHASSEVENT), ii, 559.
solubility of, in dilute nitric and sulphuric acids (COLSON), ii, 121.
hydrates of (BILTZ), ii, 356.
X-ray investigation of (JUNG), ii, 367.
sulphide, phosphorescent, economy coefficients of (SCHMIEDER), ii, 931.
containing bismuth, photo-electricity and phosphorescence of (CURIE), ii, 355.
Calcium organic compounds:—
cyanamide, pure, preparation of (YASUDA), i, 377.
action of hydrogen on (BOBROVNICKI), i, 526.
phenyl iodide, luminescence of (DUFFORD, NIGHTINGALE, and CULVERT), ii, 474.
Calcium detection, determination, and separation:—
detection of, in presence of barium and strontium (LONGINESCU and CHABORSKI), ii, 1202.
determination of, nephelometrically (KRISS), i, 852.
determination of, in blood (MYRBÄCK), i, 1485.
determination of, in blood and serum (BUDDE and FREUDENBERG; CLARK and COLLIP; SALVESEN), i, 713.
determination of phosphates and, in bone (v. EULER and JOHANSSON), i, 1489.
Calcium detection, determination, and separation:—
separation of aluminium and (KOLLO and GEORGIAN), ii, 330.
separation of, from aluminium, iron, magnesium, and phosphoric acid (JAKÓB), ii, 1095.
separation of magnesium and (RODT and KINDSCHER), ii, 158; (HEILINGÖTTER), ii, 437; (LUFF), ii, 438; (BACH), ii, 825.
Calorimeter for specific heats of gases (OSBORNE, STIMSON, and SLIGH), ii, 995.
bomb (MOUREU), ii, 427.
with platinum lining (MOUREU and LANDRIEU), ii, 995.
electrical (COHEN, MOESVELD, and HELDERMAN), ii, 151, 402.
micro-, combustion (ROTH and LASSÉ), ii, 591.
micro-bomb, use of (PADOA and FORESTI), ii, 847.
oxy- (BENEDICT and FOX), ii, 998.
Calorimetry (VERKADE and COOPS), ii, 39; (VERKADE, COOPS, and HARTMAN), ii, 490.
high-temperature, buffer method in (ROTH), ii, 949.
animal (MELLY and v. RÖTTH), i, 193, 332; (CHAMBERS and DEUEL), i, 1352.
clinical (RICHARDSON and LEVINE), i, 723.
Calumba root, alkaloids of. See under Alkaloids.
Calycanthine from *Calycanthus floridus* (SPÄTH and STROH), i, 1447.
Calycanthus floridus, calycanthine from (SPÄTH and STROH), i, 1447.
Camel, urine of. See Urine.
Campania, radioactivity of gases from the solfataras of (STOKLASA and PENKAVA), ii, 235.
Camphane, *di*chloro- (*tricyclene dichloride*) (BRUS), i, 821.
Camphane series (FORSTER and SHUKLA), i, 1161.
Camphanecarboxylic acid, esters of (RUPE and VONAESCH), i, 499.
3-Camphanecarboxylic acid, ethyl ester (RUPE and KOPP), i, 275.
Camphane-6-nitrosohydroxylamine, 6-cyano-, and its salts and derivatives (PASSERINI), i, 1290.
α-Camphanyl ethyl and **methyl ketones**, and their derivatives (RUPE and KOPP), i, 275.
Camphene, preparation of (KOMATSU and FUJIO), i, 564.
rotatory dispersion of (PARISELLE), ii, 742.

Camphene, *sec.*-*α*-amino- and -*α*-nitro- (NAMETKIN and ZABRODIN), i, 417.
*iso***Camphenilone**, structure of (NAMETKIN), i, 1079.
Campholenic acid, *α*- and *α′*-bromo-, and *α*-hydroxy-, and their salts and derivatives (BURGESS), i, 45.
Campholic acid, esters of (RUPE and VONAESCH), i, 499.
Campholic acid, cyano-, methyl ester, ketones from (HALLER and LEGAGNEUR), i, 683.
Campholytic acid, structure of (CHANDRASENA, INGOLD, and THORPE), i, 1275.
***α*-Camphomethylamine**, and its derivatives (RUPE and HODEL), i, 275.
***α*-Camphomethylaminomethylene-camphor** (RUPE and HODEL), i, 275.
Camphor, preparation of (BRINER, EGGER, and PAILLARD), i, 274.
rotatory power of (LOWRY and CUTTER), ii, 356.
latent heat of fusion of (EFREMOV), ii, 1140.
surface tension of aqueous solutions of (EDWARDS), ii, 387.
equilibria of, with nitrophenols (EFREMOV), ii, 1160.
conversion of, into fenchone (RUZICKA), i, 274.
action of magnesium *p*-anisyl and *p*-tolyl bromides on (LEDUC), i, 821.
pharmacology of (LIPSCHITZ and OSTERROTH), i, 1005.
constitution of substances having similar physiological properties to (WEDEKIND), i, 684.
cyanohydrin (PASSERINI), i, 1290.
4-*p*-tolylsemicarbazone (WHEELER and BOST), i, 318.
rotation of derivatives of (HALLER and LUCAS), ii, 742.
rotation of sulphonic derivatives of (RICHARDS and LOWRY), ii, 934.
determination of, in plants (GORI), ii, 1009.
Camphor, *α*-cyano-, catalytic reduction of (RUPE and HODEL), i, 275.
halogen derivatives of (BURGESS), i, 45; (BURGESS and LOWRY), i, 415.
rotation of (CUTTER, BURGESS, and LOWRY), ii, 743.
hydroxy-, of Manasse, constitution of (FORSTER and SHUKLA), i, 1161.
α- and *β*-hydroxy-, constitution of (KARRER and TAKASHIMA), i, 940.
Camphor oils (ONO), i, 941, 1437.
Camphor seeds, fatty acids from fat of (KOMATSU and YAMADA), i, 881.
Camphor series (KOMATSU and FUJIO), i, 564; (KOMATSU and KURATA), i, 943, 1290.
Camphor-*π*-chlorosulphoxide, *α*-bromo- (BURGESS and LOWRY), i, 416.
Camphoric acid, vanadicamphoryl salt (SCAGLIARINI and AIROLDI), i, 920.
dimethylaminoethylimide of, and its hydrochloride (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1437.
α-mononitrile, ketones from (HALLER and LEGAGNEUR), i, 683.
esters of, and their action with magnesium methyl iodide (HALLER and LEGAGNEUR), i, 924.
Camphor-*sec.*-*tert.*-nitrilic acid, and its derivatives, and chloro- (BREDT and IVANOV), i, 254; (BREDT), i, 255.
Camphorquinone, rotatory dispersion of (LOWRY and RICHARDS), ii, 265; (LOWRY and CUTTER), ii, 356.
Camphorquinone, *β*-bromo- (BURGESS and LOWRY), i, 416.
Camphor-*α*-sulphonamide, *αβ-di*bromo- (BURGESS and LOWRY), i, 416.
Camphor-*α*-sulphonic acid, *β*-bromo-, and its salts and derivatives (BURGESS and LOWRY), i, 415.
Camphorylacetic acid, esters of (RUPE and VONAESCH), i, 500.
Camphorylideneacetic acid (RUPE and VONAESCH), i, 500.
***β*-Camphorylpropionic acid**, and its derivatives (RUPE and TSCHOPP), i, 1079.
Canadite (MOLENGRAAFF and HALL), ii, 64.
Canarium strictum, oil from resin of (MOUDGIL) i, 823.
Canavalia ensiformis (jack bean), globulins of (SUMNER and GRAHAM), i, 1027.
Canavaline, preparation of (SUMNER and GRAHAM), i, 1027.
Cancer, biochemistry of (BIERICH and ROSENBOHM), i, 328.
constituents of blood and serum in (THEIS and BENEDICT), i, 724.
calcium in plasma in (ROFFO and CORREA), i, 999.
Cannizzarite (ZAMBONINI, DE FIORE, and CAROBBI), ii, 709.
Cannizzaro's reaction, mixed (ENDOH), i, 1428.
Caoutchouc, constitution of (OLIVIER), i, 566.
stretching of, and its Röntgen ray spectrum (KATZ), ii, 667.
and methylcaoutchouc, molecular refraction of (MACALLUM and WHITBY), ii, 478.

Caoutchouc, Joule effect in (HOEK; KATZ), ii, 969.
Capillarity, phenomena of (DUBRISAY), ii, 961.
evaporation and efflorescence (SCHULTZE), ii, 287.
and wetting (SCHULTZE), ii, 856.
Capillary layer, formation of (BAKKER), ii, 789.
Carbamic acid, salts, equilibria of, with carbonates (FAURHOLT), ii, 396.
esters of (OESPER, BROKER, and COOK), i, 1408.
Carbamic acids, iodo-esters of (CHINOIN FABRIK CHEMISCH-PHARMAZEUTISCHER PRODUKTE), i, 18.
Carbamic acids, *di*thio-, salts of (WHITBY and MATHESON), i, 644.
Carbamide (*urea*), formation of, from ammonium hydrogen carbonate (FICHTER and KERN), i, 796.
synthesis of (BAILEY), i, 121.
solubility of, in water (PINCK and KELLY), ii, 955.
equilibrium of methyl alcohol with (WALTON and WILSON), ii, 505.
determination of, with hypobromite (POHORECKA-LELESZ), ii, 76.
See also Urea.
Carbamides, mechanism of reactions of (DAVIS), i, 375.
***p*-β-Carbamido-β-acetoxy-*n*-propylaminophenylarsinic acid** (LES ÉTABLISSEMENTS POULENC FRÈRES), i, 601.
1-Carbamido-3:5-dimethyl-4-β-phenylethylpyrazole (v. AUWERS and MÖLLER), i, 404.
Carbazoles, hydrogenated (v. BRAUN and SCHÖRNIG), i, 1449.
Carbazones. See 5:5-Diphenyldihydroacridones.
β-Carbethoxyaminoacetamidobutyric acid, and its derivatives (LEUCHS and SANDER), i, 1249.
***n*-Carbethoxyaminobenzoic acid**, and its derivatives (KING and MURCH), i, 320.
3-Carbethoxyamino-4-carbethoxyhydroxyphenylarsinic acid (HAMILTON and SLY), i, 600.
3-Carbethoxyamino-8-ethoxy-2-*p*-methoxyphenylbenzopyranyl methyl ether (RIDGWAY and ROBINSON), i, 55.
3-Carbethoxyamino-8-ethoxy-2-*p*-methoxyphenylbenzopyrylium chloride (RIDGWAY and ROBINSON), i, 55.
ω-Carbethoxyamino-*p*-methoxyacetophenone (RIDGWAY and ROBINSON), i, 55.
3-Carbethoxyamino-8-methoxy-2-phenylbenzopyranyl ethyl and methyl ethers (RIDGWAY and ROBINSON), i, 54.
3-Carbethoxyamino-4-methylphenylarsinic acid (HAMILTON and SLY), i, 600.
Carbethoxyaminophenylarsinic acids (HAMILTON and SLY), i, 600
β-Carbethoxy-γ-benzeneazo-Δβ-pentenoic acid, ethyl ester (MACBETH and TRAILL), i, 782.
3-Carbethoxy-2:4-dimethylpyrrole-5-αω-*di*bromoethyl-ω-carboxylic acid (KÜSTER, BRUDI, and KOPPENHÖFER), i, 972.
3-Carbethoxy-2:5-dimethylpyrrole-4-glyoxylic acid, ethyl ester (KALLE & Co.), i, 297.
3-Carbethoxy-2:4-dimethylpyrrole-5-αω-*di*iodoethyl-ωω-dicarboxylic acid, ethyl ester (KÜSTER, BRUDI, and KOPPENHÖFER), i, 972.
3-Carbethoxy-2:4-dimethylpyrrole-5-vinyl-ω-carboxylic acid, and its silver salt and esters (KÜSTER, BRUDI, and KOPPENHÖFER), i, 972.
3-Carbethoxy-2:4-dimethylpyrrole-5-vinyl-ωω-dicarboxylic acid, and its silver salt and esters (KÜSTER, BRUDI, and KOPPENHÖFER), i, 972.
Carbethoxydimethylpyrryldi-(3-acetyl-2:4-dimethylpyrryl)-methanes (FISCHER and HEYSE), i, 77.
Carbethoxydimethylpyrryldi-(3-carbethoxy-2:4-dimethylpyrryl)-methanes (FISCHER and HEYSE), i, 77.
Carbethoxyglycerol carbonate (ALLPRESS and MAW), i, 4.
Carbethoxyhydroxamic acid, *p*-chloro- and nitro-benzoyl esters (OESPER and COOK), i, 523.
5-Carbethoxy-4-methyl-2-ethylpyrrole-3-acrylic acid (FISCHER and KLARER), i, 578.
5-Carbethoxy-4-methyl-2-ethylpyrrole-3-aldehyde, and its derivatives (FISCHER and KLARER), i, 578.
5-Carbethoxy-4-methyl-2-ethylpyrrole-3-α-cyanoacrylic acid (FISCHER and KLARER), i, 578.
5-Carbethoxy-4-methyl-2-ethylpyrrole-3-propionic acid (FISCHER and KLARER), i, 578.
θ-Carbethoxynonanilide (G. M. and R. ROBINSON), i, 354.
4-Carbethoxyphenylpyruvic acid, 2-nitro-, ethyl ester (KERMACK), i, 67.
δ-3-Carbethoxyphenylsemicarbazide (WILSON and CRAWFORD) i, 318.
3-ω-Carbethoxyvinyl-2-methylindole, ω-cyano- (SEKA), i, 67.

Carbides, preparation and properties of (FRIEDERICH and SITTIG), ii, 705.
effect of high temperatures on (RUFF), ii, 579.
Carbimides (SLOTTA and LORENZ), i, 1047.
Carbimides, thio-. See Thiocarbimides.
Carbobutoxyaminocarbobutoxyhydroxyphenylarsinic acids (HAMILTON and SLY), i, 600.
Carbobutoxyaminophenylarsinic acids (HAMILTON and SLY), i, 600.
Carbo-*n*-butoxyhydroxamic acid, *m*- and *p*-nitrobenzoyl esters (OESPER and COOK), i, 523.
Carbo-*o*- and -*p*-chlorophenylhydroxamic acids (OESPER and BROKER), i, 1408.
Carbocyanines, reduction of (HAMER), i, 305.
Carbodimethyldi-imide, and its salts (LECHER), i, 1391.
Carbohydrates, formation of, from proteins and fats in plants (TERROINE, TRAUTMANN, and BONNET), i, 755.
synthesis and degradation of, in the organism (GIGON), i, 463; (GIGON and BRAUCH), i, 611.
enzymic degradation and synthesis of (v. EULER, MYRBÄCK, and KARLSSON), i, 744; (v. EULER, MYRBÄCK, and NILSSON), i, 866.
photosynthesis of (GALWIALO), i, 870.
relative sweetness of (BIESTER, WOOD, and WAHLIN), i, 1498; (WILLAMAN, WAHLIN, and BIESTER), i, 1499.
fermentation of, by *Bacillus macerans* (MOSKOVITS), i, 1511.
utilisation of, by cells (MAIGE; RAYMOND), i, 1493.
induced oxidation of (PALIT and DHAR), i, 1041.
action of ammonia on (SHMOOK), i, 577.
reaction between tannin and (STOCKS and GREENWOOD), i, 1165.
alkali compounds of (SCHMID and BECKER), i, 1386.
in muscle (FURUSAWA), i, 849.
synthesis of (MEYERHOF, LOHMANN, and MEIER), i, 727.
Carboligase (NEUBERG and SIMON), i, 737.
β-Carbomethoxyaminobutyric acid, and its diamide (LEUCHS and SANDER), i, 1248.
β-Carbomethoxyaminobutyryl-*N*-phenylaminoacetic acid, and its ammonium salt and ethyl ester (LEUCHS and SANDER), i, 1248.
3-Carbomethoxyamino-4-carbomethoxyhydroxyphenylarsinic acid (HAMILTON and SLY), i, 600.
3-Carbomethoxyamino-4-methylphenylarsinic acid (HAMILTON and SLY), i, 600.
Carbomethoxyaminophenylarsinic acids (HAMILTON and SLY), i, 600.
β-Carbomethoxybutyrylaminoacetic acid, and its esters and amides (LEUCHS and SANDER), i, 1248.
Carbomethoxyglycerol carbonate (ALLPRESS and MAW), i, 4.
Carbomethoxypropionanilide (G. M. and R. ROBINSON), i, 355.
Carbon, atomic weight of (DEAN), ii, 255.
structure and valency of (WAHL), ii, 937.
spectrum of (LANG and SMITH), ii, 829.
series spectra of (BOWEN and MILLIKAN), ii, 1013.
effect of an electric field on the spark spectrum of (NAKAMURA and FUJIOKA), ii, 910.
spectra associated with (JOHNSON), ii, 723, 1024; (BIRGE), ii, 829, 836, 927.
melting point of (ALTERTHUM, FEHSE, and PIRANI), ii, 759.
vapour pressure of, in the arc (KOHN and GUCKEL), ii, 100.
diffusion of, through tungsten (ANDREWS and DUSHMAN), ii, 500.
significance of electrons in the crystallisation of (BECKENKAMP), ii, 358.
amorphous (RUFF, SCHMIDT, and OLBRICH), ii, 1125.
combustion of (SMITH and EBAUGH), ii, 888; (BILTZ), ii, 987; (SMITH), ii, 1085.
atoms, tetrahedral, stereochemistry of (KUHN and EBEL), i, 780; (KUHN and ZUMSTEIN), i, 1249.
graphitic conduction in conjugated chains of (LOWRY), ii, 299.
chains, alternating effect in (INGOLD), i, 646; (C. H. and E. H. INGOLD), i, 657; (HOLMES and INGOLD), i, 1142.
excretion of, in urine (SCHIMIZU), i, 185.
See also Graphite.
Carbon alloys with iron, equilibria of (DAWES), ii, 401.
with iron and nickel (KASE), ii, 973.
with iron and silicon (BECKER), ii, 973.
with iron and titanium (TAMARU), ii, 787.
Carbon *tetra*chloride, corrosion of metals by (RHODES and CARTY), ii, 1084.
action of benzoyl peroxide on (BÖESEKEN and GELISSEN), i, 30.

Carbon *tetra*chloride, condensation of phenol and (GOMBERG and SNOW), i,
*sub*oxide, compounds of phenylenediamines with (VAN ALPHEN), i, 81.
compounds of phenylhydrazine with (VAN ALPHEN), i, 83.
*mono*xide, formation of, by electrolysis (GERMANN), ii, 568.
from decomposition of acid chlorides (MAILHE), i, 1232.
spectrum of, at low pressures (BALDET), ii, 180, 469.
flame spectra of, and of its mixtures with hydrogen (WESTON), ii, 928.
action of the electric discharge on (OTT), ii, 579.
decomposition of, in the corona (CRESPI and LUNT), ii, 1178.
heat of oxidation of, by manganese dioxide (FRAZER and GREIDER), ii, 1064.
molecular heat of (SCHREINER), ii, 97.
specific heat of (PARTINGTON and CARROLL), ii, 373.
absorption of, in gas analysis (AMBLER; SUTTON and AMBLER), ii, 436.
combustibility of (ARMSTRONG), i, 1009.
explosion of mixtures of air and (BONE, NEWITT, and TOWNEND), ii, 800.
ignition of mixtures of air and (CROWE and NEWEY), ii, 875.
influence of chloroethylenes on inflammability of mixtures of air and (JORISSEN and VAN DER VALK), ii, 874.
explosion of ammonia with oxygen and (BEESON and PARTINGTON), ii, 682.
effect of water and of carbon dioxide on the catalytic oxidation of (LAMB and VAIL), ii, 567.
catalytic reduction of, to methane (FISCHER, TROPSCH, and DILTHEY), ii, 982.
action of, on enolates (SCHEIBLER and SCHMIDT), i, 917.
compound of auric chloride with (MANCHOT and GALL), ii, 1183.
compound of iridium chloride and (MANCHOT and GALL), ii, 232.
compounds of osmium chloride with (MANCHOT and KÖNIG), ii, 232.
compound of rhodium chloride and (MANCHOT and KÖNIG), ii, 1193.
compounds of ruthenium trihalides with (MANCHOT and KÖNIG), ii, 149.
Carbon *mono*xide, poisoning of catalysts by (PEASE and STEWART), ii, 691.
poisonous action of, on plants (WEHMER), i, 1029.
poisoning. See Poisoning.
in blood (NICLOUX), i, 321.
determination of (LEBEAU and MARMASSE), ii, 824.
determination of, by absorption in hæmoglobin (NICLOUX), ii, 824.
determination of, in blood (TERVAERT), i, 710.
*di*oxide, infra-red absorption spectrum of (ELLIS), ii, 1115.
and water vapour, action of ultraviolet light on (PORTER and RAMSPERGER), ii, 573.
scattering of light in mixtures of air and (BANERJI), ii, 1118.
magnetic susceptibility of (GLASER), ii, 82, 642.
ions in (ERIKSON), ii, 6.
equilibrium of, with carbon monoxide and oxygen in the corona discharge (WENDT and FARNSWORTH), ii, 1158.
heat of sublimation of (ANDREWS), ii, 758.
Joule effect for (KEYES and SEARS), ii, 275.
entropy of (BÄCKSTRÖM), ii, 1140.
solid, structure of (DE SMEDT and KEESOM), ii, 484; (MARK), ii, 1130.
absorption and equilibrium of, in alkaline solutions (WILLIAMSON and MATHEWS), ii, 105.
absorption of, by alkalis (LEDIG), ii, 106.
by salt solutions (IPATIEV and ANDRJUSCHTSCHENKO), ii, 956.
by glass (BANGHAM and BURT), ii, 284.
by glass wool (BANGHAM and SEVER), ii, 507.
constant mixtures of air and (JOHNSTON and WALKER), ii, 851.
equilibria of, with carbonic acid and carbonates in aqueous solution (FAURHOLT), ii, 295.
equilibrium of hydrogen and, with carbon monoxide and water vapour (PARTINGTON and SHILLING), ii, 395.
equilibrium of water and (TAMMANN and KRIGE), ii, 869.
explosion potential in, at high pressures (GUYE, MERCIER, and WEIGLÉ), ii, 490.
interaction of hydrogen and, in the electric discharge (LUNT), ii, 579.

Carbon *di*oxide, action of hydrogen with, on platinum (PRICHARD and HINSHELWOOD), ii, 564.
action of hydrogen with, on the surface of tungsten (HINSHELWOOD and PRICHARD), ii, 983.
effect of, on germination of seeds (SCHMIDT), i, 758.
in alveolar air and arterial blood (BOCK and FIELD), i, 93.
equilibrium of hæmoglobin and (ADAIR), i, 850.
equilibrium of, in the body (MURRAY and HASTINGS), i, 1342.
production of, by muscle cells (LIPSCHITZ and MEYER), i, 603.
production of, by nerve (PARKER), i, 849.
determination of (LEBEAU and MARMASSE), ii, 824.
apparatus for determination of (REED), ii, 714; (PLANTEFOL), ii, 902; (WITTIG), ii, 1094.
determination of, in small quantities (NISHI), ii, 1001.
dissolved, determination of (LEGENDRE), ii, 714.
determination of, in alveolar air (KNIPPING), i, 176.
determination of, in blood (HOLLÓ and WEISS), i, 95.
determination of, in capillary blood (VERZÁR and VÁSÁRHELYI), i, 178.
Carbonate ions, infra-red frequencies of (KORNFELD), ii, 12; (CHAPMAN and LUDLAM), ii, 1025.
Carbonates, infra-red absorption spectra of (TAYLOR), ii, 1115.
equilibria of carbamates with (FAURHOLT), ii, 396.
acid, determination of, in blood (HOLLÓ and WEISS), i, 709.
Carbon *di*sulphide, refractive index of, in the ultra-violet (BRUHAT and PAUTHENIER), ii, 478.
extinction coefficients and refractive indices of (BRUHAT and PAUTHENIER), ii, 837.
vapour pressure and specific heat of mixtures of methyl alcohol and (DRUCKER and WEISSBACH), ii, 953.
ignition of the vapour of (DIXON), ii, 683.
action of, on benzidine (ROSSI and CECCHETTI), i, 701.
reaction of benzylideneaniline with (BIGELOW), i, 242.
additive compound of triethylphosphine and (WIBAUT), i, 527.
Carbon determination:—
determination of, in organic compounds (HESLINGA), ii, 65; (WHITE and HOLBEN), ii, 240; (DESGREZ and VIVARIO; SIMON), ii, 436; (WILDE and LOCHTE), ii, 600; (LINDNER), ii, 901.
determination of, in tungsten (KING), ii, 435.
Carbon anodes. See Anodes.
Carbonates. See under Carbon.
Carbonisation, effect of catalysts on (LESSING and BANKS), i, 9.
Carbo-*m*-nitrophenoxyhydroxamic acid, and its benzoyl ester (OESPER and BROKER), i, 1408.
Carbonyl chloride (*phosgene*), formation and thermal decomposition of (BODENSTEIN and PLANT), ii, 135.
specific conductivity of (GERMANN), ii, 568.
thermal decomposition of (STOCK and WUSTROW), ii, 987.
dielectric constant of (SCHLUNDT and GERMANN), ii, 355.
photochemical reaction of hydrogen with (BREDIG and v. GOLDBERGER), ii, 142.
vapour pressure of solutions of aluminium chloride in (GERMANN and MCINTYRE), ii, 196.
compounds of chloroaluminates with (GERMANN and TIMPANY), ii, 1085.
compounds, metallic compounds of the enolic forms of (SCHEIBLER and SCHMIDT), i, 917; (SCHEIBLER, MARBENKEL, and BASSANOFF), i, 918.
Carbonyl-4:4′-*di*aminodiphenylmethane (BUTLER and ADAMS), i, 1458.
Carbophenoxyhydroxamic acid, and its silver salt and derivatives (OESPER and BROKER), i, 1408.
Carbopropoxyaminocarbopropoxyhydroxyphenylarsinic acids (HAMILTON and SLY), i, 600.
Carbopropoxyaminomethylphenylarsinic acids (HAMILTON and SLY), i, 600.
Carbopropoxyaminophenylarsinic acids (HAMILTON and SLY), i, 600.
Carbo-*n*-propoxyhydroxamic acid, *p*-chloro- and nitro-benzoyl esters (OESPER and COOK), i, 523.
Carbotolyloxyhydroxamic acids, and their silver salts and derivatives (OESPER and BROKER), i, 1408.
β-Carboxyanilinobenzylmalonic acids, ethyl esters (WAYNE and COHEN), i, 551.

dl-2′-Carboxybenzene-4-azodiphenyl-βγ-*di*amino-*n*-butanes, stereoisomeric, and their salts (MORGAN and SKINNER), i, 1192.
Carboxybutoxyaminomethylphenyl arsinic acids (HAMILTON and SLY), i, 600.
Carboxycamphoranilic acids (M. and R. SINGH), i, 1276.
5-Carboxy-2-*p*-chlorophenyl-2:1:3-triazole-4-benzoic acid (CHARRIER), i, 76; (CHARRIER, CRIPPA, TOIA, and BIANCHESSI), i, 591.
o-Carboxycinnamic acid (CHEMISCHE FABRIKEN VORM. WEILER-TER MEER), i, 1419.
2-Carboxy-4:5-dimethoxyphenylacetonitrile (HAWORTH and PINK), i, 929.
4-Carboxy-2:6-dimethylmandelic acid (PERKIN and TAPLEY), i, 42.
4-Carboxy-2:6-dimethylphenylacetic acid, and its dimethyl ester (PERKIN and TAPLEY), i, 42.
6-Carboxydiphenylamine-*N*-acetic acid, 2′-amino-, and its acetyl derivative, and 2′-nitro-, ethyl esters (LINNELL and PERKIN), i, 63.
o-Carboxydiphenylmethylarsine, and its oxide (AESCHLIMANN), i, 706.
2-Carboxy*dicyclo*-[3, 1, 0]heptane-1-acetic acid (BAKER), i, 917.
cis- and *trans*-2-Carboxy*cyclo*hexyl-1-butyric acids, and their derivatives (HÜCKEL and GOTH), i, 259.
o-Carboxyhydrocinnamic acid (STRAUS and EKHARD), i, 1139.
Carboxyhydroxamic acid, derivatives of (OESPER and COOK), i, 523.
5-Carboxy-3-hydroxy*spiro*di-1:1′-piperidinium bromide, lactone of (MANNICH and SUTTER), i, 1038.
α-Carboxy-α-hydroxyethylphosphinic acid, and its salts (BERNTON), i, 646.
Carboxylase of yeast, action of, on pyruvic acid (NEUBERG), i, 336.
2-Carboxy-5-methoxyphenylthiolacetic acid, 4-bromo- (GRIFFITH and HOPE), i, 828.
2-Carboxy-4:5-methylenedioxyphenylacetonitrile (HAWORTH and PINK), i, 929.
6-Carboxymethyl-6-ethylphenoxarsonium bromide (AESCHLIMANN), i, 706.
4(6 ?)-Carboxy-6(4 ?)-methylphthalonic acid (PERKIN and TAPLEY), i, 43.
p 4-Carboxy-6-methyl-2-quinolylphenylarsinic acid, and its ethyl and methyl esters (OGDEN and ADAMS), i, 707.
1-Carboxynaphthalene-3-sulphonic acid (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1426.
4-Carboxyphenoxyacetic acid, 2-*mono*- and 2:6-*di*-nitro- (CHRISTIANSEN), i, 817.
5-Carboxy-2-phenyl-2:1:3-oxytriazole-4-benzoic acid (CHARRIER, CRIPPA, TOIA, and BIANCHESSI), i, 591.
γ-(*o*-Carboxyphenyl)propylnitrolic acid (STRAUS and EKHARD), i, 1139.
5-Carboxy-2-phenyl-2:1:3-triazole-4-benzoic acid (CHARRIER), i, 76.
p-4-Carboxy-2-quinolylphenylarsinic acid, and its derivatives (OGDEN and ADAMS), i, 706.
5-Carboxy-2-*p*-tolyl-2:1:3-triazole-4-benzoic acid (CHARRIER, CRIPPA TOIA, and BIANCHESSI), i, 591.
5-Carboxy-1:2:3-triazole-4-*o*-benzoic acid, and its hydrate and barium salt (CHARRIER and GALLOTTI), i, 589.
Carbylamines (PASSERINI), i, 1298.
Carcinoma, metabolism of cells in (WARBURG), i, 1206.
d-Δ³-Carene, catalytic oxidation of (RAO), i, 565, 687.
Carnaubic acid, gossypyl ester (FARGHER and HIGGINBOTHAM), i, 880.
Carnosine, decomposition of, by bacteria (HEFTER), i, 1362.
in muscle in relation to excretion of iminazole (HUNTER), i, 459.
Carnotite, ionium–thorium ratio in (KAMMER and SILVERMAN), ii, 1186.
determination of uranium in (BRINTON and ELLESTAD), ii, 72.
Carotin, preparation and properties of (SCHERTZ), i, 1024.
Caryophyllaceæ, calcium oxalate crystals in (BOHN), i, 1124.
β-Caryophyllene, formic ester (ROBERTSON, KERR, and HENDERSON), i, 1293.
Casein (*paracasein*) (KONDO), ii, 518.
surface tension of (JOHLIN), ii, 857.
conductivity of solutions of (FISCHENICH and PÓLÁNYI), ii, 662.
solubility of, in hydrochloric acid (LINDERSTRÖM-LANG and KODAMA), ii, 1056.
homogeneity of (LINDERSTRÖM-LANG), ii, 1056.
acid hydrolysis of (DUNN), i, 1477.
compounds of alkalis with (GREENBERG and SCHMIDT), ii, 129.
constitution of the amino-acid from (ABDERHALDEN and SICKEL), i, 846.
compounds of chloral hydrate with (LIEBEN), i 91.
precipitation of, from milk (LINDET), i, 846.
peptic and tryptic digestion of (RONA and KLEINMANN), i, 473.

Casein, bromo- (VANDEVELDE), i, 1477.
Caseinogen, coagulation of, in presence of calcium salts (LINDET), i, 846; (PORCHER), i, 846, 847.
absorption of iodine by (LIEBEN and LÁSZLO), i, 1476.
amino-acid from (ABDERHALDEN and SICKEL), i, 846.
calcium phosphate complexes of, and their coagulation by rennin (PORCHER), i, 846, 847.
fatty compound from (KON and FUNK), i, 230.
Catalase, action of (WIELAND and HAUSSMANN), ii, 1171.
function of (DIXON), i, 1010.
decomposition of hydrogen peroxide by (NORTHROP), i, 469.
precipitation of, from liver extract (MAUBERT, JALOUSTRE, LEMAY, and ANDREOLY), i, 614.
liver, effect of radium on (MAUBERT, JALOUSTRE, and LEMAY), i, 737.
liver and blood (RONA, FIEGEL, and NAKAHARA), i, 1505.
Catalysis (HARA), i, 536; (KOMATSU and KURATA), i, 687, 942; (KOMATSU and TANAKA), i, 905; (KOMATSU and MASUMOTO), ii, 1071.
theories of (TAYLOR), ii, 562; (v. EULER, ÖLANDER, and RUDBERG), ii, 876; (AMBARD), ii, 1170.
electrical nature of (PISARSHEVSKI), ii, 210.
effect of diluents on (CONSTABLE), ii, 983.
promoter action in (ROBERTSON), ii, 690; (BOSWELL and BAYLEY), ii, 805.
of gases with metals of the platinum group (DUPARC, WENGER, and URFER), ii, 1177.
of lactone formation by acids (TAYLOR and CLOSE), ii, 1070.
by finely-divided metals (FORESTI), ii, 692.
at solid surfaces (ARMSTRONG and HILDITCH), ii, 562, 563.
lecture experiments to illustrate (KOLTHOFF), ii, 819.
contact (SWIENTOSLAWSKI), ii, 562; (REMY and SCHAEFFER), ii, 563.
heterogeneous (RICHARDSON, KNUTH, and MILLIGAN), i, 229; (GARNER), ii, 140.
and adsorption (ALEKSEEVSKI), ii, 858.
negative (UNDERWOOD), ii, 808.
of oxidation reactions (DHAR), ii, 690.
Catalysts, physical state of (SMITH; GAUGER), ii, 1072.
reciprocal excitation and inactivation of (QUARTAROLI), ii, 805.
location of the catalytic property in (MOUREU, DUFRAISSE, and LOTTE), ii, 561.
effect of, on carbonisation (LESSING and BANKS), i, 9.
for synthesis of indoles (KORCZYŃSKI and KIERZEK), i, 1097.
effect of, on chlorination of toluene (O. and C. A. SILBERRAD, and PARKE), i, 1137.
poisoning of (PEASE and STEWART), ii, 691; (CONSTABLE), ii, 881.
contact, activity of (REMY and GÖNNINGEN), ii, 1176.
metallic, for reduction of carbon monoxide (FISCHER, TROPSCH, and DILTHEY), ii, 982.
oxidising, poisoning of (MOUREU and DUFRAISSE), ii, 413.
synthetic (CUSMANO), ii, 690.
Catalytic action (HARA and KOMATSU), i, 893.
electromagnetic nature of (DITMAN), ii, 51.
decomposition, mechanism of (CONSTABLE), ii, 804.
dehydrogenation (LAZIER and ADKINS), i, 878.
hydrogenation (ZELINSKI), i, 237.
with noble metals (ZELINSKI and TUROVA-POLLAK), i, 1052.
with nickel and hydrogen (FELDMANN), i, 1263.
with palladium and platinum oxides (KERN, SHRINER, and ADAMS), i, 625.
with platinum (BODENSTEIN), ii, 216; (WALDSCHMIDT-LEITZ and SEITZ), ii, 411.
with platinum black (WASER), i, 584.
with platinum oxide (PIERCE and ADAMS) i, 824; (HECKEL and ADAMS), i, 909; (CAROTHERS and ADAMS), ii, 693.
of inorganic compounds (GALL and MANCHOT), ii, 412.
of unsaturated compounds (LEBEDEV, KOBLIANSKY, and YAKUBCHIK), i, 350.
Cataphoresis and adsorption (FROMAGEOT), ii, 128.
in colloids (SCOTT and SVEDBERG; GERASIMOV), ii, 204.
influence of valency on (FREUNDLICH and ZEY), ii, 115.
Catechin, and its derivatives (FREUDENBERG, FIKENTSCHER, and HARDER), i, 419.

Catechin, constitution of (NIERENSTEIN), i, 279; (DEAN and NIERENSTEIN), i, 280; (FREUDENBERG, FIKENTSCHER, and WENNER), i, 692.
Cathodes, arsenic, hydrogen overvoltage at (GRUBE), ii, 43.
gas, electrolysis with (GÜNTHER-SCHULZE), ii, 549.
lead, overvoltage of (GLASSTONE), ii, 43, 301.
mercury, overvoltage of (GLASSTONE), ii, 133.
mercury dropping, electrolysis with (HEYROVSKÝ), ii, 43, 133, 673, 675; (HEYROVSKÝ and SHIKATA), ii, 674; (HERASYMENKO; BAYERLE), ii, 675; (BREZINA; EMELIANOVA; SANIGAR), ii, 676; (SMRZ; PODROUŽEK), ii, 677; (GOSMAN), ii, 678.
Cathode rays. See under Rays.
Cats, calcium in (HEUBNER), i, 613.
Cell or Cells, electrochemical, electromotive force of (BUTLER), ii, 42.
electrochemical, with liquid junctions, electromotive force of (MICHAELIS and FUJITA), ii, 131.
with zinc–carbon electrodes (NYBERG), ii, 42.
zinc–sulphuric acid–carbon, effect of superposed alternating current on (ALLMAND and PURI), ii, 303.
concentration, in methyl alcohol (GRANT), ii, 301.
Weston standard, reproducibility and constancy of (VOSBURGH), ii, 672.
decrease in electromotive force of (VOSBURGH), ii, 1066.
substitutes for (VOSBURGH), ii, 1164.
Cell or Cells, photoelectric, with fluorescent liquids (GRUMBACH), ii, 549.
silver iodide (GARRISON), ii, 212; (PRICE), ii, 680.
Cell or Cells, physiological, hydrogen-ion concentration of nuclei of (REISS), i, 199.
hydrogen-ion concentration and the oxidation-reduction potential of the interior of (J. and D. M. NEEDHAM), i, 1012.
permeability of (BROOKS), i, 1004; (CHODAT), ii, 521.
differences between the sap of, and the external medium (OSTERHOUT), i, 720.
respiration of (v. SZENT-GYÖRGYI), i, 793.
fission and respiration in (MEYERHOF), i, 993.
utilisation of carbohydrates by (MAIGE; RAYMOND), i, 1493.
Cell or Cells, physiological, bioelectric, theory of (HÖBER), ii, 131.
living, electrical charges in (HEILBRUNN), i, 1492.
argon in (PICTET, SCHERRER, and HELFER), i, 1202.
Cellobiose anhydride, and its acetyl derivatives (BERGMANN and KNEHE), i, 1384.
Celluloid, molecular dimensions of (BARTON and HUNT), ii, 21.
Cellulose (HESS), i, 118; (HESS and WELTZIEN), i, 517; (HESS, WELTZIEN, and SINGER), i, 641; (HESS, SCHULTZE, and MESSMER), i, 1245; (HESS, MESSMER, and LJUBITSCH), i, 1246.
constitution of (PRINGSHEIM, KNOLL, and KASTON), i, 1385.
structure of fibres of (HERZOG), i, 1045.
structure and Röntgen spectra of, and of its hydrated and alkali forms (HERZOG), i, 639; (KATZ), i, 639, 640; (KATZ and MARK), i, 640.
kinetics of the formation of (ARRHENIUS), ii, 560.
Röntgen spectra of lichenin, tunicin, and (HERZOG and GONELL), i, 371.
action of heat on (BAIN and KAY), i, 639.
depolymerisation of (HEUSER), i, 1387.
adsorption by (LIEPATOV), ii, 385.
adsorption and swelling of (SCHWALBE and TESCHER), i, 889.
effect of swelling on the Röntgen ray spectrum of (KATZ and MARK), ii, 660.
adsorption of alkalis by (LIEPATOV), ii, 957.
adsorption of sodium hydroxide by (VIEWEG), i, 12, 119; (HEUSER), i, 119; (D'ANS and JÄGER), i, 1387.
dispersion of, in salt solutions (v. WEIMARN), ii, 515, 782.
effect of catalysts on carbonisation of (LESSING and BANKS), i, 9.
action of formic acid on (HEUSER and SCHOTT), i, 370.
mercerisation of (HESS), ii, 782.
composition of ammoniacal copper oxide solutions of (BAUR; HESS and MESSMER), ii, 662.
and its derivatives, plasticity of (SHEPPARD and CARVER), ii, 1058.
plasticity of ammoniacal copper oxide solutions of (CARVER and FOLTS), i, 662.
saccharification of (KARRER), i, 118.
enzymic decomposition of (KARRER and ILLING), i, 741, 1029.

Cellulose, degradation of, by fungi (WEHMER), i, 521.
relation between age of, and the properties of the nitrate from it (MEUNIER and BREGUET), i, 119.
β-glucosan from (VENN), i, 887.
alkali (HEUSER and NIETHAMMER; HEUSER and BARTUNEK), i, 520.
cotton, viscosity of (SMALL), ii, 499.
action of heat on (KNECHT and MULLER), i, 370.
action of strong alkalis on (DEHNERT and KÖNIG), i, 369; (KNECHT and PLATT), i, 370.
copper number of (CLIBBENS and GEAKE), ii, 906.
jute (LEHNE and SCHEPMANN), i, 518.
wood (OZAWA), i, 234.
action of dilute acids on (SIEBER), i, 519.
determination of the copper value of (BENESCH), ii, 74.
Cellulose esters, stability of (CAILLE), i, 371.
preparation of plastic material from (FARBWERKE VORM MEISTER, LUCIUS, & BRÜNING), i, 544.
acetonitrates (ATSUKI), i, 642.
nitrate, adsorption of gases by (COSTA), ii, 956.
behaviour of, in ethyl alcohol (ATSUKI), i, 1044.
nitrates (ATSUKI), i, 120.
α-Cellulose, determination of (SCHWALBE), ii, 720, 1209.
Celluloses, determination of the reducing power of (HESS, WELTZIEN, and NAKAMURA), ii, 245.
Celtium. See Hafnium.
Cementite, crystalline structure of, in pearlite (BELAIEW), ii, 768.
Cephæline, derivatives of (KELLER and BERNHARD), i, 1086.
Cereals (JODIDI and WANGLER), i, 1224.
iron, sulphur, and chlorine in the grains of (GREAVES and NELSON), i, 757.
lactic acid bacteria from (FRED, PETERSON, and STILES), i, 1014.
physiology of (JODIDI), i, 1027.
determination of lipoid phosphorus in (RASK and PHELPS), ii, 328.
Cerebroside, new (KLENK), i, 1346.
Cerebrospinal fluid, precipitation of colloidal solutions by (SHAFFER), i, 326.
arsenic in, after injection of salvarsan (FORDYCE, ROSEN, and MYERS), i, 189.
calcium in (CAMERON and MOORHOUSE), i, 857.
distribution of carbon in (POLONOVSK and GALBRUN), i, 854.
Cerebrospinal fluid, cholesterol in (LASCH), i, 456.
diastase in (COHEN), i, 721.
pathological enzymes of (DRAGANESCU and LISSIEVICI-DRAGANESCU), i, 611.
concentration of inorganic constituents of, and blood-serum (HAMILTON), i, 1352.
sugar in, in relation to blood-sugar (GOODWIN and SHELLEY), i, 853.
uric acid content of (BERNHARD), i, 326.
determination of proteins in (WUNSCHENDORFF), i, 1346.
determination of sugar in (CSAPÓ), i, 721.
determination of urea in (ROIG and HELMHOLTZ), i, 853.
Ceresin, fatty acids from (MARCUSSON), i, 349.
Cerium, preparation and properties of (KREMERS and BEUKER), ii, 581.
fluorescent *L*-spectrum of (SKINNER), ii, 5.
and its alloys, adsorption of hydrogen by (SIEVERTS and ROELL), ii, 854.
Cerium hydride (WEEKS), ii, 1186.
copper nitrate (CAROBBI), ii, 145.
sulphate, isomorphism of zirconium sulphate and (FERNANDES), ii, 748.
Cerium determination:—
determination of, electrometrically (TOMIČEK), ii, 716.
determination of, volumetrically (ŠTÉRBA-BOEHM and MATULA), ii, 716.
Cerotic acid, melting point of (KIESEL), i, 1035.
Cervix, cow's, mucous secretion of (WOODMAN and HAMMOND), i, 721.
Cetacea (FUSE), i, 1348, 1349; (TAKATA), i, 1348, 1349; (MORIMURA; OKAZAKI), i, 1348; (SUSUKI), i, 1348, 1349, 1350; (OKOHARA; MASUMIZU; OIKAWA), i, 1349.
Cetene, solubility of mixtures of liquid sulphur dioxide and (SEYER and HUGGET), ii, 504.
pyrogenic decomposition of (GAULT and ALTCHIDJIAN), i, 110.
Cetorhinus maximus, liver oil from (ANDRÉ and CANAL), i, 1373.
Cetyl alcohol, preparation of (YOUTZ), i, 1125.
Chalk, formation of flint in (LINCK and BECKER), ii, 820.
Chalkones. See Phenyl styryl ketones.
Charcoal, adsorption by (URBAIN; KROETZ), ii, 191; (RUFF and HOHLFELD), ii, 192; (RICHARDSON and ROBERTSON; KOLTHOFF), ii, 383; (HERBST), ii, 956.
from viscous media (WEISSENBERGER and WALDMANN), ii, 655.

Charcoal, adsorption and evolution of mixed gases by (LORENZ and WIEDBRAUCK), ii, 382.
adsorption of hydrobenzoins by (HERMANS), ii, 31.
adsorption of methylene-blue by (MECKLENBURG), ii, 530.
adsorption of poisons by (DINGEMANSE and LAQUEUR), i, 1500.
adsorption and detoxication by various (KAP-SOO-LEE), i, 101.
negative adsorption and oxidation by (ORYNG), ii, 656.
oxidation on the surfaces of (RIDEAL and WRIGHT), ii, 806.
oxidation of thiocarbamide by (FREUNDLICH and FISCHER), ii, 307.
animal, highly active (FIRTH and WATSON), ii, 310.
"norit," sorption and catalytic activity of (FIRTH and WATSON), ii, 880.
powdered, adsorption by various (KÖNIG), ii, 1054.
sugar, adsorption of vapours of acetic acid and of toluene by (BAKR and MCBAIN), ii, 193.
activated sugar, adsorption by (MILLER), ii, 656.
wood, decomposition of acetic acid by (KULTASCHEV and KUDRJASCHEVA), ii, 881.
new wood, adsorption of poisons by (LAQUEUR and SLUYTERS), i, 736.
Chaulmoogra oil (HASHIMOTO), i, 1234.
fractionation of (WRENSHALL and DEAN; DEAN, WRENSHALL, and FUJIMOTO), i, 1414.
physiological action of (NORD and SCHWEITZER), i, 734.
metabolic studies with (READ), i, 194.
Chaulmoogric acid, 3-hydroxybenzaldehyde-2-mercuric ester (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1154.
Cheese, Roquefort, odour of (STÄRKLE), i, 205.
ψ-Chelerythrine, and its salts, and bromo- (GADAMER and WINTERFELD), i, 285.
Chelidonic acid, ethyl ester, semicarbazone (ARNDT, SCHOLZ, and NACHTWEY), i, 58.
Chelidonine, bromo-, acetyl derivatives (GADAMER and WINTERFELD), i, 284.
Chelidonium alkaloids (GADAMER), i, 284, 287.
Chemical compounds, properties of, and atomic structure (FAJANS), ii, 623.
constants of elements (EGERTON), ii, 277.
of monatomic gases (SIMON), ii, 98.
Chemical constitution and *K*-absorption spectra (STELLING), ii, 935, 936.
and rotatory power (KENYON, PHILLIPS, and TURLEY), i, 507; (KENYON and SNELLGROVE), i, 771; (HEWITT and KENYON), i, 914.
of optically active compounds (RUPE and KOPP), i, 274; (RUPE and VONAESCH), i, 499; (RUPE and RINDERKNECHT), i, 533.
of sugars (HUDSON and KUNZ), i, 1043.
and magnetic susceptibility of organic compounds (PASCAL), ii, 634.
influence of, on thermal properties of binary mixtures (PASCAL), ii, 953.
and the parachor (SUGDEN, REED, and WILKINS), ii, 936; (SUGDEN and WHITTAKER), ii, 937.
and colour (KEHRMANN), i, 435; (JOHN), i, 1336; (MOIR), ii, 261, 634, 1121.
relation of pungency to (NOMURA and HOTTA), i, 1156.
relation between camphor-like action and (WEDEKIND), i, 684.
and resin-forming capacity (HERZOG), i, 386.
and bactericidal action (ISHIWARA), i, 750.
and physiological action (GILMAN and PICKENS), i, 333; (DUBIN, CORBITT, and FREEDMAN), i, 1502.
and trypanocidal action (KING and MURCH), i, 319.
reactions, production of (BRUTZKUS), ii, 215.
mechanism of (DHAR), ii, 214; (JÜPTNER), ii, 552; (TOLMAN), ii, 799.
temperature coefficients and mechanism of (RICE, FRYLING, and WESOLOWSKI), ii, 48.
calculation of the work of (FRENZEL), ii, 119.
induction periods in (SANYAL and DHAR), ii, 136.
critical increment of (GARNER), ii, 552, 1167; (HINSHELWOOD), ii, 874.
apparatus for carrying out (BUHTZ), ii, 427.
effect of water on (PARSONS), ii, 880.
induced (MITTRA and DHAR), ii, 576.

Chemical reactivity, radiation theory of (Roy), ii, 1167.
and conjugation (Heilbron, Kitchen, Parkes, and Sutton), i, 1320.
Chemiluminescence (Kautsky), ii, 1026.
luminous efficiency of (Adams), ii, 1117.
Chemistry, results of theoretical development of (Haber), ii, 395.
Chenodehydrodeoxycholic acid, and its esters (Windaus, Bohne, and Schwarzkopf), i, 405.
Chenodeoxybilianic acid, trimethyl ester (Windaus and Bohne), i, 554.
Chenodeoxybilianic acids, and their trimethyl esters (Windaus, Bohne, and Schwarzkopf), i, 406.
Chenodeoxycholic acid, and its salts (Windaus, Bohne, and Schwarzkopf), i, 405.
Chenopodium oil (Henry and Paget), i, 1162.
anthelmintic properties of constituents of (Smillie and Pessôa), i, 194.
Chicks, vitamin-*C* in liver of (Carrick and Hauge), i, 617.
embryo, coagulable material in (Pickering and Gladstone), i, 1343.
China wood oil, refractive index of, and its constituents (Böeseken and Ravenswaay), i, 507.
α-elæostearic acid from (Böeseken and Ravenswaay), i, 1129.
Chitin (Karrer, Schnider, and Smirnov), i, 418.
Chloral hydrate, reduction of compounds of (Meldrum and Alimchandani), i, 1272.
compound of casein with (Lieben), i, 91.
action of, on proteins of serum (Nešković), i, 716.
Chloralose (Chevalier and Cherbuliez), i, 467.
Chloralurethylane (Meldrum and Alimchandani), i, 1273.
"**Chloramine** *T*," use of, in analysis (Noll), ii, 66.
Chlorapatite in meteorites (Shannon and Larsen), ii, 321.
Chlorates. See under Chlorine.
Chlorella, synthesis of vitamin-*A* by (Coward), i, 750.
fixation of nitrogen by mixed cultures of *Azotobacter chroococcum* and (Lipman and Teakle), i, 748.
Chloric acid and Chlorides. See under Chlorine.
Chlorination, photochemical (Plotnikov), ii, 220.
by means of selenium (O. and C. A. Silberrad, and Parke), i, 1137; (O. and C. A. Silberrad), ii, 1191.
Chlorine, atomic weight of (Gleditsch), ii, 174; (Moles), ii, 346.
meteoric, atomic weight of (Harkins and Stone), ii, 921.
meteoric and terrestrial, atomic weights of (Harkins and Stone), ii, 1108; (Menzies), ii, 1109.
spectrum of (Lunt), ii, 611.
series spectra of (Bowen and Millikan), ii, 342, 610.
spark spectrum of (L. and E. Bloch), ii, 611.
ultra-violet spectrum of (Hopfield), ii, 1100.
spectral frequencies of (Holweck), ii, 336.
photo-activation of (Taylor), ii, 811, 1079; (Bowen), ii, 1079.
isotopes of (Pilley), ii, 462; (Harkins; Harkins and Stone), ii, 1108; (Menzies), ii, 1109.
and their spectra (Pfund), ii, 255.
critical potential of (Holweck), ii, 729.
activation of, by the electric discharge (Schaum and Feller), ii, 90.
dissociation of (Wohl), ii, 395; (v. Wartenberg and Weigel), ii, 668.
dissociation of, into atoms (Trautz and Geissler), ii, 294.
chemical constants of (Wohl), ii, 98; (Cox), ii, 645.
liquid, viscosity of (Steacie and Johnson), ii, 376.
solubility of, in carbon tetrachloride (Schwab and Hanke), ii, 190.
photochemical reaction between hydrogen and (Marshall), ii, 883; (Kornfeld and Müller), ii, 984; (Norrish), ii, 1080, 1179.
photochemical reaction of hydrogen and, in presence of oxygen (Norrish and Rideal), ii, 572.
effect of water vapour on the photochemical combination of hydrogen and (Coehn and Tung), ii, 142.
as an oxidising and chlorinating agent (Datta and Chatterjee), i, 891.
reaction of arsenic trioxide with (Cambi and Voltolin), ii, 148.
action of, on mercury (Getman), ii, 59.
action of, on potassium bromide or iodide (Parsons), ii, 880.

Chlorine *mon*oxide, photochemical decomposition of (BODENSTEIN and KISTIAKOVSKI), ii, 883.
action of, on organic compounds (GOLDSCHMIDT and SCHÜSSLER), i, 497.
*di*oxide, absorption spectrum and specific heat of (MAYER), ii, 12.
action of light on (BOOTH and BOWEN), ii, 573.
heats of solution and of decomposition of (BOOTH and BOWEN), ii, 299.
*hex*oxide (BODENSTEIN, HARTECK, and PADELT), ii, 991.
Hydrochloric acid, photosynthesis of (CATHALA), ii, 812; (KORNFELD and MÜLLER), ii, 984; (NORRISH), ii, 1080.
absorption spectrum of (COLBY; BECKER), ii, 1114.
ultra-red, rotation spectrum of (CZERNY), ii, 1024.
and its sodium salt, conductivities of, in methyl and ethyl alcohols (GOLDSCHMIDT and DAHLL), ii, 128.
ionisation potential of (BARKER and DUFFENDACK), ii, 1017.
liquid junction potential between potassium chloride solutions and (SCATCHARD), ii, 398.
diffusion potential and transport number of (CARTER and LEA), ii, 300.
activity coefficients of (RANDALL and VANSELOW), ii, 33; (SCATCHARD), ii, 397.
activity coefficients and transport numbers of methyl alcohol solutions of (NONHEBEL and HARTLEY), ii, 1061.
activity coefficients of, in ethyl alcohol solution (HARNED and FLEYSHER), ii, 538.
transference numbers of, in ethyl alcohol (HARNED and FLEYSHER), ii, 542.
influence of gelatin on transport numbers of (SCATCHARD), ii, 41.
dielectric constant of (COMPTON and ZAHN), ii, 1118.
specific heat of aqueous solutions of (VREVSKI and KAIGORODOV), ii, 125; (VREVSKI; VREVSKI and SAVARITZKI), ii, 126.
partial pressures of aqueous solutions of (YANNAKIS), ii, 514.
vapour pressures of aqueous solutions of (VREVSKI, SAVARITZKI, and SCHARLOV), ii, 101; (VREVSKI), ii, 102; (ZEISBERG), ii, 401; (MITSUKURI, ROKKAKU, and WATASE), ii, 1050.

Chlorine:—
Hydrochloric acid, boiling and condensation curves of aqueous mixtures of (CARRIÈRE and ARNAUD), ii, 102.
absorption of, by sulphuric acid (CUPR), ii, 655.
absorption of, in water (WHITMAN and DAVIS), ii, 106.
possible dynamic form of (v. WEIMARN), ii, 395.
reaction between bismuth sulphide and (RAMACHANDRAN), ii, 1208.
Chlorides, transport numbers of (SMITH and MACINNES), ii, 542.
electrical conductivity of, in fused antimony trichloride (KLEMENSIEWICZ), ii, 40.
fused, anode effect in electrolysis of (HEPPENSTALL and SHUTT), ii, 45.
sparingly soluble, solubility of, in chloride solutions (KENDALL and SLOAN), ii, 1052.
excretion of, in urine (TAKANOSU), i, 185.
detection and determination of, in presence of cyanides (SCHULEK), ii, 432, 712.
determination of (DOUGHTY), ii, 238.
determination of, calorimetrically (DEAN and NEWCOMER), ii, 597.
determination of, with a mercury electrode (MÜLLER and AARFLOT), ii, 65.
determination of, micro-chemically, with bromides and iodides (STREBINGER and POLLAK), ii, 823.
determination of, in plant sap (GORTNER and HOFFMAN), ii, 485.
determination of, in animal tissues (VLADESCU), i, 1113.
determination of, in blood (BENGUEREL), i, 455; (RODILLON), i, 722.
determination of, in blood and other body fluids (MISLOWITZER and VOGT; NITSCHKE), i, 1485.
Chloric acid, and its salts, reduction of, by ferrous sulphate (HARVEY), ii, 1197.
neutralisation of, with alkalis (SIMON), ii, 288.
Chlorates, determination of (WAGNER), ii, 1196.
Perchloric acid and its salts, refractivity of (MAZZUCCHELLI and VERCILLO), ii, 963.
conductivity of (LINDE), ii, 39.
use of, in analysis (YOE), ii, 902.

Chlorides:—
Perchlorates, detection of (MARVEL and DU VIGNEAUD), ii, 240.
Chlorous acid, determination of, in presence of hypochlorous acid (SCHLEICHER and WESLY), ii, 433.
Hypochlorous acid, and its alkali salts (DIETZEL and SCHLEMMER), ii, 892.
ionisation constant of (SOPER), ii, 37.
photochemical decomposition of aqueous solutions of (ALLMAND, CUNLIFFE, and MADDISON), ii, 572.
reactions of esters of (DURAND and NAVES), i, 1230.
determination of, electrometrically (SCHLEICHER and TOUSSAINT), ii, 433.
Chlorine detection and determination:—
detection of, in presence of bromine and iodine (DIMITROV), ii, 326.
determination of (CONGDON, CRABTREE, COLES, SMITH, and VEHALGO), ii, 65.
determination of, in benzaldehyde (BUKSCHNEWSKI; FAUST and SPÄNGLER), ii, 1000.
determination of, in cinnamaldehyde (FAUST and SPÄNGLER), ii, 1000.
determination of, in tissues (URBACH and FANTL), i, 1203.
Chlorine water, photochemical decomposition of (ALLMAND, CUNLIFFE, and MADDISON), ii, 572.
reactions between potassium iodide and (MÜLLER and JUNCK), ii, 584.
Chlorite, white, from Madagascar (ORCEL), ii, 821.
Chlorites, constitution of (ISKYUL), ii, 152.
Chloroamine (RASCHIG), ii, 146.
Chloroamines, hydrolysis of acyl derivatives of, in water (SOPER), i, 381.
Chloroauric acid. See under Gold.
Chloro-ethers (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
Chloroferrates. See under Iron organic compounds.
Chloroform, absorption spectrum of (DREISCH), ii, 178.
infra-red absorption spectra of (DREISCH), ii, 627.
surface tension of, and its mixtures with *cyclo*hexanol (WEISSENBERGER and SCHUSTER), ii, 648.
equilibrium of water and (TAMMANN and KRIGE), ii, 869.
parent substance of (MARCHLEWSKI), i, 604.
Chloroform, addition of, to aldehydes (HOWARD), i, 557.
action of benzoyl peroxide on (BÖESEKEN and GELISSEN), i, 30.
compound of tetrapropylammonium iodide and (STEINKOPF and BESSARITSCH), i, 495.
fixation of, by the nervous system (NICLOUX and YOVANOVITCH), i, 195.
Chlorophaerite in dolerites of Edinburgh (CAMPBELL and LUNN), ii, 1093.
Chlorophyll, effect of light on formation of, in leaves (PALLADIN), i, 1518.
development and distribution of, in roots of plants exposed to light (POWELL), i, 1221.
spectrum of, in living leaves (WLODEK), ii, 258.
effect of light on decomposition of, in autumn leaves (COMBES), i, 1120.
complex metallic derivatives of (KUNZ and SEHRBUNDT), i, 1297.
in marine algæ (LUBIMENKO), i, 216.
action of gastric juice on (KORTSCHAGIN), i, 200.
excretion and detection of degradation products of, in urine (HOFSTETTER; KITAHARA), i, 460.
Chloroplatinic acid. See under Platinum.
Chlorosulphonic acid, esters of (TRAUBE, BAUMGARTEN, BAERMANN, LANGE, and JUSTH), i, 775.
Cholesterol, molecular weight of (PARTINGTON and TWEEDY), ii, 273.
action of Röntgen rays on (ROFFO), i, 393.
rotatory power of derivatives of (ROYER), ii, 184.
and its esters, sols of (KEESER), ii, 290, 661.
sols, influence of gelatin on the stability of (KERMACK and MACCALLUM), ii, 525.
dehydrogenation of (DIELS and GÄDKE), i, 1062.
conversion of, into 4-hydroxyhyocholanic acid (WINDAUS and HOSSFELD), i, 1066.
and lecithin in relation to cell membranes (CORRAN and LEWIS), i, 198.
antirachitic properties of irradiated (HESS, WEINSTOCK, and HELMAN), i, 750; (HESS and WEINSTOCK), i, 1020.
vitamin-like properties of (DRUMMOND, ROSENHEIM, and COWARD), i, 617.
synthesis of, in the body (CHANNON), i, 1001.

Cholesterol, origin and fate of, in the organism (FOX and GARDNER), i, 859.
in blood of infants (BANU, NEGRESCO, and HERESCO), i, 452.
in blood serum (HANDOVSKY), i, 322.
in diabetes (NITZESCU, POPESCU-INOTESTI, and CADARIU), i, 462.
in urine (GARDNER and GAINSBOROUGH), i, 1204.
iodine number of (DAM), ii, 444.
serological differentiation of lecithin and (SACHS and KLOPSTOCK), i, 1486.
determination of, in blood (SACKETT), i, 995.
determination of, gravimetrically, in blood (TOMINAGA), i, 453.
and its esters, determination of, in tissues (GARDNER and FOX), i, 182.
Cholic acid, decomposition of, by *Bacillus coli* (KAZIRO), i, 1363.
*apo***Cholic acid**, preparation of (RIEDEL), i, 406.
Choline, origin and function of (GIRNDT), i, 1363.
and its derivatives, permeability and physiological action of (WERTHEIMER and PAFFRATH), i, 1211.
stability of solutions of, in ampoules (LE HEUX), i, 374.
salts of (GUTH), i, 1247.
nitrate and chloroacetyl derivative, action of, on the nervous system (HUNT and RENSHAW), i, 862.
determination of, and its hormonal action (ABDERHALDEN and PAFFRATH), i, 1016.
Cholines, proteinogenous, pharmacology of (GORDONOV), i, 1502.
Chromans. See Benzopyrans.
thio-. See Benzthiopyrans.
Chroman series (KAHIL and NIERENSTEIN), i, 52.
Chromanone chlorostannate (ARNDT and PUSCH), i, 1304.
Chromanone, 7-hydroxy-, and its derivatives (PFEIFFER, OBERLIN, and KONERMANN), i, 1303.
Chromanones, 2:3-*di*bromo-, bromothio-, and thio-, and their derivatives (ARNDT), i, 1309.
thio-, and their derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
spectrochemistry of (KROLLPFEIFFER), ii, 1028.
Chromates and **Chromatotetramminecobaltic salts**. See under Chromium.
Chrome alum, periodic crystallisation of (HEDGES and MYERS), ii, 1168.
Δ^3-Chromens, thio-, spectrochemistry of (KROLLPFEIFFER), ii, 1028.
Chromic salts. See under Chromium.
Chromium, structure of (COLLINS), ii, 18.
crystal structure of (PATTERSON), ii, 845.
K-doublets in spectrum of (SELJAKOV and KRASNIKOV), ii, 914.
spark spectrum of (L. and E. BLOCH), ii, 829.
ultra-violet spark spectrum of (KING), ii, 453.
electrolytic behaviour of (LIEBREICH and WIEDERHOLT), ii, 44; (BOUMAN), ii, 46.
electrolytic, adsorption of hydrogen by (HÜTTIG and BRODKORB), ii, 702.
Chromium alloys with aluminium (SISCO and WHITMORE), ii, 1051.
with molybdenum and nickel (SIEDSCHLAG), ii, 298.
Chromium bases (*chromium ammines*):—
Chromatopentamminecobaltic chromates (RÂY and SARKAR), ii, 816.
Chromatotetramminecobaltic chromates (RÂY and SARKAR), ii, 815.
Decamminemonoaquotrihydroxydioltrichromium thiosulphate (RÂY and SARKAR), ii, 230.
Enneamminediaquotrihydroxydioltrichromium thiosulphate (RÂY and SARKAR), ii, 230.
Chromium salts, photochemical decomposition of, in presence of gelatin (POPOVICKI), ii, 220.
Chromium chloride, magnetic properties of (WOLTJER; WOLTJER and ONNES), ii, 1038.
effect of sodium chloride on solutions of (GUSTAVSON), ii, 1086.
*di*chromate (CALCAGNI), ii, 891.
potassium fluoride, preparation of (DUBOIN), ii, 995.
hydroxide, solution of, in sodium hydroxide (FRICKE and WINDHAUSEN), ii, 35.
equilibrium of sodium hydroxide, chromite, and (MÜLLER), ii, 124.
coagulation of (SEN and MEHROTRA), ii, 665.
colloidal (BJERRUM), ii, 111.
precipitation of, electrometrically (BRITTON), ii, 1203.
*sesqui*oxide (*chromic oxide*), solid solutions of, in ferric oxide (FORESTIER and CHAUDRON), ii, 534.
*tri*oxide, equilibrium of boric acid, water, and (GILBERT), ii, 869.
Chromic salts, quantitative oxidation of, by silver oxide (HANS), ii, 316.

Chromium :—
Chromous ammonium and potassium fluorides (TRAUBE, BURMEISTER, and STAHN), ii, 990.
Chromates of the cerium group (ZAMBONINI and CAROBBI), ii, 700.
Chromium organic compounds :—
γ-mono- and *αγ-di*-bromoacetylacetones (REIHLEN, ILLEG, and WITTIG), i, 232.
Chromous pyridine chloride (TRAUBE, BURMEISTER, and STAHN), ii, 990.
Chromium detection and determination :—
detection of, without nitric acid (LONGINESCU and PETRESCU), ii, 1206.
determination of, in presence of iron and vanadium (KOLTHOFF and TOMIČEK), ii, 72.
Chromones. See Benzopyrones.
Chromonol, 2-bromothio- (ARNDT), i, 1311.
Chrysanthemum cinerariæfolium, insecticidal principle of (YAMAMOTO), i, 1522.
Chrysarobin, composition of (EDER and HAUSER), i, 948, 1160.
Chrysin, and its dimethyl ether, absorption spectra of (TASAKI), i, 1444.
Chrysinidin salts (PRATT and ROBINSON), i, 825.
Cicer arietinum, γ-galactan in seeds of (CASTORO), i, 1043.
Cicerose (CASTORO), i, 1043.
Cignolin. See Anthranol, 1:8-*di*-hydroxy-.
*iso***Cinchomeronic acid**, phenyl ester (MEYER), i, 836.
Cinchona alkaloids (GIEMSA and BONATH), i, 291.
Cinchoninic acid, derivatives of (MEYER), i, 836.
Cineole, determination of, in essential oils (CASH and FAWSITT), ii, 75.
Cinnamaldehyde benzoylhydrazone (v. AUWERS and DANIEL), i, 1181.
diphenylene-4:4′-dihydrazone (CHATTAWAY, IRELAND, and WALKER), i, 1195.
determination of chlorine in (FAUST and SPÄNGLER), ii, 1000.
Cinnamaldehyde, α-bromo-, derivatives of (v. AUWERS and OTTENS), i, 1429.
Cinnamaldoxime, *N*-aryl ethers of (BAMBERGER), i, 142.
Cinnamic acid, Claisen synthesis of (SCHEIBLER and FRIESE), i, 1417.
equilibrium of, with phenols (KREMANN, ZECHNER, and DRAZIL), ii, 650.
metallic salts of (EPHRAIM and PFISTER), i, 1148.
Cinnamic acid, theophylline salt (KNOLL & Co.), i, 828.
vanadicinnamyl salt (SCAGLIARINI and AIROLDI), i, 920.
ethyl ester, action of ammonia on (STOSIUS and PHILIPPI), i, 918.
Cinnamic acid, *p*-amino-, and *p*-nitro-, γ-dimethylamino-αβ-dimethylpropyl esters (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 1419.
o-cyano-, and its esters (CHEMISCHE FABRIKEN VORM. WEILER-TER MEER), i, 1418.
3:5-*di*hydroxy- (MAUTHNER), i, 926.
Cinnamonitrile, and α-bromo- (v. AUWERS and OTTENS), i, 1430.
Cinnamoyl cyanide (MARSH and STEPHEN), i, 1158.
m-**Cinnamoylaminoanisic acid** (SEKA and SCHRECKENTAL), i, 1316.
n-**Cinnamoylaminobenzoic acid**, and its acetyl derivative (SEKA and SCHRECKENTAL), i, 1316.
m-**Cinnamoylamino-*p*-toluic acid** (SEKA and SCHRECKENTAL), i, 1316.
7-Cinnamoyloxy-2-styryl*iso*flavone (BAKER and ROBINSON), i, 1299.
Cinnamyl alcohol, compound of, with calcium chloride (ENDOH), i, 1428.
Cinnamyl ethyl ether (BERT), i, 804.
Cinnamylideneacetic acid, polymerisation of (STOBBE, HENSEL, and SIMON), i, 1067.
Cinnamylideneacetone, polymerisation of (STOBBE, HENSEL, and SIMON), i, 1067.
Cinnamylideneacetophenone, derivatives of, and their polymerisation (GIUA), i, 1283.
Cinnamylideneacetophenone, *m*-amino- and *m*-nitro- (PFEIFFER, PRAHL, FITZ, and STOLL), i, 680.
Cinnamylideneacetylacetone, polymerisation of (STOBBE, HENSEL, and SIMON), i, 1067.
Cinnamylidenecamphor, absorption spectra of (PURVIS), ii, 627.
Cinnamylidenemalonic acid, polymerisation of (STOBBE, HENSEL, and SIMON), i, 1067.
Cinnamylidene-*p*-methoxyacetophenone, *m*-nitro- (PFEIFFER, PRAHL, FITZ, and STOLL), i, 681.
Citraconic acid, esters, action of ammonia on (STOSIUS and PHILIPPI), i, 892.
derivatives of (GOEBEL), i, 1038.
Citral, oxidation of, with ozone (VERLEY), i, 406.
Citric acid, formation of, from diketoadipic acid (FRANZEN and SCHMIDT), i, 231.

Citric acid, formation of, by moulds (BUTKEWITSCH), i, 341.
condensation of, with phenols (MÜLLER), i, 1442.
phenylhydrazoanilide of, and its phenylhydrazone salt (NAU, BROWN, and BAILEY), i, 1379.
in cow's milk (KIEFERLE, SCHWAIBOLD, and HACKMANN), i, 855.
lead salt, solubilities of (AUERBACH and WEBER), i, 1130.
tribenzyl ester (HEFTI and SCHILT), i, 394.
distinction of tartaric acid from (PARRI), ii, 162.
detection of (RODILLON), ii, 246.
detection of, in tissues (KLEIN and WERNER), i, 871.
determination of (CAMP), ii, 246.
*iso***Citric acid**, salts and derivatives of (NELSON), i, 619.
Citroanilide, salts and esters of (NAU, BROWN, and BAILEY), i, 1379.
Citrodianilidemonoamide (NAU, BROWN, and BAILEY), i, 1379.
Citromyces glaber, effect of calcium salts on growth of (KUSNETZOV), i, 746.
Citronella oil, determination of citronellal in (DUPONT and LABAUNE), ii, 75.
Citronellal, determination of, in citronella oil (DUPONT and LABAUNE), ii, 75.
Citronellol, derivatives of (RUPE and RINDERKNECHT), i, 658.
Citronellyl bromide (RUPE and RINDERKNECHT), i, 658.
Citronellylaniline. See Phenylcitronellylamine.
Citrus, extraction of pectin from (POORE), i, 619.
Claisen condensation (MORGAN, DREW, and PORTER), i, 363.
Clays, effect of heat on (HOULDSWORTH and COBB), ii, 671; (MELLOR and SCOTT), ii, 698.
mechanical composition curves of (ROBINSON), i, 224.
basic exchange in (WIEGNER), ii, 527; (UNGERER), ii, 658.
as soil colloids (JOSEPH), i, 1228.
china, Röntgen-ray investigation of (SHEARER), ii, 698.
quaternary, siliceous matter in (DEMOLON), ii, 1195.
Japanese, action of camphor white oil on (ONO), i, 941.
Coagulation, ultramicroscopy of (ROCASOLANO), ii, 523.
chemicals for prevention of (LUMIÈRE), i, 606.
of colloids (BJERRUM), ii, 111.
Coagulation of colloids, influence of valency on (FREUNDLICH and ZEH), ii, 115.
by electrolytes (RABINOVITSCH), ii, 778.
of colloidal solutions (JABŁCZYŃSKI and LORENTZ-ZIENKOWSKA), ii, 666.
Coal, structure of (MARCUSSON), i, 793.
composition of (TIDESWELL and WHEELER), i, 373; (FRANCIS and WHEELER), i, 373, 389.
effect of catalysts on carbonisation of (LESSING and BANKS), i, 9.
oxidation of (FRANCIS and WHEELER), i, 644; (OSWALD and PINTA), i, 793.
analysis of (KREULEN), ii, 240.
Cobalt, occurrence of, in arable soils (BERTRAND and MOKRAGNATZ), i, 492.
in soils, plants, and animals (MCHARGUE), i, 1023.
spectrum of (CATALÁN), ii, 611.
arc spectrum of (WALTERS), ii, 334.
spark spectrum of (L. and E. BLOCH), ii, 727.
magnetisation of iron, nickel, magnetite, and (ASHWORTH), ii, 944.
films, magnetic properties of (SORENSEN), ii, 82.
magnetostrictive effects in (MCCORKLE), ii, 487.
electro-deposition of (EMELIANOVA), ii, 676.
colloidal, catalysis with (PAAL and BOETERS), ii, 1072.
in animal organs and tissues (BERTRAND and MÂCHEBŒUF), i, 719, 996.
Cobalt alloys with iron (GRENET), ii, 973.
expansion coefficients of (HONDA and OKUBO), ii, 104.
Cobalt bases (*cobaltammines*) (EPHRAIM and FLÜGEL), ii, 61; (EPHRAIM), ii, 992.
photochemistry of (SCHWARZ and WEISS), ii, 576.
complex selenates of (MEYER, DIRSKA, and CLEMENS), ii, 422.
Aquopentamminecobaltic dichromates (RÂY and SARKAR), ii, 816.
Hexamminecobaltictriaquodisulphitosulphatocobaltiate (SCAGLIARINI and TARTARINI), ii, 1193.
Triaquotriamminecobaltictriaquotrisulphatocobaltiate (SCAGLIARINI and TARTARINI), ii, 1193.
Cobalt compounds in vegetables (BERTRAND and MOKRAGNATZ), i, 873.
Cobalt salts, rotatory dispersion of (ROBERTS), ii, 478.

Cobalt amide and nitride (BERGSTROM), ii, 231.
chloride, magnetic properties of (WOLTJER; WOLTJER and ONNES), ii, 1038.
ionisation and conductivity in solutions of, and its mixtures with barium chloride (MAZZETTI), ii, 209, 210.
colour change in solutions of (GRÓH), ii, 963.
ammoniate of (BILTZ and RAHLFS), ii, 1191.
hydroxide, precipitation of, electrometrically (BRITTON), ii, 1203.
selenates, complex (MEYER, DIRSKA, and CLEMENS), ii, 422.
selenide (MOSER and ATYNSKI), ii, 583.
sulphate, anhydrous, magnetic properties of (FOEX), ii, 346.
Cobaltic hydroxide, colloidal (PAAL and BOETERS), ii, 1090.
decomposition of hydrogen peroxide by (TRYHORN and JESSOP), ii, 807.
Cobalt organic compounds (MORGAN and SMITH), i, 1457.
Cobalt detection, determination, and separation:—
detection of (TINDAL), ii, 242; (NICHOLS and COOPER), ii, 715.
detection and determination of (DENIGÈS), ii, 826.
determination of (JÄRVINEN), ii, 602.
determination of, colorimetrically, in presence of nickel (EVANS), ii, 904.
separation of manganese, nickel, zinc, and (LEMARCHANDS), ii, 242.
Cocaine, and its derivatives, influence of sterilisation on hydrogen-ion concentration in solutions of (ROY), i, 1084.
hydrochloride, effect of sterilisation on the anæsthetic value of (LIOB), i, 862.
arsenious tartrate (DEBUCQUET), i, 1090.
Cocaines, isomeric, toxicity of, and their excretion (GRUHN), i, 736.
Coconut oil (ARMSTRONG, ALLAN, and MOORE), i, 353.
rancidity of (STÄRKLE), i, 205.
Cod, muscle of. See Muscle.
Cod-liver oil (DUBIN and FUNK), i, 1120.
anti-rachitic activity of (BILLS), i, 1019; (NELSON and STEENBOCK), i, 1020.
growth-promoting and anti-rachitic value of (SOAMES), i, 210.
Cod-liver oil, effect of heat on vitamins of (SOUTHGATE), i, 1515.
Codeine, and its isomerides, action of thionyl chloride on (SPEYER and ROSENFELD), i, 961.
arsenious tartrate (DEBUCQUET), i, 1090.
Codeine, bromo- and chloro-, preparation and catalytic reduction of (SPEYER and ROSENFELD), i, 961.
Codeinone, bromo-, action of sodium hyposulphite on (SPEYER and ROSENFELD), i, 961.
Coke, determination of nitrogen in (TER MEULEN), ii, 599.
Collagen (HERZOG and GONELL), i, 1488.
thermolability of (THOMAS and KELLY), ii, 520.
nitrogen distribution in hydrolysis products of (SADIKOV), i, 176.
Collisions, termolecular, resulting from bimolecular collisions (TRAUTZ and SCHUETER), ii, 552.
Collodion membranes. See Membranes.
Colloids (SVEDBERG), ii, 196.
structure of (v. WEIMARN), ii, 660.
chemistry of (FRIED and PAULI), ii, 390; (KÜHNL and PAULI), ii, 776.
nomenclature of (ZACHARIAS), ii, 196.
electrical synthesis of (BÖRJESON), ii, 197.
birefringency in (FREY), ii, 200; (NEUBERT), ii, 201.
coagulation of (JABŁCZYŃSKI), ii, 203.
by electrolytes (GHOSH and DHAR), ii, 511; (RABINOVITSCH), ii, 778.
velocity of coagulation of (JABŁCZYŃSKI), ii, 34, 35.
influence of valency on coagulation and cataphoresis of (FREUNDLICH and ZEH), ii, 115.
filtration of (ZAKARIAS), ii, 862.
plasticity of (BINGHAM), ii, 1157.
swelling of (BILTZ), ii, 520; (KATZ and MARK), ii, 666.
electricity produced in (KOPACZEWSKI), ii, 978.
effect of ammonium salts on (FULMER), i, 1508.
osmotic properties and coagulation of (BJERRUM), ii, 111.
crystallisation of aqueous suspensions of (FREUNDLICH and OPPENHEIMER), ii, 203.
basic exchange in (WIEGNER), ii, 527.
increase of imbibition by (POPOV and SEISOV), i, 606.
fixation of water in (KUHN; FISCHER; SCHADE), ii, 36.

Colloids, water-combination in (HÜTTIG), ii, 516.
solution of, in mixed liquids (MARDLES), ii, 34.
effects of dilution on (KOPACZEWSKI), ii, 111.
effect of dielectrics on stability of (DEUTSCH), ii, 525.
action of ions on (MICHAELIS), ii, 1154.
mobility of particles in (GERASIMOV), ii, 204.
purification of (BECHHOLD and ROSENBERG), ii, 668.
protection of, by small quantities of electrolytes (BOUTARIC and PERREAU), ii, 526.
sensitisation and protection of, by lipoids (BECK), ii, 527.
protective action of soaps on (BHATNAGAR, PRASAD, and BAHL), ii, 1155.
decomposition of neutral salts by (HÜMMELCHEN and KAPPEN), i, 218.
of clay, electrical charge on (DAYHUFF and HOAGLAND), i, 219.
in mineralogy and geology (DOELTER), ii, 514.
heat of wetting of, in soils (ANDERSON), i, 219; (BOUYOUCOS), i, 1228.
dispersoid, effect of added salts on the stability of (v. WEIMARN and UTZINO), ii, 664.
quantitative filtration (OSTWALD), ii, 198.
facultative and obligatory, and the electric charge thereon (MICHAELIS and DOKAN), ii, 963.
hydrophilic, effect of agitation on coagulation of (FREUNDLICH and BASU), ii, 522.
inorganic, action of ozone on aqueous solutions of (RIESENFELD and HAASE), ii, 988.
lyophilic, action of electrolytes on (KRUYT and TENDELOO), ii, 1059.
and Poiseuille's law (KRUYT and ROBINSON), ii, 391; (KRUYT), ii, 515.
mixed (JABŁCZYŃSKI and LORENTZ-ZIENKOVSKA), ii, 1060.
protective (SEN), ii, 666.
action of (TRAUBE and RACKWITZ), ii, 968.
suspensoids, therapeutic action of (LOISELEUR), i, 197.
determination of, in soils (BOUYOUCOS), i, 348.
Colloidal colouring matters, electrocapillary analysis of (KOPACZEWSKI), ii, 828.
Colloidal electrolytes, dispersion of (MESTREZAT and JANET), i, 198.
elements, preparation of (DEDE and WALTHER), ii, 197.
metals, conductivity of (ANDRÉ), ii, 976.
sols, cataphoresis of (EVERS), ii, 668.
in non-dissociating liquids (HATSCHEK and THORNE), ii, 197.
colour of suspensions of (JOBST), ii, 777.
particles, size of (SVEDBERG), ii, 528.
properties, development of (ALEXANDER), ii, 779.
reactions, electromagnetic nature of (DITMAN), ii, 51.
solutions, viscosity of (OSTWALD), ii, 291, 663; (MATTHÄUS) ii, 663; (DE WAELE), ii, 777.
viscosity and elasticity of (SZEGVARI), ii, 111; (FREUNDLICH and SCHALEK), ii, 112.
electrophoresis of (SCHAUM and FRIEDERICH), ii, 220.
surface tension of, and of their mixtures with mineral waters (HENRIJEAN and KOPACZEWSKI; D'ARSONVAL and BORDAS), ii, 291.
stability of (SEN), ii, 664; (SEN and MEHROTRA), ii, 665.
effect of added substances on (BOUTARIC and MANIÈRE), ii, 778.
in presence of electrolytes (BOUTARIC and PERREAU), ii, 863.
similarities of true solutions and (BANCROFT), ii, 858.
size and granular distribution of particles in (AUDUBERT and RABATÉ), ii, 775.
orientation of particles in (ZOCHER), ii, 966.
determination of molecular dimensions and Avogadro's number from (DU NOUY), ii, 844.
adsorption of sugars by (PRASAD, SHRIVASTAVA, and GUPTA), ii, 957.
coagulation of (HENRY and MORRIS), ii, 34; (JABŁCZYŃSKI and LORENTZ-ZIENKOWSKA), ii, 666.
effect of low temperatures on (BOTTAZZI and BERGAMI), ii, 965.
by electrolytes (MUKHERJEE and GHOSH), ii, 394.
by hydrogen ions (WEIR), ii, 1155.
by Röntgen rays (DOGNON), ii, 665.

Colloidal solutions, coagulation of, flocculation of (BOUTARIC), ii, 393; (BOUTARIC and MANIÈRE), ii, 394.
effect of addition of stable colloids on (BOUTARIC and PERREAU), ii, 1155.
in nitrobenzene (BROWN and BURY), ii, 1055.
emulsoid, determination of the size of particles in (KRUYT and TENDELOO), ii, 113.
unstable, dialysis of (GUTBIER), ii, 965.
suspensions, stability of (KERMACK and WILLIAMSON), ii, 523.
effect of light on the settling of (MORISON), ii, 774.
distribution of particles in (BARKAS), ii, 289; (COUTTS), ii, 290.
Colophony from the firs of Bucovina (CZERNY), i, 253.
American, pyrogenic decomposition of of (VESTERBERG and BORGE), i, 252.
Colorimeter, modified Duboscq–Pellin, for biochemical work (WU), ii, 899.
Colostrum (HÖLLEN), i, 1490.
bacteriolytic power of (J. and M. BORDET), i, 616.
Colour, theory of (ZINTL and RAUCH), ii, 182; (STIEGLITZ), ii, 840.
and chemical constitution (MOIR), ii, 261; (KEHRMANN), i, 435.
and molecular geometry (MOIR), ii, 634, 1121.
Colours, temper (MASON), ii, 108.
Colouring matter, $C_{14}H_6O_2N_2Br_4$, from 3:5-dibromo-2-aminopyridine (TSCHITSCHIBABIN), i, 159.
$C_{16}H_{14}O_2N_2$, from 2-amino-3-methylpyridine (TSCHITSCHIBABIN), i, 159.
$C_{17}H_{10}O_3NBrS$, from isatin and 4-bromo-2-carboxy-5-methoxyphenylthiolacetic acid (GRIFFITH and HOPE), i, 828.
$C_{20}H_{10}O_4$, from dinaphthyl derivatives and aluminium chloride (BADISCHE ANILIN- & SODA-FABRIK), i, 1290.
$C_{24}H_{15}ON_2$, from 3-hydroxy-4-keto-1-indoxenyl-1:4-dihydronaphthalene and *o*-phenylenediamine (SANDER), i, 982.
$C_{24}H_{24}N_2Cl_2$, and its derivatives, from acetoethylanilide and phosphoryl chloride (FISCHER, MÜLLER, and VILSMEIER), i, 440.
$C_{25}H_{29}N_2I$, from ethyl orthoformate and 2:3:3-trimethyl-ψ-indole methiodide (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 839.
Colouring matter, $C_{26}H_{16}O_2N_2S$, from 5-acetamido-1:4-naphthaquinone-4-anil and oxythionaphthen (SANDER), i, 982.
$C_{27}H_{30}O_3N_2$, from 4-phenyltetrahydro-1:4-oxazine, benzaldehyde, and hydrochloric acid (ADKINS and SIMINGTON), i, 986.
Colouring matters, (AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION), i, 1330.
preparation of (VOSWINCKEL), i, 572.
physical chemistry of (FÜRTH), ii, 1057.
absorption spectra and constitution of (KEHRMANN and SANDOZ), i, 983.
action of ultra-violet light on (HEERMANN), ii, 144.
extinction of fluorescence of (VAVILOV), ii, 474.
polarised fluorescence of (VAVILOV), ii, 739.
from solutions of (LEVSCHIN), ii, 13, 629, 1117; (WEIGERT and KÄPPLER), ii, 1026.
diffusion of (AUERBACH), ii, 28.
adsorption of, by aluminium hydroxide (WOOD and WOOLLER), ii, 285.
by glass (SCHELTE), ii, 286.
effect of hydrogen-ion concentration on, by mordants (MARKER and GORDON), ii, 31.
by soils (WILKINSON and HOFF), i, 1227.
effect of salts on, by tissues (MANN), ii, 35.
by wool and cotton (SPEAKMAN and BATTYE), ii, 284.
insoluble in water (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 587, 599.
effect of light on, in cotton fabrics (CUNLIFFE), ii, 812.
kinetics of bleaching of (PREDVODITELEV and NETSCHAJEVA), ii, 575.
change in conductivity of films of, on bleaching (SCHTSCHODRO), ii, 1134.
reduction of, by alcoholic sodium hyposulphite (EYMER), ii, 582.
effect of, on growth of bacteria (BURNET), i, 1117.
effect of, on the multiplication of infusoria (ROBERTSON), i, 1012.
staining of the walls of plant cells by (SCHWARZ), i, 755.
colloidal. See Colloidal colouring matters.
of the flavone series, absorption spectra of (TASAKI), i, 1444, 1445.
of flesh and blood (SCHUMM), i, 1347.

Colouring matters of fungi (KÖGL and POSTOWSKY), i, 50, 1083, 1439; (KÖGL and v. TAEUFFENBACH), i, 1440.
mordant, co-ordination theory applied to (MORGAN and SMITH), ii, 841.
from poison gases (BOGERT and CHERTCOFF), i, 80, 315.
sulphide, structure of (HODGSON), i, 1104.
synthetic, diffusion of (KOPACZEWSKI), ii, 529.
vat (KALLE & Co.), i, 1334.
detection of, on cotton (JONES and KILBY), ii, 608.
vegetable, fluorescence of (MEUNIER and BONNET), i, 1439.
detection of, spectrophotometrically (HOLMES), ii, 1212.
Colouring matters. See also :—
Aetioporphyrin.
Aetiourinoporphyrin.
Atromentin.
Bilirubin.
Carotin.
Chrysin.
Coproporphyrin.
Cytochrome.
Galangin.
Hæmatoporphyrin.
Hæmatoidin.
Hæmin.
Hæmochromogen.
Hæmoglobin.
Hæmoporphyrin.
Helicorubin.
Mesobilirubinogen.
Mesoporphyrin.
Methæmoglobin.
Ooporphyrin.
Oxyhæmin.
Oxyhæmocyanin.
Oxyhæmoglobin.
Phycocyanine.
Phycoerythrin.
Phylloerythrin.
Pyocyanine.
Sulphæmoglobin.
Urobilin.
Urobilinogen.
Urochromogen.
Xanthophyll.
Xanthopterin.
Xylindein.
Colpidium colpoda, effect of washing on the reproduction of (CUTLER and CRUMP), i, 1012.
Columbamine, constitution of (SPÄTH and DUSCHINSKY), i, 1313.
Combustion of gases at high pressures (BONE, NEWITT, and TOWNEND), ii, 880.
Combustion of gases, electrification in (DICKINSON), ii, 740.
of mixed gases, effect of infra-red radiation on (DAVID), ii, 980.
Comenic acid, manganous salt (VERKADE), i, 421.
Comet, Daniel's, cyanogen spectrum in (BALDET), ii, 928.
Comets, spectrum of the tails of (BALDET), ii, 180, 469.
Commutator for potentiometric measurements (ERNEST), ii, 236.
Compounds of high molecular weight, chemistry of (BERGMANN and KNEHE), i, 1384; (BERGMANN, MIEKELEY, and KANN), i, 1474.
*spiro***Compounds**, formation and stability of (BAKER), i, 1277.
Compressibility of organic liquids (HEBEISEN), ii, 763.
chemical affinity, and internal pressure (SAERENS), ii, 91.
Compressors, chemical reactions in (BRUTZKUS), ii, 314.
Compton effect (WEBSTER and ROSS), ii, 92, 1034; (ROSS and WEBSTER), ii, 269, 270; (WOO; JAUNCEY), ii, 368; (BECKER, WATSON, SMYTHE, BRODE, and MOTT-SMITH), ii, 1128.
intensity of (JAUNCEY; DAVIS), ii, 747.
width of modified spectral lines in (JAUNCEY), ii, 483.
Concanavaline, preparation of (SUMNER and GRAHAM), i, 1027.
Condensers, effect of diffusion of gaseous ions on the current-voltage curves of (JAFFÉ), ii, 253.
water (PATTERSON), ii, 151.
Conductivity of metals, theory of (CASSEL; WOLF), ii, 942.
Conductivity water. See under Water.
Conductors, good, dielectric constants of (FÜRTH), ii, 631.
Congo-paper, highly sensitive (HORST), ii, 1196.
Congo-red, sensitisation of, by gelatin (ETTISCH and RUNGE), ii, 864.
Conhydrine (HESS and GRAU), i, 425.
Coniine hydrochloride, optical properties of (KEENAN and HANN), i, 1093.
Contact detectors, rectifying action of (STRANSKI), ii, 55.
Cooling, theories of (SEELIGER), ii, 492.
Co-ordination and residual affinity (MORGAN and YARSLEY), i, 378; (MORGAN and SMITH), i, 1457; (MORGAN, CARTER, and HARRISON), ii, 1042.
Co-ordination compounds (HAHN and WOLF), ii, 578; (REMY and ROTHE), ii, 1088.

Co-ordination numbers, geometry of (STRAUBEL; HÜTTIG), ii, 362.
Copper, occurrence of, in soils, plants, and animals (MCHARGUE), i, 1023.
atomic weight of (RUER and BODE), ii, 620.
spectrum of (BELL), ii, 470.
arc spectrum of (LOWERY), ii, 4; (SHENSTONE), ii, 453, 1014.
low-voltage arc spectra of (SHENSTONE), ii, 77.
Röntgen ray spectrum of (ALLISON and ARMSTRONG), ii, 1015.
spark spectrum of (L. and E. BLOCH), ii, 829.
ultra-violet absorption spectrum of (ZUMSTEIN), ii, 453.
conductivities of (SCHOFIELD), ii, 273.
potential of, in cyanide solutions (WALKER, SORRELS, and BRECKENRIDGE), ii, 1066.
effect of dissolved elements on electrical resistivity of (NORBURY), ii, 273.
expansion coefficient of (BORELIUS and JOHANSSON), ii, 27.
diffusion of, into gold and silver (THOMPSON and DEARDEN), ii, 29.
atoms, spatial arrangements round (SCHLESINGER), i, 1249.
recrystallisation of, after hot deformation (HANEMANN), ii, 1134.
strained, Röntgen ray analysis of (ONO), ii, 746.
catalytic action of (PALMER and CONSTABLE; CONSTABLE), ii, 311.
reduced, catalytic activity of (KOMATSU and KURATA), i, 687, 942; (KOMATSU and YUKITOMO), i, 687; (KOMATSU and TANAKA), i, 905; (KOMATSU and MASUMOTO), ii, 1071.
corrosion of, in sea-water (BENGOUGH and MAY), ii, 218.
anomalous protection against oxidation of (SHEPPARD), ii, 1084.
action of iron on (SIEBE; HANSON and FORD), ii, 317.
action of nitrogen peroxide on (KLEMENC and SCHROTH), ii, 228.
effect of colloids on the displacement of, by zinc (GRAY), ii, 578.
action of natural waters on (HENSTOCK), ii, 696.
in the animal organism (ZANDA), i, 719.
Copper alloys, electrolysis of (KREMANN and GRUBER-REHENBURG), ii, 678.
with aluminium (MASING and KOCH), ii, 787.
dilatation of (CHEVENARD), ii, 768.
Copper alloys with aluminium and zinc (HANSON and GAYLER), ii, 974.
with antimony (KURNAKOV and BELOGLAZOV), ii, 787.
with gold (SEDSTRÖM), ii, 104.
gold–copper compound in (STERNER-RAINER), ii, 651.
with iron and manganese (OSTERMANN), ii, 1050.
with magnesium and zinc, determination of magnesium in (SCHÜRMANN and SCHOB), ii, 902.
with manganese, crystal structure of (PATTERSON), ii, 1130.
with mercury (TAMMANN and STASSFURTH), ii, 377.
with nickel (CHEVENARD), ii, 851.
oxidation of (PILLING and BEDWORTH), ii, 689.
with palladium, structure of (HOLGERSSON and SEDSTRÖM), ii, 20.
with tin (ISIHARA), ii, 122.
hardness of (BAUER and VOLLENBRUCK), ii, 104.
α-phase boundary in (STOCKDALE), ii, 973.
with zinc (GENDERS and BAILEY), ii, 297; (IITSUKA), ii, 651.
β-transformations in (HAUGHTON and GRIFFITHS), ii, 973.
Röntgen ray analysis of (WESTGREN and PHRAGMEN), ii, 746.
Copper salts, overvoltage in electrolysis of (GORDON), ii, 549; (MILLER), ii, 798.
reduction of, by dextrose (FLEURY and TAVERNIER), ii 605.
distribution of, with vitamin-*A* (MCHARGUE), i, 1515.
toxic action of, on protoplasm (VOEGTLIN, JOHNSON, and DYER), i, 1116.
Copper chlorides, oxidation-reduction potential of (CARTER and LEA), ii, 403.
iodide, band spectrum of (MULLIKEN), ii, 833.
nitrate, equilibrium of ammonium nitrate, water, and (MEIGER; SCHREINEMAKERS, BERKHOFF, and POSTHUMUS), ii, 123.
double nitrates with metals of the cerium group (CAROBBI), ii, 145, 222.
selenides (MOSER and ATYNSKI), ii, 584.
sulphate, equilibrium of aluminium sulphate, water, and (CAVEN and MITCHELL), ii, 396.
tervalent copper compound from oxidation of, in alkaline solution (VRTIS), ii, 694.

Copper sulphate, manurial experiments with (DENSCH and HUNNIUS), i, 489; (DENSCH), i, 766.
See also Anhydrite.
sulphates (KRUGER), ii, 58.
Cupric chloride, reaction of magnesium organic halides with (GILMAN and PARKER), i, 237.
antiseptic action of, in various solvents (KLISSIUNIS), i, 1500.
halides, ammoniates of (BILTZ, BRÖHAN, and WEIN), ii, 1182.
hydroxide, catalysis of the dehydration of (QUARTAROLI), ii, 806.
equilibrium of silver nitrate, water, and (MALQUORI), ii, 697.
compounds of quinine with (ERBEN), i, 573.
precipitation of, electrometrically (BRITTON), ii, 1204.
oxide, solubility of, in water (REMY and KUHLMANN), ii, 119.
sulphide, conversion of, to cuprous sulphide (HAHN), ii, 160.
Cuprous salts, reaction of ferrous salts with (WELLS), ii, 148.
bromide, crystalline (BRIGGS), ii, 319.
chloride, vapour pressure of hydrochloric acid solutions of (YANNAKIS), ii, 401.
hydroxide (KLASON), ii, 318.
Cupro-sulphites and **-thiosulphates** of the rare earths (CANNERI and FERNANDES), ii, 888.
Copper organic compounds:—
with diacetyldioxime (PANETH and THILO), i, 1132.
Copper detection, determination, and separation:—
detection of (SCHERINGA), ii, 326; (NICHOLS and COOPER), ii, 715; (SPACU), ii, 1003.
detection of, in distilled water (POIROT), ii, 242.
detection and determination of (HAHN), ii, 1096.
determination of, potentiometrically (ZINTL and RAUCH), ii, 1003.
determination of, volumetrically, with potassium iodide (HERSCHKOVITSCH), ii, 904.
determination of, electrolytically, in presence of antimony, lead, and tin (LUKAS and JÍLEK), ii, 241.
determination of, electrolytically, in presence of lead (BILTZ), ii, 715.
determination of, in tissues (CURRIE), i, 183.
determination of, and its separation from cadmium and zinc (JÍLEK and LUKAS), ii, 903.
Copper detection, determination, and separation:—
separation of antimony, lead, tin, and (LASSIEUR), ii, 328.
separation of cadmium and (SACCARDI), ii, 159.
separation of, from iron (ARDAGH and BROUGHALL), ii, 603.
separation of lead and (LASSIEUR), ii, 159.
separation of mercury and (SPACU), ii, 1004.
Coproporphyrin, synthesis of, by yeast (FISCHER and FINK), i, 105, 866.
absorption coefficient of (NIEMANN), i, 1206.
Coprosterol, iodine value of (DAM), i, 856.
Cordierite from India (KRISHNAN), ii, 322.
Corn offal, nitrogenous constituents of (RANDOIN, ALQUIER, ASSELIN, and CHARLES), i, 210.
Corresponding states, theory of (BOITARD), ii, 865.
Corrosion (MAASS and LIEBREICH), ii, 140; (WHITNEY; SHIPLEY, McHAFFIE, and CLARE), ii, 688; (WHITMAN and RUSSELL), ii, 689; (BEENY; ENOS), ii, 1068; (UTIDA and SAITO), ii, 1069.
report of the Committee on (BENGOUGH and MAY), ii, 218.
water-line (EVANS), ii, 687, 688.
of metals by naphtha solutions of sulphur and its compounds (WOOD, SHEELY, and TRUSTY), ii, 980.
of ferrous metals in electrolysis (THORNTON and HARLE), ii, 303.
device for determination of (FETZER), ii, 996.
Cortex limonis (lemon), vitamin content of (WILLIMOTT and WOKES), i, 1220.
Corundum, crystal structure of (PAULING and HENDRICKS), ii, 368.
n- and *iso*-**Corybulbines**, and their ethyl ethers (SPÄTH and DOBROWSKY), i, 1085.
Corydalis alkaloids (SPÄTH and MOSETTIG), i, 1447.
Corydalis cava, alkaloids from (SPÄTH and DOBROWSKY), i, 1085.
Corydinecarboxylic acid, benzyl ester, and its methyl ether (OSADA), i, 284.
ethyl ester, methyl ether (OSADA), i, 283.
Corypalmine, constitution of, and its ethyl ether (SPÄTH and MOSETTIG), i, 1447.
Cotton, swelling of (COLLINS and WILLIAMS; COLLINS), ii, 781.

Cotton, viscosity of cuprammonium solutions of (FARROW and NEALE), ii, 773.
sorption by (COWARD, SPENCER, and WOOD), ii, 507.
absorption and desorption of water by (URQUHART and WILLIAMS), ii, 780, 781.
adsorption of dyes by (SPEAKMAN and BATTYE), ii, 284.
tendering of, by acids (COWARD, WOOD, and BARRETT), i, 643.
effect of sulphuric acid on the breaking load of (VINCENT), ii, 783.
fading of dyed (CUNLIFFE), ii, 812.
Egyptian and upland, chlorides in the leaf-tissue fluids of (HARRIS; J. V. and Z. W. LAWRENCE), i, 216.
analysis of (BIRTWELL, CLIBBENS, and RIDGE), i, 234; (CLIBBENS and GEAKE), ii, 906.
Cotton cellulose. See under Cellulose.
Cotton plant, odorous constituents of (POWER and CHESNUT), i, 1026.
reaction of (POWER and CHESNUT; HARRIS, HOFFMAN, and JOHNSON), i, 758.
Cotton seed, proteins of (JONES and CSONKA), i, 1225.
Cotton wax, American, constituents of (FARGHER and PROBERT; CLIFFORD and PROBERT), i, 879.
Egyptian, constituents of (FARGHER and HIGGINBOTHAM), i, 879.
Coulometer (FISCHBECK), ii, 1166.
Coumaran, 3-amino-6-hydroxy-, 6-acetyl derivative, and 6-hydroxy- (SONN and PATSCHKE), i, 282.
Coumaranone, 4-amino-, acetyl derivative (DIRKS), i, 148.
*di*bromo- (DEAN and NIERENSTEIN), i, 953.
Coumaran-3-one, 6-hydroxy-, oxime of (SONN and PATSCHKE), i, 282.
Coumarin, determination of (RADCLIFFE and SHARPLES), ii, 1210.
Coumarin, 3-bromo-7-hydroxy- (FRIES and NÖHREN), i, 955.
Coumarin-4-acetic acids, and their esters, reactivity of the methylene group in (DEY and ROW), i, 149, 953.
Coumarincarboxylic acid, *p*-toluidide of (WAYNE and COHEN), i, 551.
Coumarinic acid (DEY and ROW), i, 149.
3(3′-Coumaryl)-6′-methylbenzfuran-2-carboxylic acid, bromo- (DEY and ROW), i, 150.
3′-Coumaryl-4-naphthapyrones, and bromo-, chloro-, and nitro- (DEY and ROW), i, 149.
Cows, origin of lactose and of lactosuria in (CAMPUS), i, 327.
Cows, mineral metabolism of, in reference to diet (MONROE and PERKINS; MILLER, YATES, JONES, and BRANDT), i, 1498.
effect of proteins in diet of (PERKINS and MONROE), i, 1354.
lactating, blood-sugar concentration in (WIDMARK and CARLENS), i, 608.
Co-zymase (v. EULER and NILSSON), i, 1361.
Cream, electrical conductivity of (FRICKE and MORSE), i, 608.
Creatine, equilibrium of creatinine and (EDGAR and SHIVER), ii, 533.
in muscle (REISSER and HAMANN), i, 860.
influence of polyneuritis on (KUDRJAVZEVA), i, 329.
function of, in muscle contraction (TIEGS), i, 1003.
reciprocal conversion of creatinine and (HAHN and FASOLD), i, 1496.
effect of carbohydrate- and protein-free diets on excretion of (PALLADIN), i, 1211; (PALLADIN and KRATINOVA), i, 1514.
excretion of, by sheep (PALLADIN), i, 327.
sodium salt of (HAHN and FASOLD), ii, 653.
Creatinine (KAPFHAMMER), i, 797.
tautomerism of, and its derivatives (GREENWALD), i, 839.
equilibrium of creatine and (EDGAR and SHIVER), ii, 533.
reciprocal conversion of creatine and (HAHN and FASOLD), i, 1496.
effect of carbohydrate- and protein-free diets on excretion of (PALLADIN), i, 1211.
effect of a maize diet on excretion of (PALLADIN and KRATINOVA), i, 1514.
excretion of, by sheep (PALLADIN), i, 327.
Jaffe's reaction for (GREENWALD), ii, 1212.
***o*-Cresaurin.** See 3:3′:3″-Trimethylaurin.
***o*-Cresol**, 4:6-*di*bromo-, and its benzoyl derivative (KOHN and JAWETZ), i, 135.
nitro derivatives, and their salts and derivatives (GIBSON), i, 388.
***m*-Cresol**, 2-amino-, and 2-nitro- (HODGSON and BEARD), i, 540.
***p*-Cresol**, oxidation of (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1262.
determination of, in blood (HAAS and SCHLESINGER), i, 334.
***p*-Cresol**, bromo derivatives (KOHN and WIESEN), i, 539.
5-chloro-3-amino-, derivatives of (RAIFORD and LANKELMA), i, 809.

p-**Cresol**, *o*-iodo-, and its benzoate (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1262.
Cresols, molecular compounds of, with alcohol, ether, acetone, and benzene (WEISSENBERGER and PIATTI), i, 538, 539.
o- and *p*-**Cresols**, equilibrium between (HILL and MOSBACHER), ii, 1161.
o-, *m*-, and *p*-**Cresols**, bromo- and bromonitro-derivatives of, and their derivatives (KOHN and WEISSBERG), i, 655.
n- and *iso*-*o*-**Cresol***tetra***chlorophthaleins**, and their derivatives (ORNDORFF and PATEL), i, 672.
p-**Cresoldisulphonic acid**, action of sodium hypochlorite on (RASCHIG), i, 249.
p-**Cresolisatein anhydride** (SEN and SIRCAR), i, 555.
Cresolmercurisulphonic acid (SACCHARIN-FABRIK AKTIEN-GESELLSCHAFT VORM. FAHLBERG, LIST, & Co.), i, 1197.
Cresol-red, salt error of (RAMAGE and MILLER), ii, 712.
o-**Cresolsulphonephthalein** diethyl and dimethyl ethers (ORNDORFF and SHAPIRO), i, 251.
Cretins, fat and cholesterol in blood of (HECKSCHER), i, 999.
Cristobalite (LONGCHAMBON), ii, 1131.
synthesis of (WEIL), ii, 1193.
crystal structure of (WYCKOFF), ii, 638.
$\alpha\beta$-transformation of (WEIL), ii, 757.
Critical solution temperature of ternary mixtures (BOUTARIC and CORBET), ii, 103.
state, properties of systems near the (GAY and PERRAKIS), ii, 669.
temperature, determination of, from coefficient of expansion of liquids (VAN LAAR), ii, 950.
and melting point (VAN LAAR and LORENZ), ii, 374.
relation between melting point, boiling point, and (PRUD'HOMME), ii, 99.
and expansion of liquids (DE KOLOSOVSKI), ii, 646.
relation between molecular volume and (LORENZ and HERZ), ii, 25, 183.
Crookes' tubes, fluorescence experiments with (DAUVILLIER), ii, 1116.
Crops, yield and mineral content of, influenced by rotation (BURGESS), i, 1519.
Crotin (KARRER, WEBER, and VAN SLOOTEN), i, 1226.
Crotonaldehyde, and *a*-bromo-, benzoylhydrazones (v. AUWERS and DANIEL), i, 1181.
Crotonic acids, isomerism of (GONZÁLEZ), i, 629.
Crucibles, silica, for filtration (HÜTTIG and KÜKENTHAL), ii, 998.
Crustacea, dissociation of oxyhæmoglobin in blood of (STEDMAN and STEDMAN), i, 1199.
Cryogenine, colour reactions of, with metallic salts (BORNET) ii, 164.
Cryolite, equilibrium of alumina and (ROUSH and MIYAKE), ii, 974.
Cryoscopy in mixed solvents (WRIGHT), ii, 1144.
of solutions of gases in various solvents (GARELLI), ii, 1151.
with benzene (JONES and BURY), ii, 1040.
with nitrobenzene (BROWN and BURY), ii, 32; (BROWN), ii, 296.
with sodium sulphate (TURNER and PATTERSON), ii, 273.
Cryostat (WALTERS and LOOMIS), ii, 1091.
and hydrogen liquefier (LATIMER, BUFFINGTON, and HOENSHEL), ii, 818.
Cryptopine, pharmacological action of (HEATHCOTE), i, 734.
Crystals, structure of, and chemical constitution (WEISSENBERG), ii, 1129, 1130.
form and lattice structure of (YAMADA), ii, 94.
structure of, in relation to physical properties (VAN ARKEL), ii, 749.
relation between atomic number and structure of (SCOTT), ii, 369.
structure, dissolution velocity and etched figures on (TAMMANN; TAMMANN and KRINGS), ii, 942.
doubly refracting, refractive index of (PERRIER), ii, 1028.
band spectra of gases and of (KAHLER), ii, 626.
photo-electric properties of (GUDDEN and POHL), ii, 344, 943.
reflection of Röntgen rays by (HARTREE; BRAGG), ii, 735.
powdered, *X*-ray analysis of (BRENTANO), ii, 483.
apparatus for (LANGE), ii, 482.
magnetism of (FORREST), ii, 1133.
passage of electrons through (LENZ), ii, 920, 1019.
electrolysis of (LUKIRSKY, SČUKAREV, and TRAPESNIKOV), ii, 369.
thermal expansion of (HENGLEIN), ii, 935.
dynamics of (WAELSCH), ii, 485.
grating energy of (WESSEL), ii, 640.
deformation of, on hardening (PÓLÁNYI), ii, 370.

Crystals, migration in the lattice of (HÜTTIG), ii, 640.
molecular symmetry in (SMITH), ii, 271.
aggregation and polymorphism of (SCHAUM and RÖRIG), ii, 95.
orientation of, in conglomerates (TAMMANN), ii, 1132.
effect of strain and heat treatment on (ELAM), ii, 945, 946.
measurement of absolute dimensions of (SELJAKOV), ii, 270.
growth of, of different species (ROYER), ii, 749.
growth and diminution in size of (FRIEDEL), ii, 271.
modification of, due to foreign matter (GAUBERT), ii, 271.
molecular volumes of (HENGLEIN), ii, 477.
surface tension of, against saturated solutions (SOEP), ii, 1046.
spreading of films of, on water (CARY and RIDEAL), ii, 1046, 1047, 1048.
plasticity of (DAVEY), ii, 1039.
dynads in (HERZOG and WEISSENBERG), ii, 942.
of complex and pseudo-complex compounds (SCHLEICHER), ii, 22.
formation of, in the organism (HERZOG and GONELL), i, 718.
cubic, effect of cold rolling on the structure of (WEBER), ii, 93.
hydrated, electrical conductivity of (JAKUBSOHN and RABINOVITSCH), ii, 847.
mixed, distribution of atoms in (TAMMANN), ii, 20.
optical properties of (PORTER), ii, 945.
diffusion in (BRAUNE and HELLWEG), ii, 103.
solution of (LE BLANC and RÖSSLER), ii, 365.
binary, thermal expansion of (JOHANSSON), ii, 487.
organic, vapour pressures of (SWAN and MACK), ii, 951.
perfect, reflection of Röntgen rays by (WEBER), ii, 1034.
single, flow of (GEISS), ii, 96.
Crystallisation, van't Hoff's diagram of (BELOGLAZOV), ii, 788.
induced (DENIGÈS), ii, 906.
periodic (HEDGES and MYERS), ii, 1168.
spontaneous (TANCOV), ii, 868.
in binary systems (RUER), ii, 125.
Crystallography, Röntgen ray methods of correcting data of (YARDLEY), ii, 1033.
Culture fluids, hydrogen-ion concentration of (CHRISTENSEN and FULMER), i, 1216.
effect of seeds and plants on reaction and hydrogen-ion concentration of (RUDOLFS; HOAGLAND), i, 1368.
Cumidic acid, derivatives of (DE DIESBACH and ZURBRIGGEN), i, 1427.
3-ψ-Cumylrhodanylidene-$\Delta^{5:3'}$-oxindole (HANN), i, 987.
Cupferron. See Phenylhydroxylamine, nitroso-.
Cupric compounds. See under Copper.
Cuprite, crystal structure of (GREENWOOD), ii, 93.
Cuprous salts. See under Copper.
Cuskhygrine, derivatives of (HESS and BAPPERT), i, 425.
Cutic acid, and its copper salt (LEGG and WHEELER), i, 1025.
Cutinic acid, and its metallic salts (LEGG and WHEELER), i, 1025.
Cyanamide, action of ammonia on (COUDER), i, 525.
as source of plant nitrogen (BIALOSUKNIA), i, 1366.
derivatives of (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 594.
determination of (PINOK), ii, 607.
determination of, in calcium cyanamide (FOSSE, HAGENE, and DUBOIS), ii, 76.
Cyanamidoacetic acid (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 596.
Cyanidin, synthesis of (WILLSTÄTTER ZECHMEISTER, and KINDLER), i, 54.
conversion of, into catechin (FREUDENBERG, FIKENTSCHER, HARDER, and SCHMIDT), i, 1165.
chloride, synthesis of, and its pentamethyl ether (PRATT and ROBINSON), i, 422.
and its 3:3′:4′-trimethyl ether (PRATT and ROBINSON), i, 827.
*epi***Cyanilic acid** (WIELAND), i, 1049.
*iso***Cyanilic acid,** and its salts and derivatives (WIELAND), i, 1048.
Cyanine colouring matters, colour of (MOIR), ii, 1121.
Cyanite, crystal structure of (NORTON), ii, 1127.
formation of mullite from (GREIG), ii, 987.
Cyano-compounds (OTT and FINKEN), i, 1251.
catalytic reduction of (RUPE and GISIGER), i, 1095.
Cyanogen, band spectrum of (MULLIKEN), ii, 18.
thio-. See Thiocyanogen.

Cyanogen compounds, determination of, iodometrically (LANG), ii, 1009.
Cyanogen bromide, apparatus for preparation of (STEINKOPF, OHSE, and BUCHHEIM), ii, 590.
action of, on thebaine (SPEYER and ROSENFELD), i, 962.
iodide, formation and determination of, in iodometric analysis (LANG), ii, 713.
Hydrocyanic acid, preparation of (BICHOWSKY), i, 236.
specific heat of (PARTINGTON and CARROLL), ii, 373.
saturated vapour pressure of (HARA and SINOZARI), ii, 279.
critical constants and vapour pressure of (BREDIG and TEICHMANN), ii, 950.
liquid, decomposition of (WALKER and ELDRED), i, 1393.
catalytic oxidation of (HARA and SINOZARI), ii, 983.
stimulation of plants by (GASSNER), i, 1029.
fate of, in the organism (DANCKWORTT and PFAU), i, 196.
alkali salts, hydrolysis of, in aqueous solution (HARMAN and WORLEY), ii, 783.
double molybdenum salts, electrolytic oxidation of (COLLENBERG and ANDERSEN), ii, 1165.
potassium salt, reactions of halogens with (MÜLLER and SCHUCH), ii, 825.
potassium and sodium salts, purification and melting point of (GRANDADAM), ii, 704.
sodium salt, preparation of (HARA and MIURA), i, 645; (GUERNSEY and SHERMAN), ii, 889.
detection of (STAMM), ii, 75, 76; (MAGNIN), ii, 607.
*iso*Hydrocyanic acid (ENKLAAR), i, 1394.
Cyanides, complex, electrolysis of (SANIGAR), ii, 676.
determination of (KANÔ), ii, 1010.
determination of, bromometrically (OBERHAUSER), ii, 828.
determination of, in mixtures with halides (DEAN and NEWCOMER), ii, 597.
Cyanates, determination of, colorimetrically (K. C. and D. F. H. BAILEY), ii, 447.
determination of, in blood (MONTGOMERY), i, 455.
Cyanophyceæ, pigments of the (RICHTER), i, 1218.
Cyanuric compounds (OTT and FINKEN), i, 1251.
Cyanurtriazide, preparation of (OTT), i, 599.
Cyclic compounds, formation of from halogenated open-chain derivatives (INGOLD), i, 357; (HAERDI and THORPE), i, 923.
magneto-chemistry of (PASCAL), ii, 1123.
and unsaturation (MEREJKOVSKI), i, 1291.
with double linkings, order of addition to (NAMETKIN), i, 250.
Cymbopogon caesius (inchi grass), oil from (RAO and SUDBOROUGH), i, 1164; (MOUDGILL), i, 1293.
Cymene, electrochemical oxidation of (FICHTER and MEYER), i, 800.
Cyperus rotundus, essential oil of (RAO, PANICKER, and SUDBOROUGH), i, 1164.
Cypridina, effect of light on luminescence of (HARVEY), i, 1212.
Cysteine, oxidation of, in the organism (ROSE, SHIPLE, and SHERWIN), i, 190.
effect of traces of iron on oxidation of (HARRISON), i, 13.
detection of (SULLIVAN), ii, 1211.
Cystine, specific rotation and oxidation of (ANDREWS), i, 1389.
oxidation of, in the organism (ROSE, SHIPLE, and SHERWIN), i, 190.
content of, in proteins (JONES, GERSDORFF, and MOELLER), i, 98.
effect of, on growth in rats (SHERMAN and MERRILL), i, 730.
effect of, on sulphur metabolism (LEWIS), i, 1354.
detection of (SULLIVAN), ii, 1211.
determination of, in urine (MAGNUS-LEVY), i, 610.
Cytochrome (KEILIN), i, 1112.
Cytolysis, production of acid by (DRZEWINA and BOHN), i, 1512.
Cytosylic acid, brucine salt (PEISER), i, 1477.

D.

Dacrydium cupressinum, constituents of oil from (MCDOWALL and FINLAY), i, 418.
Damourite from Tasmania (DITTLER), ii, 323.
Darapskite (FOOTE), ii, 786.
Datisca cannabina, glucoside from (CHARAUX), i, 823.
Datiscetin, synthesis of, and its derivatives (KALFF and ROBINSON), i, 1302.
Datiscetinidin chloride, and its 3:2′-dimethyl ether (PRATT and ROBINSON), i, 826.

Datiscin (CHARAUX), i, 823.
Decacyclene, hydrogenation of (DZIEWOŃSKI and SUSZKO), i, 242.
Decahydroacridone (PERKIN and SEDGWICK), i, 65.
Decahydroanthracene (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 128.
Decahydronaphthalene (*decalin*), and its derivatives (HÜCKEL), i, 258.
and chloro- (ZELINSKI and GAVEDOVSKAJA), i, 123.
isomerism of (WIGHTMAN), i, 894.
isomerisation and dehydrogenation of (ZELINSKI and TUROVA-POLLAK), i, 1053.
surface tension of (GRUNMACH and SCHWEIKERT), ii, 31.
Decahydronaphthalenes (HÜCKEL and GOTH), i, 260.
heats of combustion of (ROTH and LASSÉ), ii, 275.
stereoisomeric (HÜCKEL), i, 1254.
Decahydro-β-naphthol (ZELINSKI and TUROVA-POLLAK), i, 1053.
5-β-Decahydronaphthoylbenzene-1:2:4-tricarboxylic acid, and its derivatives (PHILIPPI, SEKA, and FUNKE), i, 556.
Decahydronaphthylamines. See Decalylamines.
Decahydro*iso*quinoline, phenylcarbimide derivative (SKITA and REITMEYER), i, 140.
Decalin. See Decahydronaphthalene.
Decalols, and their derivatives (HÜCKEL), i, 258.
Decalones, and their derivatives (HÜCKEL), i, 258.
β-Decalones, heats of combustion of (ROTH and LASSÉ), ii, 275.
***trans*-α-Decalone-β-carboxylic acid**, ethyl ester, and its phenylpyrazolone (HÜCKEL and GOTH), i, 260.
α-Decaloneoxalic acid, ethyl ester, and its pyrrolidone derivative (HÜCKEL and GOTH), i, 260.
Decalylamines, and their derivatives (HÜCKEL), i, 258.
αα′-Decamethylene*di*iminodi*iso*butyric acid (SCHLESINGER), i, 1251.
Decamminemonoaquotrihydroxydioltrichromium thiosulphate. See under Chromium.
Decoic anhydride (HOLDE and GENTNER), i, 1035.
Decomposition apparatus (REMY), ii, 589.
Decomposition processes, transference of hydrogen as a basis of (KLUYVER and DONKER), ii, 1173.
Dehydracetic acid, structure of (RASSWEILER and ADAMS), i, 299.
Dehydrating agents, colloidal solutions of, in nitrobenzene (BROWN and BURY), ii, 1055.
Dehydration, dynamic study of (GUICHARD), ii, 427, 559.
Dehydrobis (*N*-tetramethylthiuronium) *per*chlorate (LECHER), i, 1391.
Dehydrocholane (WIELAND), i, 1066.
Dehydro-ψ-codeinone, and its derivatives (SPEYER and ROSENFELD), i, 961.
Dehydroemodinanthranol methyl ester, and its acetyl derivatives (EDER and HAUSER), i, 1160.
Dehydroeseretholemethine, and its salts (STEDMAN and BARGER), i, 292.
Dehydrofluorocyclene, *αα′-di*bromo-, and *di*bromo*di*hydroxy-, tetrasulphonic acid, and *di*bromo*tetra*nitro- (DZIEWOŃSKI and SUSZKO), i, 649.
Dehydrogenation and autoxidation (MANCHOT and GALL), i, 561.
Dehydroindigotin, 4:4′-*di*chloro-, 4:4′-*di*chloro-5:7:5′:7′-*tetra*iodo-, and 6:6′-*di*iodo-, and their derivatives (KALB and VOGEL), i, 161.
5:7:5′:7′-*tetra*iodo-, potassium and sodium hydrogen sulphites (KALB and BERRER), i, 160.
Dehydrothiotoluidines. See Phenyl methylbenzthiazoles, amino-.
Dehydrothio-*m*-xylidines, constitution of (ANSCHÜTZ and SCHULTZ), i 315.
Deliquescence of salts (SCHERINGA), ii, 296.
Delnoline (MARKWOOD), i, 762.
Delphinicæ, urine of (SUZUKI), i, 1349.
Delphinidin, chloride, synthesis of, and its hexamethyl ether (PRATT and ROBINSON), i, 422.
and its 3:3′:4′:5′-tetramethyl ether (PRATT and ROBINSON), i, 827.
Delphinium, alkaloids from species of (KELLER), i, 830.
Delphinium consolida, constituents of seeds of (MARKWOOD), i, 762.
De-*N*-methyldihydrocodeinone, oxime of (WIELAND and KOTAKE), i, 1092.
De-*N*-methyldihydrothebainone, piperonylidene derivative (WIELAND and KOTAKE), i, 1093.
Demethylechitamine, and its salts and derivatives (GOODSON and HENRY), i, 1166.
7-Demethylo-ψ-corydaline, and its methiodide (HAWORTH and PERKIN), i, 971.
7-Demethylomethylpapaverine (HAWORTH and PERKIN), i, 971.
7-Demethylomethylpapaverinol (HAWORTH and PERKIN), i, 971.

7-Demethylomethyltetrahydropapaverine, and its derivatives (HAWORTH and PERKIN), i, 971.
Density (*specific gravity*), rotation dispersion, and absorption spectra of homologous compounds (KRETHLOW), ii, 1029.
relation of temperature to (HERZ), ii, 494, 1141.
of gases by the interferometer (BARUS), ii, 25.
of liquids (VAN LAAR), ii, 278.
of binary solids (PANICHI), ii, 493.
Deoxybenzoin *p*-bromophenylhydrazone (BODFORSS), i, 699.
Deoxybenzoin, cyano-, aldimine from (RUPE and GISIGER), i, 1096.
Deoxybilianic acids, trimethyl esters (WINDAUS and BOHNE), i, 554.
Deoxyepicatechin tetramethyl ether (FREUDENBERG, FIKENTSCHER, and HARDER), i, 419.
Deoxyglucose, formation of, from glucal in rabbits (KONDO), i, 99.
Deoxytetrahydro-α-methylmorphimethines, and their derivatives (SPEYER and KOULEN), i, 60.
Dermocybe sanguinea, colouring matters from (KÖGL and POSTOWSKY), i, 1083.
Dermocybin, and its derivatives (KÖGL and POSTOWSKY), i, 1083.
Derris root, active principle of (TAKEI), i, 761.
Desmotropy, keto-enolic (KAUFMANN and RICHTER), i, 231.
Detonation of mixed gases (WENDLANDT), ii, 135.
Dextrin, nature of (LING and NANJI), i, 516.
limit I, and its acetyl derivative (SYNIEWSKI), i, 368.
Dextrose, structure of (HAWORTH), i, 1133.
mutarotation of (KUHN and JACOB), ii, 49.
effect of phosphates on the rotation of (v. EULER and NILSSON), i, 1042.
dissociation constant of (BRITTON), ii, 977.
reduction of copper salts by (FLEURY and TAVERNIER), ii, 605.
fermentation of (LEMOIGNE), i, 1361.
argon in (PICTET, SCHERRER, and HELFER), i, 865.
lactic acid fermentation of (VIRTANEN), i, 866.
effect of adrenaline and insulin on the utilisation of, by animals (GOTTSCHALK), i, 481.
action of ammonia on (SHMOOK), i, 577.
Dextrose, decomposition of, by bacilli (AUBEL and SALABARTAN), i, 747.
effect of insulin and muscle tissue on (LUNDSGAARD and HOLBØLL), i, 208.
action of yeast extracts on (KUHN and v. GRUNDHERR), i, 203.
αζ-*di*chlorohydrin, and its derivatives (HELFERICH, SPROCK, and BESLER), i, 792.
phenylhydrazones, structure of (FRÈREJACQUE), i, 635.
p-toluenesulphonylhydrazone (FREUDENBERG and BLÜMMEL), i, 52.
in blood in health and in diabetes (LUNDSGAARD and HOLBØLL), i, 1206, 1207.
in blood and body fluids (LUNDSGAARD and HOLBØLL), i, 1494.
oxidation of, in muscle (AHLGREN), i, 482.
in physiological fluids (LUNDSGAARD and HOLBØLL), i, 1207.
in urine (LUND and WOLF), i, 1205.
clinical detection of, in urine (RUOSS), i, 185.
determination of (IONESCU and SPIRESCU), ii, 331; (FLEURY and TAVERNIER; KNECHT and HIBBERT), ii, 605.
determination of, polarimetrically and by copper reduction (WHITE), ii, 1006.
influence of nitrogenous substances on determination of (ROSENTHALER), ii, 1006.
determination of, in blood (MILROY), i, 1486.
determination of, in presence of sucrose in organic liquids (BUFANO), i, 453.
Dextrosedibenzylmercaptal γδ-*iso*butylidene ether (PACSU), i, 1242.
Diabetes (*glycosuria*), effect of induced oxidation in (MITTRA and DHAR), ii, 576.
cholesterol in (NITZESCU, POPESCU-INOTESTI, and CADARIU), i, 462.
dextrose in blood in (LUNDSGAARD and HOLBØLL), i, 1207, 1494.
glycolysis in blood in (BIERRY, RATHERY, and KOURILSKY), i, 1207.
action of insulin in (LAWN and WOLF), i, 483.
lactic acid metabolism in (COLLAZO and LEWICKI), i, 1364.
mineral metabolism in (MEYER-BISCH and GÜNTHER), i, 328.
purine metabolism in (LE BRETON and KAYSER), i, 610.
sugar in blood and urine in, after insulin treatment (MAJOR and DAVIS), i, 1491.
uricolytic index in (LANGFELDT and HOLMSEN), i, 1207.

Diabetes (*glycosuria*), infection in (RICHARDSON and LEVINE), i, 723.
determination of sugar in urine in (WILLIAMS and CASEY), i, 998.
phloridzin, metabolism of glycerol in (CHAMBERS and DEUEL), i, 1352.
excretion of sugars in (DEUEL and CHAMBERS), i, 1352.
Diacetalmalonic acid, and its ethyl ester (PERKIN and PINK), i, 359.
2:3-Diacetanilido-1:4-diacetoxynaphthalene (FRIES and BILLIG), i, 940.
Diacetoacetylnaphthylenediamines (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 587.
Diacetoacetyl-*p*-phenylenediamine (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 587.
Diacetonamine, preparation of (HAESELER), i, 644.
Diacetone alcohol, electrolytic reduction of (READ and FLETCHER), i, 627.
Diacetonemannose. See Mannose di*iso*propylidene ether.
2:4-Diacetoxyacetophenone, ω-chloro- (NIERENSTEIN, WANG, and WARR), i, 34.
***s*-Di(acetoxyformanilidophenyl) *tri*sulphide** (NAIK and PATEL), i, 122.
Diacetyl. See Dimethyl diketone.
Diacetylacetone *cyclodi*sulphide, *tri*thio- (ARNDT, NACHTWEY, and PUSCH), i, 1307.
4:4′-Diacetylarsenobenzene, and **3:3′-*di*hydroxy-**, derivatives of (MARGULIES), i, 448.
Diacetylbenzylamine (HOLMES and INGOLD), i, 1144.
Diacetyldibenzyliminophthalimidine, and its derivatives (WEISS and FREUND), i, 139.
1:3-Diacetyl-2:2-dimethyl*cyclo*pentane, and its disemicarbazone (HALLER and LEGAGNEUR), i, 925.
Diacetyldioxime, copper and nickel compounds of (PANETH and THILO), i, 1152.
Diacetylene, and its silver derivatives (LESPIEAU and PRÉVOST), i, 493.
*hexa*bromide (LESPIEAU and PRÉVOST), i, 626.
Diacetyl-ψ-glucal, acetals from (BERGMANN), i, 887.
Diacetylglyoxime peroxide, peroxide of the dioxime of (PONZIO and BERNARDI), i, 79.
***s*-Diacetylhydrazine**, *s-hexa*chloro- (NAIK and PATEL), i, 121.
Diacetylphenylarsine (JOB, REICH, and VERGNAUD), i, 173.
Diacetylsuccinic acid, ethly ester, azo compounds with (BÜLOW and BAUR), i, 1327.
1:4-Dialanylpiperazine, and its derivatives (ABDERHALDEN and ROSSNER), i, 975.
4:4-Dialdehydoarsenobenzene, and its semicarbazone (MARGULIES), i, 447.
Dialdehydobenzenedicarboxylic acids, and their derivatives (DE DIESBACH and ZURBRIGGEN), i, 1427.
αγ-Dialdehydopropane-β-carboxylic acid, and its di-*p*-nitrophenylhydrazone (PERKIN and PINK), i, 359.
αγ-Dialdehydopropane-ββ-dicarboxylic acid, and its ethyl ester and their di-*p*-nitrophenylhydrazones (PERKIN and PINK), i, 359.
Dialkyl phosphites, tautomerism of (MIŁOBĘDZKI), i, 1051.
Diallyl *penta*sulphide, and its derivatives (THOMAS and RIDING), i, 4.
Diallylacetophenone (HALLER, BAUER, and RAMART), i, 261.
α-Diallylaminomethyl-α-ethylacetoacetic acid, ethyl ester (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1249.
Diallylbarbituric acid (VOLWILER), i, 1174.
diethylamine salt (HOFFMANN, LA ROCHE & Co.), i, 300.
Diallyl*iso*butyrone (HALLER, BAUER, and RAMART), i, 261.
αα-Diallylbutyrophenone (HALLER, BAUER, and RAMART), i, 261.
αα-Diallylpropiophenone (HALLER, BAUER, and RAMART), i, 261.
Dialyser, rotating (ASTRUC and CANALS), ii, 896.
Dialysis, use of tap water in (WILKE-DÖRFURT and DEKER), ii, 528.
electrolytic, laboratory apparatus for (FUCHS and HONSIG), ii, 897.
Diamagnetism of gases (GLASER), ii, 82.
Diamidoacetic acid, *dic*yano-. See Guanidoacetic acid, cyano-.
Diamines, compounds of stannic halides with (HIEBER and WAGNER), i, 1326.
aromatic stereoisomeric, nitration of (MORGAN and HICKINBOTTOM), i, 156.
Di(2-amino-4-methylthiazolyl)-5-phenylmethane (BOGERT and CHERTCOFF), i, 315.
Di(2-amino-4-phenylthiazolyl)-5-*p*-chlorophenylmethane (BOGERT and CHERTCOFF), i, 316.
Di(2-aminophenylthiazolyl)-5-*p*-dimethylaminophenylmethane (BOGERT and CHERTCOFF), i, 316.

Di(2-amino-4-phenylthiazolyl)-5-hydroxyphenylmethanes (BOGERT and CHERTCOFF), i, 316.
Di(2-amino-4-phenylthiazolyl)-5-nitrophenylmethanes (BOGERT and CHERTCOFF), i, 316.
Di(2-amino-4-phenylthiazolyl)-5-phenylmethane, and its derivatives (BOGERT and CHERTCOFF), i, 315.
Diamminoethylenediaminobisacetylacetonocobaltic salts (MORGAN and SMITH), i, 1457.
Diamond, photo-electric properties of (GUDDEN and POHL), ii, 344.
Hall effect with (LENZ), ii, 920.
crystal structure of zinc blende and (BECKENKAMP), ii, 271.
transformation of, into graphite (LEBEAU and PICON), ii, 136.
black and white, heats of combustion of (ROTH and NAESER), ii, 1140.
Di-*n*-amylacetal (BĚDOWÉ), i, 513.
Di*iso*amylamine hydrochloride (RUPE and HODEL), i, 275.
Di*iso*amylammonium iodide (STEINKOPF and BESSARITSCH), i, 495.
***s*-Di*iso*amylhydrazine, salts of** (MAZOUREVITCH), i, 1247.
***α*-Diamylose *hexa*nitrate** (PRINGSHEIM, LEIBOWITZ, and SILMANN), i, 1244.
Dianhydrostrophanthidinic acid (JACOBS and COLLINS), i, 1082.
Dianilino*di*aminostilbene (ELBS, NACKEN, and HOFMANN), i, 168.
9:10-Dianilinoanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1399.
Dianilino-*p*-azoxystilbene (ELBS and GAUMER), i, 167.
and its derivatives (ELBS, NACKEN, and HOFMANN), i, 168.
***s*-Di-4-anilinocarbamide, 3:5-*di*nitro-** (LINDEMANN and WESSEL), i, 1099.
2:3-Dianilino-1:4-diacetoxynaphthalene (FRIES and BILLIG), i, 940.
9:10-Dianilino-9:10-dihydroanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
1:1-Dianilinodihydro-α-naphthafurandione-2-anil (PASSERINI), i, 1298.
***PP'*-Dianilino-*PP'*-dioxotetrahydrotetrazdiphosphinium** (AUTENRIETH and BÖLLI), i, 1469.
Di-β-anilinoethyl ether (CRETCHER, KOCH, and PITTENGER), i, 627.
3:5-Dianilino-4-methoxyphenol, 2:6-*di*nitro- (KOHN and MARBERGER), i, 1265.
2:3-Dianilino-1:4-naphthaquinone (FRIES and BILLIG), i, 939.
α-Dianisidine hydroferrocyanide (CUMMING), i, 122.
4:6-Di-*p*-anisoyl-1:3-dimethylbenzene (DE DIESBACH and STREBEL), i, 1436.
Dianisyldi-α-naphthylethane (CONANT, SMALL, and TAYLOR), ii, 874.
9:12-Dianisyldiphensuccindanes (BRAND and KREY), i, 904.
9:12-Di-*o*-anisyl-Δ^{10}-diphensuccindene (BRAND and KREY), i, 904.
2:6-Dianisyl*cyclo*hexanone (GARLAND and REID), i, 1281.
2:7-Di-*p*-anisylideneaminophenanthraquinone (SIRCAR and GUPTA), i, 984.
Dianisylidene*cyclo*hexanone, and its hydrochloride (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 268.
Dianthranyl oxide and ***tetra*sulphide** (COOKE, HEILBRON, and WALKER), i, 1410.
Dianthraquinone, *di*hydroxy-, and its derivatives (PERKIN and YODA), i, 1160.
1:1-Dianthraquinonyl (ECKERT), i, 414.
***s*-2-Dianthraquinonylethane**, and ***di*-4-chloro-** (ECKERT), i, 413.
Diaquocobaltousethylene*di*aminobisacetylacetone (MORGAN and SMITH), i, 1457.
Diarsinoanilinoformyl-*s*-diphenylcarbamides (HAMILTON and MAJOR), i, 991.
***o:o'*-Di-4-arsinobenzeneazo*di*bromofluorescein** (CHRISTIANSEN), i, 1193.
***o:o'*-Di-4-arsinobenzeneazofluorescein** (CHRISTIANSEN), i, 1193.
***o:o'*-Di-4-arsinobenzeneazophenol*tetra*chlorophthalein** (CHRISTIANSEN), i, 1193.
***o:o'*-Di-4-arsinobenzeneazophenolphthalein** (CHRISTIANSEN), i, 1193.
4:4'-Di-*p*-arsino-*o*-methylanilinoformyl-*s*-diphenylcarbamide (HAMILTON and MAJOR), i, 991.
5:5'-Diarsinosulphonanilide-*N:N'*-disulphonic acid, 2:2'-*di*hydroxy-, barium salts (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471.
Diaryl*di*chlorosilicanes, action of mercuric oxide on (VYLE and KIPPING), i, 172.
ββ-Diarylethyl alcohols, preparation and dehydration of (RAMART and AMAGAT), i, 658.
Diarylthiocarbamides, preparation of (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 133.
Diastase (SYNIEWSKI), i, 469.
malt, optimum temperature for the action of, on starch (LECOQ), i, 470.
determination of (GORE), i, 335.

Diastase, salivary, hydrolysis of glycogen by (PAECHTNER), i, 738.
determination of activity of (SYNIEWSKI), i, 470.
determination of, in fæces (FRANK and DOLESCHALL), i, 461.
α-Diastase, action of, on amylopectin (SYNIEWSKI), i, 470.
Diatoms, silicon metabolism of (BRIEGER), i, 341.
2:7- and 4:5-Diazidophenanthraquinones, and their derivatives (BRASS and NICKEL), i, 273.
Diazoacetic acid, ethyl ester, decomposition of, by copper acetylide (MÜLLER and GOTTFRIED), i, 893.
Diazoamino-conversion (GOLDSCHMIDT, JOHNSEN, and OVERWIEN), ii, 138.
Diazobenzenebismuth chloride (SUPNIEWSKI), i, 1473.
Diazo-compounds, thermochemistry of (SWIENTOSLAWSKI; SWIENTOSLAWSKI and BLASZKOVSKA), ii, 1044.
coupling of aromatic nuclei with (LEVI), i, 436, 1186.
analogies between organic peroxides and (GELISSEN and HERMANS), i, 813.
reactions of secondary aromatic amines with (LEVI and FALDINO), i, 171.
aliphatic, formation of (BERK and HERMANS), i, 794.
Diazoles, complex, colour of (CHAKRAVARTI), i, 162.
Diazomethane, action of, on aromatic acyl chlorides (NIERENSTEIN, WANG, and WARR), i, 34; (LEWIS, NIERENSTEIN, and RICH), i, 935.
action of, on hippuryl chloride (KARRER and WIDMER), i, 593.
4:4′-Di*iso*barbituric acid, and its salts (DAVIDSON and BAUDISCH), i, 1188.
3:4:6:7-Dibenzacridine-5-carboxylic acid. See Dinaphthacridine-14-carboxylic acid.
Dibenzhydroxamic acid, *pp′-di*bromo- (SCHEUING and HENSLE), i, 28.
Dibenzimide, *di-p*-hydroxy-, and its diacetyl derivative (ANSCHÜTZ and ZERBE), i, 667.
Dibenzofulvene (*diphenylene-ethylene*), preparation of, and ω-bromo- and ω-nitro- (WIELAND and KRAUSE), i, 902.
Dibenzohomopyran (SIEGLITZ and KOCH), i, 279.
Dibenzo-Δ⁶-suberen-1-one-2:2′-spiran, preparation of (LEUCHS and SANDER), i, 1432.
Dibenzoylbenzenedicarboxylic acid, bromo- (PHILIPPI, SEKA, and BAUER), i, 555.
2:5-Dibenzoyl-3:4-benzofuran (WEISS and SONNENSCHEIN), i, 938.
βδ-Dibenzoyl-αε-diketo-*n*-pimelic acid. See Methylenebenzoylpyruvic acid.
αβ-Dibenzoylethane, *tetra*bromo- and *di*-4-chloro- (CONANT and LUTZ), i, 682.
αα′-Dibenzoylethylene, *hexa*hydroxy- (BOGERT and RITTER), i, 816.
αβ-Dibenzoylethylene, amino, halogen and hydroxy derivatives of (CONANT and LUTZ), i, 681.
Dibenzoylglyoxime *per*oxide (RUGGERI), i, 79.
dioxime, diacetyl derivative (PONZIO), i, 1075.
peroxide of (PONZIO and BERNARDI), i, 80.
Di-β-benzoyloxyethyl ether (CRETCHER and PITTENGER), i, 228.
3:9-Dibenzoylperylene, 4:10-*di*chloro-3:9-*di-p*-bromo-, and -3:9-*di-p*-chloro- (ZINKE, FUNKE, and PONGRATZ), i, 819.
3:4-Dibenzoyl-1-phenyl-2:5-dimethylpyrrole (SEKA), i, 57.
Dibenzoylterephthalic acid, *tetra*bromo-2:5-*di-p*-hydroxy- (DE DIESBACH and STREBEL), i, 1436.
1:3-Dibenzoyl-1:2:2-trimethyl*cyclo*pentane, and its derivatives (HALLER and LEGAGNEUR), i, 683.
Dibenzoylxylenes (DE DIESBACH and STREBEL), i, 1435.
4:6-Di-2-benztriazolylresorcinol (ELBS), i, 164.
Dibenzyl *penta*sulphide, and its derivatives (THOMAS and RIDING), i, 5.
γγ-Dibenzylacetylacetone, and its salts (MORGAN and TAYLOR), i, 634.
Dibenzylamines, *di*nitro-, and their salts (HOLMES and INGOLD), i, 1143.
4-β-Dibenzylaminoethylglyoxaline, and its hydrobromide (GERNGROSS), i, 441.
Dibenzylcitric acid (HEFTI and SCHILT), i, 394.
2:6-Dibenzyl-*p*-cresol (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.
3:5-Dibenzyl-*p*-cresol (CLAISEN), i, 1410.
Dibenzyldixanthyl, and its *per*oxide (CONANT and SLOAN), i, 955.
Dibenzyl*cyclo*hexanol, *di-p*-hydroxy-, and its salts (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 268.
2:6-Dibenzyl*cyclo*hexanone, 2:6-*di-p*-chloro- (GARLAND and REID), i, 1281.
***N-exo*-Dibenzylhistamine**. See 4-β-Dibenzylaminoethylglyoxaline.
Dibenzylideneacetone. See Distyryl ketone.

2:7-Dibenzylideneaminophenanthraquinone, and 2:7-*di-o*-hydroxy- (SIRCAR and GUPTA), i, 984.
Dibenzylidene*cyclo*hexanone, *di-p*-hydroxy-, and its derivatives (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 268.
2:6-Dibenzylidene*cyclo*hexanone, *di-p*-bromo- and *tetra*bromo- (GARLAND and REID), i, 1280.
Dibenzylidenemethyl*cyclo*hexanone, *di-p*-hydroxy-, and its salts (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 268.
Dibenzylidene*cyclo*pentanone, *di-p*-hydroxy-, derivatives of (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 267.
1:2-Dibenzylindazolium iodide (v. AUWERS and PFUHL), i, 1101.
1:1-Dibenzyl-ψ-*iso*indole, 3-amino-, and its hydrochloride (WEISS and FREUND), i, 139.
Dibenzylmethylamines, *di*nitro-, and their salts (HOLMES and INGOLD), i, 1143.
Dibenzylmethylcarbinol (TROTMAN), i, 382.
ββ-Dibenzyloxydiethylmalonic acid, and its salts (BENNETT), i, 884.
2:5-Dibenzyloxydihydropyrazine, reduction of (KARRER and GRÄNACHER), i, 302.
Di(benzyloxy)phenylmethane, *di*-α-cyano- (STOLLÉ), i, 815.
2:4-Dibenzylphenol (v. BRAUN and REICH), i, 1405.
Dibenzylphthalimidine (WEISS and FREUND), i, 139.
4:4-Dibenzyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), i, 634.
Di-ββ′-benzylthioldiethyl sulphides (FROMM and JORG), i, 352.
αβ-Dibromo compounds, action of inorganic iodides on (VAN DUIN), i, 802; (CONANT, KIRNER, and HUSSEY), i, 803.
Dibutadiene (ASCHAN and KROHN), i, 49.
Di-β-butoxyethyl ether (CRETCHER and PITTENGER), i, 228.
Di-*n*-butyl sulphide (GILMAN, SMITH, and PARKER), i, 657.
Di-*n*-butylacetal (BÉDOWÉ), i, 513.
Di-*n*-butylacetoacetic acid, ethyl ester (HESS and BAPPERT), i, 349.
Di-*n*-butylamine *m*-nitrobenzenesulphonamide (MARVEL, KINGSBURY, and SMITH), i, 245.
[redacted] salts of (MAZOUREVITCH), i, 1247.
β-Di-*sec.*-butylaminoethyl alcohol, and its benzoates (ADAMS, VOLWILER, and JENKINS), i, 399.
γ-Di-*sec.*-butylaminopropyl *p*-aminobenzoate hydrochloride (ADAMS, VOLWILER, and JENKINS), i, 399.
Di*iso*butylammonium *tri*iodide (STEINKOPF and BESSARITSCH), i, 497.
Dibutyldixanthyl, and its peroxide (CONANT and SLOAN), i, 955.
s-Di*iso*butylhydrazine, salts of (MAZOUREVITCH), i, 1247.
αβ-Di-*n*-butylhydroxylamine, and its hydrochloride (NEUFFER and HOFFMAN), i, 891.
αβ-Di-*m*-butylhydroxyurethane (NEUFFER and HOFFMAN), i, 891.
5:5-Dibutyrylarsenobenzene, 3:3′-*di*nitro-4:4′-*di*hydroxy- (MARGULIES), i, 447.
s-Di*iso*butyrylhydrazine (NAIK and PATEL), i, 121.
Di*iso*butyrylmethane, and its copper salt (MORGAN and TAYLOR), i, 634.
αβ-Di-*iso*butyryl-*o*-nitrophenylhydrazide (VAN ALPHEN), i, 82.
3:4-Dicarbethoxy*di*aminophenylarsinic acid (HAMILTON and SLY), i, 600.
Dicarbethoxyglycerol (ALLPRESS and MAW), i, 4.
Dicarbethoxyglycol (ALLPRESS and MAW), i, 4.
9-Dicarbethoxyhydrazinophenanthrene (STOLLÉ and ADAM), i, 1470.
γδ-Dicarbethoxy-γ-hydroxy-ββ-dimethylbutane-α-carboxylic acid, anhydride and lactone of (ROTHSTEIN, STEVENSON, and THORPE), i, 885.
δε-Dicarbethoxy-δ-hydroxy-γγ-dimethylpentane-β-carboxylic acid, γ-lactone of (ROTHSTEIN, STEVENSON, and THORPE), i, 884.
Dicarbethoxymethyl-*N*-phenylnitrone (BURKHARDT and LAPWORTH), ii, 937.
Dicarbethoxytartaric acid, diethyl ester (ALLPRESS and MAW), i, 4.
dl-Dicarbethoxytyrosine (HAVESTADT and FRICKE), i, 163.
α-Dicarbethoxytyrosylamino-β-glyoxaline-4(or 5)-propionic acid, methyl ester (HAVESTADT and FRICKE), i, 163.
3:4-Dicarbobutoxy*di*aminophenylarsinic acids (HAMILTON and SLY), i, 600.
3:4-Dicarbomethoxy*di*aminophenylarsinic acid (HAMILTON and SLY), i, 600.
Dicarbomethoxyglycol (ALLPRESS and MAW), i, 4.
α-Dicarbomethoxyhydrazinoanthracene (STOLLÉ and ADAM), i, 1469.

9-Dicarbomethoxyhydrazinophenanthrene (STOLLÉ and ADAM), i, 1469.

Dicarbomethoxytyrosine (HAVESTADT and FRICKE), i, 163.

α-Dicarbomethoxytyrosylaminopropionic acid, ethyl ester (HAVESTADT and FRICKE), i, 163.

Dicarbomethoxytyrosylaminosuccinic acid, methyl ester (HAVESTADT and FRICKE), i, 163.

3:4-Dicarbopropoxy*di*aminophenylarsinic acids (HAMILTON and SLY), i, 600.

2:5-Di-*p*-carboxybenzoylterephthalic acid, and its barium salt (DE DIESBACH and STREBEL), i. 1436.

3:3′-Dicarboxydiphenyl *di*sulphoxide, 4:4′-*di*hydroxy- (BERE and SMILES), i, 22.

Dicarboxylamidobenzenedicarboxylic acid, sodium salt (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 130.

Dicarboxymethylmandelic acid (PERKIN and TAPLEY), i, 43

3:4-Dicarboxy-5-methylpyrazole-1-benzeneazoacetoacetic acid, ethyl ester, and its derivatives (BÜLOW and BAUR), i, 1327.

***p*:*p*′-Di-4-carboxy-6-methyl-2-quinolylarsenobenzene** (OGDEN and ADAMS), i. 707.

***p*:*p*′-Di-4-carboxy-2-quinolylarsenobenzene** (OGDEN and ADAMS), i, 706.

αα′-Dicellosylsulphone, and its tetradecylacetyl derivative (WREDE and ZIMMERMANN), i, 1384.

***dl*-Dicentrine**, synthesis of, and its derivatives (HAWORTH, PERKIN, and RANKIN), i, 1314.

2:7-Dicinnamylideneaminophenanthraquinone (SIRCAR and GUPTA), i, 984.

4:3′-Dicoumaryl, 6′-bromo-7-hydroxy- and 7-hydroxy-, and their derivatives (DEY and ROW), i, 150.

Di-*o*-cresolisatin, diacyl derivatives of (HOFFMANN, LA ROCHE & Co.), i, 66.

Dicyanodiamide, effect of, on plants (ALLISON, SKINNER, and REID), i, 1030.

Dicyanoimide, and its salts (BURDICK), i, 1048.

Didehydrobromochelidonine, and its salts (GADAMER and WINTERFELD), i, 285.

Didehydrochelidonine, and its salts (GADAMER and WINTERFELD), i, 285.

Di-β-3:4-dimethoxyphenylethyl ketone, and its oxime (NOMURA and HOTTA), i, 1156.

2:6-Di-*p*-dimethylaminobenzylidene-*cyclo*hexanone, and its perchlorates (PFEIFFER), i, 411.

αγ-Di-dimethylaminopropan-β-ol methiodides (CALLSEN), i, 1389.

Di-*p*-dimethylaminostyryl ketone, salts of (PFEIFFER), i, 411.
additive compound of, with resorcinol (PFEIFFER, GOEBEL, and ANGERN), i, 262.

2:6-Di-2′:4′-dimethylbenzyl-*cyclo*hexanone (GARLAND and REID), i, 1281.

2:6-Di-2′:4′-dimethylbenzylidene-*cyclo*hexanone (GARLAND and REID), i, 1280.

***s*-Di(diphenyl) *di*sulphide, *di*amino-**, acetyl derivative (NAIK and PATEL), i, 121.

αβ-Didiphenylacetylmethylhydrazide (VAN ALPHEN), i, 82.

αβ-Didiphenylacetylphenylhydrazide (VAN ALPHEN), i, 82.

Di-(β-diphenylethyl)amine, and its derivatives (RUPE and GISIGER), i, 1095.

***l*-Di-diphenylethylethylene oxide** (MCKENZIE and ROGER), i, 26.

***l*-Di-diphenylmethylethylene oxide** (MCKENZIE and ROGER), i, 26.

Di-di*iso*propylidenegalactosylamine, and its derivatives (FREUDENBERG and DOSER), i, 366.

Dielectric constants, determination of (HELLMANN and ZAHN), ii, 1117.
of good conductors (FÜRTH), ii, 631.
of electrolytes (WALDEN, ULICH, and WERNER), ii, 512, 773; (ULICH), ii, 964.
of liquids (GRÜTZMACHER; SAYCE and BRISCOE), ii, 263; (BELL and POYNTON), ii, 477; (HARRIS), ii, 631.
of organic liquids (GRENACHER; FRANCKE), ii, 741; (LANGE), ii, 840.
of aqueous solutions, effect of temperature on (KOCKEL), ii, 932.

Diet, balance of carbohydrates and mineral salts in (RANDOIN, ALQUIER, ASSELIN, and CHARLES), i, 1002.
importance of iron in (HART, STEENBOCK, ELVEHJEM, and WADDELL), i, 1352.
rich in vitamins, effect of ions on growth on (TSUKAMOTO), i, 210.
required for reproduction (SURE), i, 212, 752.
of cows, protein content of (PERKINS and MONROE), i, 1354.
of parents, influence of, on young (KORENCHEVSKI and CARR), i, 210, 463.

Diet, relation between loss of fur and, in rats (HARTWELL), i, 464.
synthetic, preparation of (HARTWELL), i, 1514.
2:9-Diethoxyacridine (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 429.
2:3-Diethoxybenzaldehyde, nitration of (RUBENSTEIN), i, 1428.
***o*:*o*′-Di(ethoxybenzoyl)benzils**, and their derivatives (BRAND and KREY), i, 904.
Di-β-ethoxyethyl ether (CRETCHER and PITTENGER), i, 228.
Di-*m*-and-*p*-ethoxymethylbenzylamines, and their salts and derivatives (v. BRAUN and REICH), i, 1405.
Di-(β-ethoxymethylphenylethyl)amines and their salts and nitroso-derivatives (v. BRAUN and REICH), i, 1405.
ββ-Diethoxypropionic acid, ethyl ester (INGOLD), i, 779.
Di-*o*-γ-ethoxypropylbenzylamine (v. BRAUN and KAISER), i, 1414.
***d*-Diethoxysuccinic acid**, dissociation constant of (FAIRWEATHER), i, 631.
Diethyl ether. See Ethyl ether.
sodium phosphite (NYLÉN), i, 1135.
selenides, ββ′-*di*bromo- and ββ′-*di*chloro-, and their halides (BELL and GIBSON), i, 1126.
*di*sulphide, compounds of gold chloride with (RÂY), ii, 184.
ββ′-*di*hydroxy-, dibenzoate (FROMM and JÖRG), i, 352.
2:5-Diethylacetophenoneoxime (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
ββ-Diethylacrylic acid. See β-Ethyl-Δα-pentenoic acid.
Diethylamine, condensation of phenylthiocarbamide with (HUNTER), i, 805.
m-nitrobenzenesulphonamide (MARVEL, KINGSBURY, and SMITH), i, 244.
Diethylaminoacetic acid, phenylethyl ester (WEIL), i, 157.
9-Diethylaminoanthrone, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1399.
γ-Diethylamino-γ-diethylnonan-η-one, and its derivatives (BLAISE and MONTAGNE), i, 633.
2:2′-Diethylamino-5:5′-dimethyldiphenyl *di*sulphide, 2:2′-diacetyl derivative (CLARK), i, 841.
2:2′-Diethylaminodiphenyl *di*sulphide, 2:2′-diacetyl derivative (CLARK), i, 841.
3-β-Diethylaminoethoxy-4-diallyl-5-hydroxybenzene (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 301.
Diethylaminoethoxyethyl alcohol, and its derivatives (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 374.
3-β-Diethylaminoethoxy-1-phenyl-4-dimethyl-5-pyrazolone (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 301.
Diethylaminoethylcarbamic acid, esters of, and their hydrochlorides (HARTMANN and KÄGI), i, 1046.
Diethylaminoethyliminodicarboxylic acid, phenylethyl ester (HARTMANN and KÄGI), i, 1046.
***N*-Diethylaminoethyl-linoleamide** (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
9-Diethylamino-6-hydroxy-5-keto-7:12-naphthaphenthiazine (HELLER), i, 315.
α-Diethylaminomethyl-α-allylacetoacetic acid, ethyl ester (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1249.
α-Diethylaminomethyl-α-ethylacetoacetic acid, ethyl ester (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1249.
5-Diethylaminophenyl hydrogen thiosulphate, 2-amino-, and its derivatives (HELLER), i, 314.
Diethylaniline, vapour pressure of (NELSON and WALES), ii, 494.
Diethylaniline, *di*-β-hydroxy-, salts of (GABEL), i, 536.
Diethylanthraquinone (QUAYLE and REID), i, 1289.
Diethylbarbituric acid, choline and methylamine salts (HOFFMANN, LA ROCHE & Co.), i, 300.
ββ-Diethylbutan-α-ol, γ-amino-, and its hydrochloride and benzoyl derivative (BILLON), i, 120.
***s*-Diethylcarbamide**, ββ-*di*chloro- (MELDRUM and ALIMCHANDANI), i, 1273.
Diethyldihydroresorcinol. See 3:5-Diketo-1:1-diethyl*cyclo*hexane.
Diethylenediamineplatinous iodide, decomposition of, by acids (SCHLEICHER and SCHMITZ), ii, 704.
αα′-Diethylglutaric acid, dianilide and di-*p*-toluidide of (v. AUWERS), i, 892.
ββ-Diethylglutarylfluorescein (DUTT and THORPE), i, 141.
ββ-Diethylglutarylrhodamine (DUTT and THORPE), i, 142.
Diethylketen *per*oxide (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 933.
Diethyloxonium *per*bromide (KEHRMANN and FALKE), i, 351.
γγ-Diethylpentane (MORGAN, CARTER, and DUCK), i, 877.

6:6-Diethylphenoxarsonium iodide (AESCHLIMANN), i, 706.
2:6-Diethylpyridine, and its salts (BLAISE and MONTAGNE), i, 836.
αα-**Diethylsuccinic acid** (DUTT and THORPE), i, 142.
as-**Diethylsuccinylfluorescein** (DUTT and THORPE), i, 141.
as-**Diethylsuccinylrhodamine** (DUTT and THORPE), i, 142.
Diethyl*di*thiocarbamic acid, salts of (WHITBY and MATHESON), i, 644.
s-**Diethylthiocarbamide**, *ββ*-*di*chloro-, and *βββ*-*tri*chloro-*α*-hydroxy- (MELDRUM and ALIMCHANDANI), i, 1273.
Diethylthiocarbamylmalic acids (HOLMBERG), i, 1239.
3:7-Diethylxanthine, and 8-chloro- (BILTZ and PEUKERT), i, 1463.
4:6-Diethyl-*m*-xylene, 2-*mono*- and 2:5-*di*-bromo- (PHILIPPI, SEKA, and BAUER), i, 555.
Di*iso*eugenol, constitution of, and *tetra*chloro-, diethyl ether, and *hexa*-chloro- (PUXEDDU), i, 1266.
Diffusion, Stokes–Einstein law for (MILLER), ii, 28.
of coloured substances (AUERBACH), ii, 28.
in mixed crystals (BRAUNE and HELLWEG), ii, 103.
of gases by the interferometer (BARUS), ii, 25.
of mixed gases (LORENZ and MAGNUS), ii, 501.
of ions (MESTREZAT and GARREAU), ii, 543.
in metals (HEVESY and OBRUTSHEVA), ii, 500.
of solids (THOMPSON and DEARDEN), ii, 29.
thermal, measurement of (IBBS), ii, 376.
Diffusion coefficients (COHEN and BRUINS), ii, 28.
determination of (MACK), ii, 1124.
Digalactosylamine and its bisphenylhydrazone (FREUDENBERG and DOSER), i, 367.
αα′-**Digalactosylsulphone**, and its octa-acetyl derivative (WREDE and ZIMMERMANN), i, 1384.
p-**Digallic acid** (NIERENSTEIN, SPIERS, and HATCHER), i, 693.
Digestion, gastric, effect of avitaminosis on (GROEBBELS and SPERFELD), i, 1514.
peptic, influence of ions on (RONA and KLEINMANN), i, 103.
salivary, effect of halides and other substances on (CLIFFORD; WALKER), i, 738.
Digestion, tryptic (EHRENBERG), i, 202; (HUNTER and SMITH; STANDENATH), i, 473.
Digitalis, gitogenin in leaves of (WINDAUS and BRUNKEN), i, 873.
gitoxin from leaves of (WINDAUS and SCHWARTE), i, 1295.
Digitonin, and its degradation products (WINDAUS and WILLERDING), i, 1082.
αα′-**Diglucosylsulphone**, and its octa-acetyl derivative (WREDE and ZIMMERMANN), i, 1384.
ζ-**Diglucosylsulphone** hexa-acetyldimethylglucoside (WREDE and ZIMMERMANN), i, 1384.
Diguaiacolisatin, diacyl derivatives of (HOFFMANN, LA ROCHE & Co.), i, 66.
Diheptacyclene *di*sulphide, *ms*-*di*bromo- (COOKE, HEILBRON, and WALKER), i, 1411.
s-**Dihexoylhydrazine** (NAIK and PATEL), i, 121.
Di*cyclo*hexyl ether, *di*chloro- (GOLDSCHMIDT and SCHÜSSLER), i, 498.
Dihydrazines (v. BRAUN and BAYER), i, 1382.
9:10-Dihydroanthracene, bromo- and chloro-*di*nitro derivatives (BARNETT), i, 1259.
Dihydroanthranol, 1:8-*di*chloro-9(or 10)-nitro- (BARNETT and MATTHEWS), i, 18.
cis- and *trans*-**9:10-Dihydroanthraquinols**, 1:5-*di*chloro-, and their derivatives (BARNETT, COOK, and MATTHEWS), i, 901.
cis-**9:10-Dihydroanthraquinyl** diacetate, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 818.
9:10-Dihydroanthraquinyl-9:10-di-pyridinium *di*bromides, 1- and 2-chloro- (BARNETT and MATTHEWS), i, 18.
*di*chloride, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
Dihydrobenzenes, structure of (LELY), i, 1396.
2:3-Dihydrobenzquinazolone-4, and its salts and derivatives (SEIDE), i, 159.
Dihydrobromo-ψ-chelerythrine. See Anhydrodidehydrobromochelidonine.
Dihydrochaulmoogric acid, and its ethyl ester (DEAN, WRENSHALL, and FUJIMOTO), i, 1414.
Dihydro-ψ-chelerythrine. See Anhydrodidehydrochelidonine.
Dihydrocitronellyl bromide (BECHERER), i, 664.
Dihydrocodeine, bromo- and chloro- (SPEYER and ROSENFELD), i, 961.
3:5-Dihydrocoumarin, 5- and 7-hydroxy- (CHAPMAN and STEPHEN), i, 669.

1:2-Dihydrocoumarone, 3:5-*di*hydroxy-, and its diacetyl derivative (DEAN and NIERENSTEIN), i, 281.

Dihydrocupreine-5-azobenzene-*p*-arsinic acid, and its sodium salt and hydrochloride (ERBEN and SCHNIDERSCHITSCH), i, 707.

***α*- and *β*-Dihydrocuskhygrines**, and their derivatives (HESS and BAPPERT), i, 425.

Dihydrode-*N*-methyldihydrocodeine, and its salts (WIELAND and KOTAKE), i, 1093.

Dihydrode-*N*-methyldihydrocodeinone, and its derivatives (WIELAND and KOTAKE), i, 1092.

Dihydrode-*N*-methyldihydrothebaine, and its derivatives (WIELAND and KOTAKE), i, 1092, 1448.

Dihydrode-*N*-methyldihydrothebainone, and its derivatives (WIELAND and KOTAKE), i, 1093.

Dihydro-7-demethylo-ψ-dehydrocorydalinium salts (HAWORTH and PERKIN), i, 971.

Dihydrodeoxytetrahydro-*α*-methylmorphimethine, and its derivatives (SPEYER and KOULEN), i, 59.

Dihydro-4:4′-dipyridyl (EMMERT, JUNGCK, and HÄFFNER), i, 73.

Dihydrohydnocarpic acid (DEAN, WRENSHALL, and FUJIMOTO), i, 1415.

Dihydro-6-methylcoumarin (THOMPSON and EDEE), i, 1442.

1:2-Dihydro-2-methylquinoline, synthesis of (MASON), i, 834.

Δ¹-Dihydronaphthalene, and its derivatives, and 2-nitro- (STRAUS and EKHARD), i, 1138.

3:4-Dihydronaphthalene-1:2-dicarboxylic acid, and its silver salt, esters, and anhydride (v. AUWERS and MÖLLER), i, 403.

2:3-Dihydronaphthen, and its derivatives (FRICKE and SPILKER), i, 1311.

Dihydronaphthoic acids, ethyl esters (v. AUWERS and MÖLLER), i, 404.

3:4-Dihydronaphthyl-1-acetic acid, and its ethyl ester (SCHROETER, ZADEK, and HOFFMANN), i, 677.

1:2-Dihydronaphthyridine, and its hydrochloride (RÄTH), i, 437.

Dihydro-oxeserolene (POLONOVSKI and POLONOVSKI), i, 696.

Dihydroisopelletierines (HESS and GRAU), i, 427.

Dihydrophenanthrene, structure and spectrochemistry of (v. AUWERS and KRAUL), i, 900.

Dihydrophenazine, 3-nitro-7- and -8-[illegible]-, and their derivatives (KEHRMANN and HAENNY), i, 1330.

Dihydroquinoxaline, hydroxy- (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1324.

Dihydrosafroeugenol. See 4-Ethoxypropylbenzene, 3-hydroxy-.

Dihydrothebenine, and its derivatives (SPEYER and ROSENFELD), i, 961.

2:3-Dihydrothionaphthen, its sulphone (v. BRAUN, BAYER, and KAISER), i, 1446.

Dihydrothio-2-perimidone (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 133.

Dihydrotrianhydrostrophanthidin (JACOBS and COLLINS), i, 566.

***αα*-Di-indandionylethane**, and its tetraoxime (RADULESCU and GEORGESCU), i, 1286.

Di-indandionylmethane, and its salts and derivatives (RADULESCU and GEORGESCU), i, 1286, 1287.

***ββ*-Di-indandionylpropane** (RADULESCU and GEORGESCU), i, 1286.

Di-indazole, *di*-3-hydroxy-, and its 1-acetyl derivative (HANTZSCH), i, 702.

Di-indene, and its derivatives (STOBBE and FÄRBER), i, 19.

Di-indolylethane, and its derivatives (ODDO), i, 297.

Di-indolylmethane, and its silver derivative (ODDO), i, 296.

Di-indone, derivatives of (RADULESCU and GEORGESCU), i, 1285, 1286.

3:5-Di-indyl*iso*oxazole (ODDO), i, 297.

3:5-Di-indylpyrazole (ODDO), i, 297.

Diketoadipic acid, formation of citric acid from (FRANZEN and SCHMITT), i, 231.

Diketo*cyclo*butane, absorption spectra of derivatives of (LARDY), ii, 88.

Diketobutyric acid phenylosazone (GOEBEL), i, 1038.

Diketocineole, reduction of (CUSMANO and MASSA), i, 686.

3:3′-Diketodibenz-Δ$^{2:2'}$-dicoumarans (*dibenzoxindigo*) (FRIES and PUSCH), i, 569.

3:3′-Diketo-Δ$^{2:2'}$-dicoumaran (FRIES), i, 567.

3:5-Diketo-1:1-diethyl*cyclo*hexane (KON and LINSTEAD), i, 633.

***αδ*-Diketo-*αδ*-di-2-hydroxy-4:6-dimethylphenylbutane** (FRIES and BARTENS), i, 569.

***αδ*-Diketo-*αδ*-di-2′-hydroxy-*m*-tolylbutane**, and *βγ-di*bromo-, and their derivatives (FRIES and BARTENS), i, 568.

2:2′-Diketo-3:3′-diphenyl-3:3′-dicoumaranyl (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.

2:2′-Diketo-3:3′-diphenyl-3:3′-dicoumaranyls, radical dissociation of (LÖWENBEIN and FOLBERTH), i, 552.
2:2′-Diketo-3:3′-diphenyl-5-methyl-3:3′-dicoumaranyl (LÖWENBEIN and FOLBERTH), i, 552.
Diketohydrindene, derivatives of (RADULESCU and GEORGESCU), i, 1285, 1286.
2:5-Diketo-6-methyl-3-methylenepiperazine, diacetates and tetrapeptide derivatives of (BERGMANN, MIEKELEY, and KANN), i, 1474.
Diketonates of metalloids (DILTHEY), i, 1473.
1:4-Diketones, unsaturated (CONANT and LUTZ), i, 681.
α- and **β-Diketones**, absorption spectra of (LARDY), ii, 88.
β-Diketones, structure of enolic forms of (SIDGWICK), i, 630.
δ-Diketones, preparation of (BLAISE and MONTAGNE), i, 633.
acyclic, pyridine derivatives from (BLAISE and MONTAGNE), i, 835.
4:7-Diketo-1-phenyl-5-methylbenztriazole (CHATTAWAY and PARKES), i, 985.
2:5-Diketopiperazines, hydrolysis of (LÜDTKE), i, 450.
oxidation of (ABDERHALDEN and KOMM), i, 848.
Diketotetramethyldicoumarans (FRIES and BARTENS), i, 568.
3:5-Diketo-4:4:6:6-tetraphenylhexahydropyridazine-1:2-dicarboxylic acid, ethyl ester (INGOLD and WEAVER), i, 580.
4:7-Diketo-1-*o*-tolyl-5-methylbenztriazole (CHATTAWAY and PARKES), i, 985.
Dilactyl-lactic acid (DIETZEL and KRUG), i, 1036.
1:4-Dileucylpiperazine, and its derivatives (ABDERHALDEN and ROSSNER), i, 975.
Dimercuribis-*o*-chloroanilines (VECCHIOTTI and MICHETTI), i, 1058.
2:5-Dimethoxyacetanilide, 4-bromo-, and 4-nitro- (RUBENSTEIN), i, 1279.
αγ-Dimethoxyacetoacetic acid, ethyl and methyl esters (PRATT and ROBINSON), i, 422.
Dimethoxyacetophenones, and their semicarbazones (PRATT and ROBINSON), i, 826.
2:5-Dimethoxyaniline, 4-bromo-, and 4-nitro-, and their salts (RUBENSTEIN), i, 1279.
β-Dimethoxyanilinopropenyl methyl ketones, and the 6-bromo-derivative of the 3:4-compound (LIONS, PERKIN, and ROBINSON), i, 831.
2:3-Dimethoxybenzaldehyde dimethylacetal (HAWORTH and PERKIN), i, 968.
2:3-Dimethoxybenzaldehyde, 5- and 6-nitro-, and their derivatives (PERKIN, ROBINSON, and STOYLE), i, 39.
2:4-Dimethoxybenzaldehyde, 5-nitro-, and its derivatives (RAO, SRIKANTIA, and IYENGAR), i, 676.
2:5-Dimethoxybenzaldehyde, bromo- and nitro-, and their *p*-nitrophenylhydrazones (RUBENSTEIN), i, 1279.
Di-*o*-methoxybenzimide (ANSCHÜTZ, RIEPENKRÖGER, and KUCKERTZ), i, 667.
2:5-Dimethoxybenzoic acid, 3-amino-, and its hydrochloride, 3- and 6-bromo-, and 3- and 6-nitro- (RUBENSTEIN), i, 1279.
7:8-Dimethoxybenzopyrone, 3-hydroxy- (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.
2:3-Dimethoxybenzoyl chloride (HAWORTH and PERKIN), i, 968.
6:7-Dimethoxy-2-benzoyl-1:2-dihydro-*iso*quinoline, 1-cyano- (HAWORTH and PERKIN), i, 968.
3:9-Di-*p*-methoxybenzoylperylene (ZINKE, FUNKE, MATSCHER, WOLFBAUER, and LORBER), i, 1436.
***s*-Di-*p*-methoxybenzpinacone** (TIFFENEAU and ORÉKHOV), i, 680.
2:3-Dimethoxybenzyl bromide, and its derivatives (HAWORTH and PERKIN), i, 968.
3:4-Dimethoxybenzyl bromide (HAWORTH, PERKIN, and RANKIN), i, 969.
Dimethoxybenzylcoumarone phenylhydrazone (FREUDENBERG, FIKENTSCHER, and HARDER), i, 420.
2:3-Dimethoxybenzylideneaniline, 5- and 6-nitro-, and their hydrochlorides (PERKIN; ROBINSON and STOYLE), i, 39.
3′:4′-Dimethoxy-2′-benzylidene-1-hydrindone, 2′- and 6′-nitro- (LIONS, PERKIN, and ROBINSON), i, 832.
2:3-Dimethoxybenzylidene-*p*-toluidine, 5- and 6-nitro- (PERKIN, ROBINSON, and STOYLE), i, 39.
***p:p′*-Dimethoxy-*α*-benzylmandelic acid** (MALKIN and ROBINSON), i, 560.
6:6′-Dimethoxy-2:2′-bisoxythionaphthen, 5:5′-*di*bromo- (GRIFFITH and HOPE), i, 827.
5:6-Dimethoxy-2-(5′-bromo-2′-hydroxyphenyl)phthalide (JACOBSON and ADAMS), i, 272.
5:6-Dimethoxy-2-(bromohydroxytolyl)-phthalides (JACOBSON and ADAMS), i, 272, 1077.

7:8-Dimethoxychromanone (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.
3:4-Dimethoxycinnamic anhydride (ROBINSON and SHINODA), i, 1302.
***pp'*-Dimethoxycinnamylideneacetophenone**, and its dimethylacetal (STRAUS and HEYN), i, 1431.
3:5-Dimethoxycoumaran-2-one, hydrazone of (DEAN and NIERENSTEIN), i, 281.
***αα*-Dimethoxy-*αε*-di-*p*-anisyl-*βδ*-pentadiene** (STRAUS and HEYN), i, 1431.
***γγ*-Dimethoxy-*αγ*-di-*p*-anisylpropane** (STRAUS and HEYN), i, 1430.
***γγ*-Dimethoxy-*αγ*-di-*p*-anisylpropylene** (STRAUS and HEYN), i, 1430.
Dimethoxydianthraquinone (PERKIN and YODA), i, 1160.
3:5-Dimethoxy-1:2-dihydrocoumarone (DEAN and NIERENSTEIN), i, 281.
Dimethoxydihydrothebeninemethine, salts of (SPEYER and ROSENFELD), i, 962.
6:6'-Dimethoxydiketodicoumarans, and 5:5'-*di*bromo- (FRIES and SAFTIEN), i, 570.
4:6-Dimethoxy-2(3':4'-dimethoxybenzoyl)coumarone (FREUDENBERG, FIKENTSCHER, and WENNER), i, 692.
5:6-Dimethoxy-2-(3':4'-dimethoxybenzyl)benzoic acid (JACOBSON and ADAMS), i, 1077.
4:6-Dimethoxy-2-(3':4'-dimethoxybenzyl)coumarone, and bromo- (FREUDENBERG, FIKENTSCHER, and WENNER), i, 692.
Dimethoxy-2:4-dimethylquinolines, and their salts and derivatives (LIONS, PERKIN, and ROBINSON), i, 831.
Dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinolines, and their salts and derivatives (LIONS, PERKIN, and ROBINSON), i, 831.
3:3'-Dimethoxydiphenoquinone-4:4'-*di*chlorodi-imine (BLASZKOVSKA), ii, 1043.
2:3'-Dimethoxydiphenyl-5:6'-dicarboxylic acid (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1262.
Dimethoxy-3:3'-diphenyl-5:5'-dimethyl-3:3'-dicoumaranyls, 2:2'-*di*hydroxy- (LÖWENBEIN and FOLBERTH), i, 552.
3:4-Dimethoxydiphenylmethane-2-carboxylic acid, 2'-hydroxy- (JACOBSON and ADAMS), i, 272.
Dimethoxydipropyldiphenyl, *di*hydroxy- (RICHTER and CHRISTEN), i, 813.
3:4'-Dimethoxy-2:4-distyrylbenzopyrylium chloride, 7-hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.
Di-β-methoxyethyl ether (CRETCHER and PITTENGER), i, 228.
3:4'-Dimethoxyflavone, 5:7-*di*hydroxy- (ROBINSON and SHINODA), i, 1302.
3:3'-Dimethoxyflavylium chloride, 5:7-*di*hydroxy- (PRATT and ROBINSON), i, 826.
4:5-Dimethoxyhomophthalamic acid (HAWORTH and PINK), i, 929.
4:5-Dimethoxyhomophthalimide (HAWORTH and PINK), i, 929.
5:6-Dimethoxy-2-(4'-hydroxy-3'-methoxybenzyl)benzoic acid (JACOBSON and ADAMS), i, 1077.
5:6-Dimethoxy-2-(hydroxymethylbenzyl)benzoic acids (JACOBSON and ADAMS), i, 1077.
5:6-Dimethoxy-2-(2'-hydroxy-5'-nitrophenyl)phthalide (JACOBSON and ADAMS), i, 1077.
5:6-Dimethoxy-2(6'-hydroxy-*m*-tolyl)-phthalide (JACOBSON and ADAMS), i, 1077.
5:6-Dimethoxy-2(2'-hydroxy-3':5'-xylyl) phthalide (JACOBSON and ADAMS), i, 1077.
Dimethoxyindenoquinoline, and its hydrochloride (LIONS, PERKIN, and ROBINSON), i, 832.
2:3-Dimethoxyindophenazine, and its salts (ARMIT and ROBINSON), i, 1172.
6:6'-Dimethoxy-3-keto-$\Delta^{2:3'}$-dicoumaran, 5:5'-*di*bromo-, and its derivatives (FRIES and SAFTIEN), i, 571.
6:6'-Dimethoxy-3-keto-2:3-dihydro-2:3'-dicoumaran, and its oxidation product (FRIES and SAFTIEN), i, 570.
1:2-Dimethoxymethoxyanthraquinones, hydroxy- (JACOBSON and ADAMS), i, 1077.
5:7-Dimethoxy-4-*p*-methoxyphenylcoumarin (BARGELLINI), i, 1299.
3:7-Dimethoxy-4-*p*-methoxyphenyl-2-methylbenzopyrylium ferrichloride (ALLAN and ROBINSON), i, 148.
1:2-Dimethoxy-6-methylanthraquinone, 8-bromo-5-hydroxy- and 5-hydroxy- (JACOBSON and ADAMS), i, 272.
1:2-Dimethoxy-6-methyl-9-anthrone, 8-bromo-5-hydroxy- and 5-hydroxy- (JACOBSON and ADAMS), i, 272.
1:2-Dimethoxymethyl-9-anthrones, 5-hydroxy- (JACOBSON and ADAMS), i, 1077.
3:7-Dimethoxy-2-methylbenzopyrone (ALLAN and ROBINSON), i, 148.
Dimethoxymethylenefluorene, bromo- (WIELAND and KRAUSE), i, 902.
2:3-Dimethoxy-6-methylindophenazine methohydroxide (ARMIT and ROBINSON), i, 1173.

2:3-Dimethoxy-5(or 11)-methyl*iso*indophenazine, and its salts (ARMIT and ROBINSON), i, 1173.

4:6-Dimethoxy-2-methylpyridine-5-carboxylic acid (SPÄTH and KOLLER), i, 1446.

β-2:3-Dimethoxyphenoxypropionic acid (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.

β-4:5-Dimethoxyphenylacrylic acid, 3-amino-, and 3-nitro- (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.

3:4-Dimethoxyphenyl-5′-bromo-2′-hydroxy-*m*-tolylmethane-2-carboxylic acid (JACOBSON and ADAMS), i, 272.

β-3:4-Dimethoxyphenylethyl *n*-amyl ketone, and its oxime (MURAI), i, 1157.

β-3:4-Dimethoxyphenylethyl butyl ketones, and their derivatives (NOMURA and HOTTA), i, 1157.

β-3:4-Dimethoxyphenylethyl ethyl ketone, and its derivatives (NOMURA and HOTTA), i, 1157.

Di-3-methoxyphenylethyl ketone, *di*-β-4-hydroxy-, and its dibenzoyl derivative (NOMURA and HOTTA), i, 1156.

β-3:4-Dimethoxyphenylethyl *n*-propyl ketone, and its oxime (NOMURA and HOTTA), i, 1157.

Di(*p*-methoxyphenyl)hydantoins (COGHILL and JOHNSON; COGHILL), i, 583.

3′:4′-Dimethoxyphenyl β-2-hydroxy-4:6-dimethoxyphenylethyl ketone (FREUDENBERG, FIKENTSCHER, and WENNER), i, 692.

2:4-Dimethoxyphenyl 2-hydroxy-4:6-dimethoxystyryl ketone (PRATT and ROBINSON), i, 825.

3:4-Dimethoxyphenyl *o*-hydroxystyryl ketone benzoate (FREUDENBERG, FIKENTSCHER, and HARDER), i, 420.

3:4-Dimethoxyphenyl-2′-hydroxy-*m*-tolylmethane-2-carboxylic acid (JACOBSON and ADAMS), i, 272.

3:7-Dimethoxy-4-phenyl-2-methylbenzopyrylium ferrichloride (ALLAN and ROBINSON), i, 148.

5:7-Dimethoxy-2-phenyl-4-methylbenzopyrylium salts (WALKER and HEILBRON), i, 693.

2:6-Di-*p*-methoxyphenyl-3-methyltetrahydro-4-pyrone (RYAN and CAHILL), i, 558.

3-*mp*-Dimethoxyphenylpyrazoline, and its derivatives (FREUDENBERG and FIKENTSCHER), i, 69.

5:7-Dimethoxy-2-phenyl-4-styrylbenzopyrylium chloride, 2′- and 4′-hydroxy- (WALKER and HEILBRON), i, 693.

Di-(*p*-methoxyphenyl)-2-thiohydantoins (COGHILL and JOHNSON), i, 582.

:4-Dimethoxyphenyl *o*-tolyl ketone (DE DIESBACH and STREBEL), i, 1435.

3:4-Dimethoxyphenyl β-2:4:6-trimethoxyphenylethyl ketone, and its oxime (FREUDENBERG, FIKENTSCHER, and HARDER), i, 421.

4:6-Dimethoxyphenyl 3:4:5-trimethoxyphenylethyl ketone, 2-hydroxy- (DEAN and NIERENSTEIN), i, 952.

3:4-Dimethoxyphenyl 2:4:6-trimethoxystyryl ketone (FREUDENBERG, FIKENTSCHER, and HARDER), i, 421.

4:6-Dimethoxyphenyl 3:4:5-trimethoxystyryl ketone, 2-hydroxy-, and its derivatives (SONN, MÜLLER, BÜLOW, and MEYER), i, 933; (DEAN and NIERENSTEIN), i, 952.

1:4-Dimethoxyphthalazine (RADULESCU and GEORGESCU), i, 1185.

4:5-Dimethoxyphthalide, 6-amino-, 6-bromo-, and 6-nitro- (RÂY and ROBINSON), i, 1153.

3:4-Dimethoxypropylbenzene, 6-amino-, and its derivatives (THOMS and KEMP), i, 789.

3:5-Dimethoxy-*n*-propylbenzene (MAUTHNER), i, 25.

4:6-Dimethoxypyridine-2-carboxylic acid, 5-cyano- (SPÄTH and KOLLER), i, 1446.

6:7-Dimethoxy*iso*quinoline methiodide (FORSYTH, KELLY, and PYMAN), i, 1167.

6:7-Dimethoxy*iso*quinoline-1-carboxylamide (HAWORTH and PERKIN), i, 969.

3:4-Dimethoxystilbene (DEY and ROW), i, 954.

2′:4′-Dimethoxystilbene, 2:4-*di*nitro- (PFEIFFER, KALCKBRENNER, and BEHR), i, 548.

Dimethoxystilbenes, *di*nitro-, *tri*nitro-, and nitroamino- (GULLAND and ROBINSON), i, 1188.

Dimethoxystilbenecarboxylic acids, nitro-, and their salts and derivatives (PFEIFFER, KALCKBRENNER, and BEHR), i, 548.

3:4′-Dimethoxy-2-styrylchromone, 5:7-*di*hydroxy- (ROBINSON and SHINODA), i, 1302.

Dimethoxystyryl ketone, additive compounds of β-naphthol and resorcinol with (PFEIFFER, GOEBEL, and ANGERN), i, 271.

Di-3-methoxystyryl ketone, *di*-4-hydroxy-, and its hydrate (NOMURA and HOTTA), i, 1156.

3:2-β-4′-Dimethoxystyrylquinoline, and its salts (TRÖGER and DUNKER), i, 434.

Dimethoxysuccinic acid, esters, rotation of (PATTERSON and FULTON), ii, 1120.

methyl-*n*-hexylcarbinyl esters (PATTERSON and BUCHANAN), i, 115.

6:7-Dimethoxy-1:2:3:4-tetrahydro*iso*quinoline, and its hydrochloride (FORSYTH, KELLY, and PYMAN), i, 1167.

Dimethoxytetraphenylmethanes (GOMBERG and FORRESTER), i, 1267.

6:6′-Dimethoxy-3:3′-*di*thiochromanol (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.

2:5-Dimethoxytoluene, 3-bromo-4:6-*di*nitro- (KOHN and MARBERGER), i, 1265.

3:5-Dimethoxy-*p*-toluic acid, 2:6-*di*bromo-, methyl ester (WAGENHOFER), i, 550.

Dimethoxytriphenylcarbinols, derivatives of (GOMBERG and FORRESTER), i, 1267.

Dimethoxytriphenylmethyls, and their peroxides (GOMBERG and FORRESTER), i, 1267.

2:5-Dimethoxytriphenyl-α-naphthyl methane (GOMBERG and FORRESTER), i, 1267.

Dimethoxy*iso*violanthrone, and chloro- (ZINKE, FUNKE, MATSCHER, WOLFBAUER, and LORBER), i, 1436.

Dimethyl ether. See Methyl ether.

2:5-Dimethyl-4-acetamidomethylpyrrole-3-carboxylic acid, ethyl ester (FISCHER and NENITZESCU), i, 835.

3:5-Dimethylacetophenone, and 2-hydroxy-, and their derivatives (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.

2:3-Dimethyl-5-aldehydopyrrole-4-carboxylic acid, and its derivatives (FISCHER and BELLER), i, 1333.

2:4-Dimethyl-3-aldehydopyrrole-5-carboxylic acid, ethyl ester (KALLE & Co.), i, 297.

αα-Dimethylallyl alcohol. See γ-Methyl-Δ^α^-buten-γ-ol.

αγ-Dimethylallyl alcohol. See Δ^β^-Penten-δ-ol.

2:3-Dimethyl-1-allylpyrazolium iodide (v. AUWERS and DANIEL), i, 1180.

1:3-Dimethyl-9-allyluric acids (GATEWOOD), i, 1189.

9-Dimethylaminoanthrone, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 819.

Dimethylaminoazobenzene hydroferricyanide (CUMMING), i, 122.

***p*-Dimethylaminobenzene-*p*′-azodiphenyl**, and its hydrochloride (VORLÄNDER), i, 1258.

***p*-Dimethylaminobenzoic acid**, phenyl [illegible] (RIVIER and RICHARD), i, 1416.

[illegible]**-dimethylaminobenzophenone** *per*[illegible] (PFEIFFER), i, 410.

[illegible]**-dimethylaminobenzthiazole** (HELLER), i, 314.

***p*-Dimethylaminobenzylidene-*p*-aminobenzoic acid** (WAYNE and COHEN), i, 551.

7-*p*-Dimethylaminobenzylideneaminophenanthraquinone, 2-amino- (SIRCAR and GUPTA), i, 984.

2-*p*-Dimethylaminobenzylidene-6-*p*-anisylidene*cyclo*hexanone, and its *per*chlorates (PFEIFFER), i, 411.

2-*p*-Dimethylaminobenzylidene-6-benzylidene*cyclo*hexanone, and its *per*chlorates (PFEIFFER), i, 411.

2-*p*-Dimethylaminobenzylidene*cyclo*hexanone (PFEIFFER), i, 411.

***p*-Dimethylaminobenzylidenemalonic acid**, ethyl ester (WAYNE and COHEN), i, 551.

Dimethylamino-*o*-bromo-*p*-aminobenzoylethanol (FREJKA and VITHA), i, 1416.

α-Dimethylaminobutan-γ-one (MANNICH), i, 375.

4-Dimethylamino-2′-chloroindophenyl thiosulphates (HELLER), i, 314.

γ-*p*-Dimethylaminocinnamoyl-β-*o*-hydroxyphenylpropane-αα′-dicarboxylic acid (HEILBRON, FORSTER, and WHITWORTH), i, 1285.

4′-Dimethylamino-5:7-dimethoxy-2-phenyl-4-styrylbenzopyrylium salts (WALKER and HEILBRON), i, 694.

α-Dimethylamino-β-dimethylaminomethylbutan-γ-one, and its picrate (MANNICH), i, 375.

2:2′-Dimethylaminodiphenyl *di*sulphide, 2:2′-diacetyl and -dibenzoyl derivatives of (CLARK), i, 841.

***p*-Dimethylaminodiphenyl**, *p*′-amino-, hydrochloride, and derivatives of, and *mono*- and *di*-nitro- (VORLÄNDER), i, 1258.

4′-Dimethylaminodiphenylamine-4-sulphonic acid, 2-nitro-, sodium salt (BATTEGAY and VÉCHOT), i, 1467.

***p*-Dimethylaminodistyryl ketone**, salts of (PFEIFFER), i, 410.

3-β-Dimethylaminoethoxy-4-diethyl-5-pyrazolone (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 301.

Dimethylaminoethoxyethyl alcohol, and its derivatives (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 374.

α-Dimethylamino-β-ethylbutan-γ-one, and its hydrochloride (MANNICH), i, 375.

Dimethylaminoethylcarbamic acid, benzyl ester, and its hydrochloride (HARTMANN and KÄGI), i, 1046.

***N*-Dimethylaminoethylstearamide** (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.

Dimethylamino*cyclo*hexanols, and their derivatives (HECKEL and ADAMS), i, 909.
4′-Dimethylamino-3-hydroxyindonaphthyl-7-sulphonic acid hydrogen 2′-thiosulphate, and its potassium salt (HELLER), i, 314.
9-Dimethylamino-6-hydroxy-5-keto-7:12-naphthaphenthiazine, and its hydrochloride (HELLER), i, 314.
9-Dimethylamino-6-hydroxy-5-keto-7:12-naphthaphenthiazine-2-sulphonic acid, potassium salt (HELLER), i, 314.
4′-Dimethylamino-5:7-*di*hydroxy-2-phenyl-4-styrylbenzopyrylium salts (WALKER and HEILBRON), i, 693.
5-Dimethylamino-1-iminobenzthiazole, and its derivatives (HELLER), i, 314.
4-Dimethylaminoindophenyl sodium thiosulphate (HELLER), i, 314.
4″-Dimethylamino-4′-methoxy-2:4-distyrylbenzopyrylium chloride, 7-hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.
-Dimethylaminomethylphenylarsinic acid (LES ÉTABLISSEMENTS POULENC FRÈRES, FOURNEAU, and MADINAVEITIA), i, 990.
Dimethylaminomethyl-γ-valerolactone, and δ-bromo-, derivatives of (MANNICH and SUTTER), i, 1037.
9-Dimethylaminophenthiazone (HELLER), i, 314.
5-Dimethylaminophenyl hydrogen thiosulphate, 2-amino- (HELLER), i, 313.
3-*N*-Dimethylaminophenylamino-6-methylbenzthiopyrone, *N*-acetyl and -propionyl derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
9-Dimethylaminophenylanthracene (BARNETT, COOK, and MATTHEWS), i, 648.
9-Dimethylaminophenylanthrone, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 819.
2-*p*-Dimethylaminophenylbenztriazole, and its derivatives (ELBS), i, 164.
3-*p*-Dimethylaminophenyl-5-*p*-dimethylaminostyryl-Δ⁵-*cyclo*hexen-1-one-2-carboxylic acid, ethyl ester (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
3-*p*-Dimethylaminophenyl-5-(2′-hydroxy-3′- and -5′-methoxy)styryl-Δ⁵-*cyclo*hexen-1-one-2-carboxylic acids, ethyl esters (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
3-*p*-Dimethylaminophenyl-5-*o*-hydroxystyryl-Δ⁵-*cyclo*hexen-1-one (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
3-*p*-Dimethylaminophenyl-5-*o*-hydroxystyryl-Δ⁵-*cyclo*hexen-1-one-2-carboxylic acid, and its ethyl ester (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
3-*p*-Dimethylaminophenyl-5-*o*-methoxystyryl-Δ⁵-*cyclo*hexen-1-one-2-carboxylic acid, ethyl ester (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
3-*p*-Dimethylaminophenyl-5-methyl-*cyclo*hexen-5-ol-1-one-2-carboxylic acid, ethyl ester, and its phenylhydrazone (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
3-*p*-Dimethylaminophenyl-5-methyl-Δ⁵-*cyclo*hexen-1-one-2-carboxylic acid, ethyl ester (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
4′-Dimethylaminostilbene-4-carboxylic acid, 2-nitro-, esters of (PFEIFFER, KALCKBRENNER, and BEHR), i, 549.
***p*-Dimethylaminostyryl *p*-methoxystyryl ketone**, and its salts (PFEIFFER), i, 410.
4′-Dimethylamino-2-styryl-4-methylbenzopyrylium chloride, 7-hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.
4′-Dimethylamino-2-styryl-1-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
4-*p*-Dimethylaminostyryl-α-naphthapyrone, and its hydrochloride (DEY and ROW), i, 954
2-*p*-Dimethylaminostyrylquinoline, derivatives of (PFEIFFER, RHEINBOLDT, and WOLF), i, 412.
***C*-Dimethylaminotetrahydroanthranil**, and its salts (v. AUWERS, BAHR, and FRESE), i, 312.
Dimethylaminothiolbenzene (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.
***p*-Dimethylaminothiolbenzoic acid**, and its derivatives (RIVIER and RICHARD), i, 1416.
5-Dimethylamino-1-thiolbenzthiazole, and its salts and derivatives (HELLER), i, 313.
Dimethylammonium chloroferrates (REMY and ROTHE), ii, 1089.
Dimethylaniline, vapour pressure of (NELSON and WALES), ii, 494.
action of acid chlorides on (RIVIER and RICHARD), i, 1416.
influence of acetyl chloride on nitration of (CHRZASZCZEWSKA and BIATU), i, 1058.
and *p*-bromo-, and *p*-nitroso-, hydroferri-, and hydroferro-cyanides of (CUMMING), i, 122.
Dimethylaniline, 2-bromo-4:6-*di*nitro- (SANÉ and JOSHI), i, 134.

9:10-Di(methylanilino)-9:10-dihydroanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
2-*p*-Dimethylanilino-6-methoxy-2-thiol-3-ketocoumaran (FRIES and SAFTEIN), i, 571.
4:6-Dimethylbenzaldehydeanil-2-carboxyanilide (PERKIN and TAPLEY), i, 43.
2:6-Dimethylbenzaldehydeanil-4-carboxylic acid (PERKIN and TAPLEY), i, 43.
4:6-Dimethylbenzaldehyde-2-carboxyanilide (PERKIN and TAPLEY), i, 43.
2:6-Dimethylbenzaldehyde-4-carboxylic acid, and its phenylhydrazone (PERKIN and TAPLEY), i, 43.
3:3′-Dimethylbenzophenone, 4:4′-*di*hydroxy-, and its derivatives (GOMBERG and ANDERSON), i, 1064.
2:5-Dimethylbenzophenoneoxime (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
4:6-Dimethylbenzoylformic acid, 2-hydroxy-, derivatives of (FRIES and BARTENS), i, 568.
6:8-Dimethylbenzthiopyran, and its sulphone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.
2:6-Dimethylbenzthiopyrone, and 3-bromo- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
2:6-Di-*p*-methylbenzyl*cyclo*hexanone (GARLAND and REID), i, 1281.
2:6-Di-*p*-methylbenzylidene*cyclo*hexanone (GARLAND and REID), i, 1280.
Dimethylbenzylindazolium salts, and *di*bromo-, and iodo- (v. AUWERS and LOHR), i, 74.
Dimethylbilirubin (KÜSTER, HAAS, and MAURER), i, 307.
$\beta\gamma$-Dimethyl-Δ^{α}-buten-γ-ol (CLAISEN), i, 278.
2:6-Di-*a*-methyl-Δ^{β}-butenyl-*p*-cresol (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.
2:6-Dimethyl-4-*iso*butyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester, ψ-cyanide (MUMM), i, 965.
$\beta\gamma$-Dimethyl-Δ^{β}-butylene, dinitrate of (HAINES and ADAMS), i, 801.
1:6-Dimethyl-4-*iso*butylmethylenedihydropyridine, and its salts and derivatives (MUMM), i, 965, 967.
2:4-Dimethyl-5-carbethoxypyrrole-3-propionic acid (FISCHER and NENITZESCU), i, 835.
2:4-Dimethyl-5-carbethoxypyrryl-3:3-methylmalonic acid, and its diethyl [illegible] (FISCHER and NENITZESCU), i, 835.
[illegible]methylcarboxysuccinic acid, and its ethyl ester (INGOLD), i, 357.
Dimethylchloroacetamidomethylpyrrole-3-carboxylic acids, ethyl esters (FISCHER and NENITZESCU), i, 835.
1:4-Dimethyl-5-chloromethyluracil (SCHMEDES), i, 435.
2:8-Dimethylchromanone, 2- and 3-amino- (WITTIG), i, 279.
2:6-Dimethylchromone (HALL), i, 23.
4:6-Dimethylcoumaranoneanils (FRIES and BARTENS), i, 567, 568.
4:6-Dimethylcoumaran-3-one-2-*p*-dimethylaminoanil (FRIES and BARTENS), i, 567.
4:7-Dimethylcoumarin, preparation of (MÜLLER), i, 1442.
4:6-Dimethylcoumarophenazine (FRIES and BARTENS), i, 568.
Dimethylcreatinine picrate (GREENWALD), i, 839.
3:5-Dimethyl-*p*-cresol, 2:6-*di*bromo-3:5-*di*hydroxy- (KOHN and WEISSBERG), i, 655.
$\beta\epsilon$-Dimethyl-$\Delta\zeta$-decen-ϵ-ol (GRIGNARD and DUBIEN), i, 111.
9:10-Dimethyldianilinoanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1399.
1:8-Dimethyldibenzocopyrine, 10:15-*di*amino-, and its hydrochloride (GULLAND and ROBINSON), i, 1187.
2:5-Dimethyl-4-diethylaminomethylpyrrole-3-carboxylic acid, ethyl ester, and its perchlorate (FISCHER and NENITZESCU), i, 835.
***s*-Dimethyldiethylsuccinic acid**, and its derivatives (DOX), i, 797.
$\alpha\alpha'$-Dimethyl-$\beta\beta'$-diethylthiocarbamide (LECHER), i, 1391.
***N*:*S*-Dimethyl-*N*:*N*′-diethyl-ψ-thiocarbamide** (LECHER, GRAF, and GNÄDINGER), i, 1393.
2:6-Dimethyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester, ψ-cyanide (MUMM), i, 965.
Dimethyl diketone (*diacetyl*), decomposition of (HURD and TALLYN), i, 885.
1:4-Dimethyl-2:5-diketopiperazine, 1:4-*di*hydroxy-, diacetate (BERGMANN, MIEKELEY, and KANN), i, 1134.
2:2′-Dimethyldiphenyl (*ditolyl*), 5:5′-*di*amino-, and 5:5′-*di*hydroxy- (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1262.
3:5:3′:5′-*tetra*amino- and -*tetra*nitro-4:4′-*di*hydroxy-, and their derivatives (STEINKOPF, ZEMISCH, WINKLER, and POHL), i, 1413.
3:3′-Dimethyldiphenyl, 5:5′-*di*amino-4:4′-*di*hydroxy-, dihydrochloride (STEINKOPF, ZEMISCH, WINKLER, and POHL), i, 1414.

3:3′-Dimethyldiphenyl, 6:6′-*di*hydroxy-, and its derivatives (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1263.

pp′-**Dimethyldiphenyl-3:3′-disulphonamide** (HARDING), i, 670.

2:5-Dimethyl-3-diphenylhydroxymethylpyrrole-4-carboxylic acid, ethyl ester (SEKA), i, 57.

Dimethyldiprene (ASCHAN and KROHN), i, 49.

5:5′-Dimethyl-2:3′-dipyrrole-4:4′-dicarboxylic acid, 3-hydroxy-, ethyl ester, derivatives of (FISCHER and HEYSE), i, 78.

Dimethyl-2:2′-diquinolyls, and their derivatives (CONOLLY), i, 1329.

7:7′-Dimethyldisulphisatide (WAHL and FAIVRET), i, 588.

Dimethyldodecahydrocarbazole, and its salts (v. BRAUN and SCHÖRNIG), i, 1449.

Dimethyldodecaoxymethylene ether (STAUDINGER and LÜTHY), i, 361.

Dimethylene-1:3-oxaimines, synthesis and division of (INGOLD), i, 840.

3:5-Dimethyl-2-ethylcoumaran (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.

2:6-Dimethyl-4-ethyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester, *ψ*-cyanide (MUMM), i, 965.

ββ-Dimethyl-α-ethylglutaric acid, derivatives of (KON, SMITH, and THORPE), i, 509.

3:5-Dimethyl-2-ethyl-7-α-methyl-Δβ-butenylcoumaran (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.

1:6-Dimethyl-4-ethylmethylenedihydropyridine, and its *per*chlorate (MUMM), i, 965.

3:5-Dimethyl-1-ethylpyrazole, and its picrate (v. AUWERS and DANIEL), i, 1180.

Dimethyl-1-ethylpyrazoles, chloro-, and their *per*chlorates (v. AUWERS and NIEMEYER), i, 1177.

3:5-Dimethyl-1(2)-ethyl-2(1)-propylpyrazole, and its *per*iodide (v. AUWERS and DANIEL), i, 1180.

2:6-Dimethyl-3-ethylpyridine, and its salts (KOENIGS and HOFFMANN), i, 299.

Dimethylethyltetrahydroindazoles, and their picrates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.

1:7-Dimethyl-3-ethyluric acid, 8-thio- (BILTZ and PEUKERT), i, 1463.

1:7-Dimethyl-3-ethylxanthine, and its salts, and 8-chloro- (BILTZ and PEUKERT), i, 1463.

2:5-Dimethylfuran-3:4-dicarboxylamide (SEKA), i, 57.

2:5-Dimethylfuro-2:2′:5:5′-tetramethyltetrahydrofuran (SEKA), i, 57.

2:5-Dimethylfuro-2:2′:5:5′-tetraphenyltetrahydrofuran (SEKA), i, 57.

3:7-Dimethyl-5-furyl-5:10-dihydroacridine, 2:8-*di*amino- (MAHOOD and HARRIS), i, 302.

αα-Dimethylglutaric acid, dinaphthylides and di-*p*-toluidide of (v. AUWERS), i, 892.

ββ-Dimethylglutarylfluorescein (DUTT and THORPE), i, 141.

ββ-Dimethylglutarylrhodamine (DUTT and THORPE), i, 142.

4:5-Dimethylglyoxaline, 2-amino-, and its salts and derivatives (BURTLES and PYMAN), i, 1326.

Dimethylglyoxalines, 4- and 5-nitro-, and their salts (BHAGWAT and PYMAN), i, 1174, 1175.

2-thiol- (BURTLES, PYMAN, and ROYLANCE), i, 697.

Dimethylglyoxime, preparation of (SEMON and DAMERELL), i, 1039.

dimethyl ether (AVOGADRO and TAVOLA), i, 1040.

Dimethylhaemin, bromo-, bromide (KÜSTER and HEESS), i, 993.

βζ-Dimethylheptan-ε-ol (THOMS and KAHRE), i, 789.

βζ-Dimethyl-Δγ-hepten-ε-one, and its semicarbazone (THOMS and KAHRE), i, 789.

l-**βε-Dimethylhexan-βε-diol**, γ-amino-, benzoyl derivative (KARRER, JÄGGI, and TAKAHASHI), i, 1046.

βδ-Dimethylhexane-βδ-diol, compound of boric acid and (HERMANS), i, 500.

cis-**1:4-Dimethyl*cyclo*hexane-4:5-diol** (NAMETKIN and BRIUSOVA), i, 1146.

Dimethyl*cyclo*hexanetricarboxylic acid, and its trimethyl ester (RUZICKA, MEYER, and PFEIFFER), i, 1419.

l-**βε-Dimethylhexan-β-ol**, γ-amino-, benzoyl derivative (KARRER, JÄGGI, and TAKAHASHI), i, 1046.

1:3-Dimethyl*cyclo*hexan-4-ol, and its derivatives (GODCHOT and BEDOS), i, 537.

1:3-Dimethyl*cyclo*hexan-4-ones, and their derivatives (GODCHOT and BEDOS), i, 537.

1:4-Dimethyl-Δ¹-*cyclo*hexene, derivatives of (NAMETKIN and BRIUSOVA), i, 1146.

l-**βε-Dimethylhexen-β-ol**, γ-amino-, benzoyl derivative (KARRER, JÄGGI, and TAKAHASHI), i, 1046.

Dimethylhydroxyglyoxime, metallic salts of (PONZIO and RUGGERI), i, 1041.

1:3-Dimethyl-4-hydroxymethylene*cyclo*hexan-5-one, and its derivatives (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.

Dimethylhydroxymethylpyrrole-3-carboxylic acids, ethyl esters (FISCHER and NENITZESCU), i, 834.

2:5-Dimethylindazole, 3-bromo-, and its picrate (v. AUWERS and LOHR), i, 75.

1:2-Dimethylindazolium bromide and chloride (v. AUWERS and PFUHL), i, 1101.

7:7′-Dimethylindigotin, ferric chloride derivatives (KUNZ and STÜHLINGER), i, 1319.

7:7′-Dimethyl*iso*indigotin (WAHL and FAIVRET), i, 588.

Di(2-methylindolyl)ethane, and its dioxime (ODDO), i, 297.

Di(2-methylindolyl)methane (ODDO), i, 297.

3:3′-Dimethylindophenol, 6:4′:6′-*tri*hydroxy- (HENRICH and GÖTZ), i, 913.

3:5-Di(2-methylindyl)*iso*oxazole (ODDO), i, 297.

Di-2-methylindylphthalide (ODDO), i, 588.

3:5-Di(2-methylindyl)pyrazole (ODDO), i, 297.

Dimethylketen, additive and polymerisation reactions of (STAUDINGER), i, 786.

*per*oxide (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 933.

1:3-Dimethyl-4-methoxymethylene*cyclo*hexan-5-one, and its methylsemicarbazone (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.

Dimethylmethylenedihydropyridines, and their derivatives (MUMM), i, 965, 967.

1:6-Dimethylmethylenedihydropyridine-3:5-dicarboxylic acid, ethyl ester, and its derivatives (MUMM), i, 966.

Dimethylmethylenestannane (KRAUS and GREER), i, 1394.

3:3-Dimethyl-β-naphthindolenyl-2-formoxime, and its derivatives (PLANCHER, COLACICCHI, and BARBIERI), i, 579.

2:6-Dimethyl*iso*nicotinic acid, 3-amino-, and its salts (GULLAND and ROBINSON), i, 1186.

4:4′-Dimethyl*di*nitroaminobenzophenone, 3:5:3′:5′-*tetra*bromo-(ELION), i, 262.

βδ-Dimethyl-Δ$^{\alpha\epsilon}$-nonadiene (GRIGNARD and DUBIEN), i, 112.

βδ-Dimethyl-Δ$^{\alpha}$-nonen-δ-ol (GRIGNARD and DUBIEN), i, 111.

6:9-Dimethyl-1:2:3:4:5:6:7:8-octahydrocarbazole (v. BRAUN and SCHÖRNIG), i, 1449.

1:3-Dimethyl*cyclo*pentane-3-carboxylic acid, and its copper salt and amide (ZELINSKI and RJACHINA), i, 29.

βδ-Dimethylpentane-βδ-diol, compound of boric acid and (HERMANS), i, 500.

3:6-Dimethyl-2:10-phenoxazone, 7-hydroxy-, and its derivatives (HENRICH and GÖTZ), i, 913.

Di-(β-methylphenylethyl)amines, *o*- and *m*-chloro-, hydrochlorides and derivatives (v. BRAUN and REICH), i, 1407.

γ-2:4- and **γ-3:4-Dimethylphenylpropinenes** (BERT, DORIER, and LAMY), i, 1373.

2.5-Dimethyl-1-phenylpyrrolo-2:2′:5:5′-tetramethyltetrahydrofuran (SEKA), i, 57.

***o*:*p*-Dimethylphenylquinoxaline**, 2:3-*o*-*di*hydroxy- (FRIES and BARTENS), i, 568.

4:6-Dimethylphthalonic acid, and its dimethyl ester (PERKIN and TAPLEY), i, 43.

2:5-Dimethyl-4-*N*-piperidinomethylpyrrole-3-carboxylic acid, ethyl ester, and its *per*chlorate (FISCHER and NENITZESCU), i, 835.

3-*aa*-Dimethylpropionyl-1:2:4-benzoxadiazine, 7-nitro- (KHEINBOLDT and SCHMITZ-DUMONT), i, 1132.

2:4-Dimethylpropiophenone-*p*-nitrophenylhydrazone (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.

3:5-Dimethyl-1-propylpyrazole, and its picrate (v. AUWERS and DANIEL), i, 1180.

3:5-Dimethylpyrazole-1-carboxylic acid, ethyl ester (v. AUWERS and DANIEL), i, 1181.

1:5-Dimethylpyrazol-3-one picrate (v. AUWERS and NIEMEYER), i, 1177.

1:3-Dimethylpyridofluorene, and its hydriodide (MILLS, PALMER, and TOMKINSON), i, 69.

1:3-Dimethylpyridofluorenone, and its 4-carboxylic acid (MILLS, PALMER, and TOMKINSON), i, 69.

1:6-Dimethyl-α-pyridone (MUMM), i, 966.

Dimethylpyrone, action of hydrazine on (KIJNER), i, 1105.

3:4-Dimethylpyrrole, 5-chloroacetyl derivative (KALLE & Co.), i, 297.

Dimethylpyrroles, *mono-* and *di*-iodo-, and the carboxylic acids of the former (PIERONI and NOCENTINI), i, 1096.

2:3-Dimethylpyrrole-5-aldehyde (FISCHER and BELLER), i, 1333.

2:3-Dimethylpyrrole-5-carboxylic acid, ethyl ester (FISCHER and BELLER), i, 1334.

Dimethylstannane, disodium derivative (KRAUS and GREER), i, 1394.

Dimethylstibine, derivatives of (MORGAN and DAVIES), i, 1395.

***as*-Dimethylsuccinylfluorescein** (DUTT and THORPE), i, 141.

***as*-Dimethylsuccinylrhodamine** (DUTT and THORPE), i, 142.

2:6-Dimethyl*cyclo*telluropentane-3:5-dione, and its dioxime (MORGAN and TAYLOR), i, 634.

Dimethylterephthalonic acid, and its derivatives (PERKIN and TAPLEY), i, 42.

Dimethyl-1:2:3:4-tetrahydrocarbazoles (v. BRAUN and SCHÖRNIG), i, 1449.

Dimethyltetrahydroindazoles, and their picrates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.

4:6-Dimethyltetrahydroindazole-2-carboxylamide (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.

4:6-Dimethyl-4:5:6:7-tetrahydroindazole-2-carboxylic acid, esters (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.

Di(7-methyl-4:5:6:7-tetrahydroindazyls), and their derivatives (v. AUWERS, BAHR, and FREESE), i, 311, 313.

6:6′-Dimethyl*dithio*benzopyrone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

Dimethylthiocarbamylmalic acids, and their derivatives (HOLMBERG), i, 1238.

4:6-Dimethylthiochroman-4-ol (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

6:6′-Dimethyl-3:3′-*dithio*chromanol, and its *di*bromide (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.

2:6-Dimethylthiochromanone, and its derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.

4:6-Dimethyl-Δ^3-thiochromene (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

Dimethyl*dithio*ethylene, metallic halides of (MORGAN, CARTER, and HARRISON), ii, 1042.

4:6-Dimethylthioflavan-4-ol, and its *per*chlorate (ARNDT, PUSCH, and SCHWARZ), i, 1304.

3:4-Dimethylthiophen-2:5-dicarboxylic acid, and its salts (SEKA), i, 1299.

Dimethyltoluene, *di*chloro- (SOMMELET), i, 803.

$\beta\delta$-Dimethyl-$\Delta\delta$-tridecene (THOMS and AMBRUS), i, 790.

***N*:*N*′-Dimethyl-*N*:*N*″:*N*″-triethylguanidine** (LECHER, GRAF, and GNÄDINGER), i, 1393.

1:3-Dimethyluric acid, oxidation of, in alkaline solution (PIAUX), i, 165.

1:1′-Dimethyl*streptovinylene*-2:2′-oxacyanine, and its salts and ethyl ether (KÖNIG and MEIER), i, 705.

1:1′-Dimethyl*streptovinylene*-2:2′-thiocyanine, and its salts (KÖNIG and MEIER), i, 705.

Dimethyl*iso*violanthrones (ZINKE, FUNKE, MATSCHER, WOLFBAUER, and LORBER), i, 1436.

Dimethyl-yellow, effect of salts on the dissociation of (RICHTER), ii, 237.

Dinaphthacridine-14-carboxylic acid (SAFTIEN), i, 1318.

Di-*α*- and -*β*-naphthacylfumarodilactones (BOGERT and RITTER), i, 256.

Dinaphthadiphenazine (KEHRMANN and SCHEDLER), i, 442.

Di-*α*-naphthafluorenone chloride (MAGIDSON), i, 384.

Di-*α*-naphthafluorenyl chloride (MAGIDSON), i, 385.

Dinaphthafluorindine, and its hydrochloride (KEHRMANN and SCHEDLER), i, 442.

Dinaphthalylbenzidine (SHIMOMURA), i, 982.

Dinaphthanthracene series (PHILIPPI, SEKA, and BAUER), i, 555; (PHILIPPI, SEKA, and FUNKE), i, 556.

Dinaphthanthracene-5:7:12:14-diquinone-3:10-dicarboxylic acid (DE DIESBACH and STREBEL), i, 1436.

Dinaphthanthra-5:7:12:14-diquinone, *tetra*bromo-2:9-*di*hydroxy- (DE DIESBACH and STREBEL), i, 1436.

Dinaphthanthradiquinones (DE DIESBACH and STREBEL), i, 1435.

Dinaphthanthradiquinonedisulphonic acid, and its salts (PHILIPPI, SEKA, and FUNKE), i, 556.

***s*-$\alpha\beta$-Dinaphthazine** (LEVI), i, 1186.

$\alpha\alpha'\beta\beta'$-Dinaphthazine, 3:3′- and 5:5′-*di*hydroxy- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 305.

$\alpha\alpha'\beta\beta'$-Dinaphthazinesulphonic acids (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 305.

Di-*α*-naphthenylazosulphine. See 2:5-Di-*α*-naphthyl-1:3:4-thiodiazole.

$\beta\beta$-Dinaphthoxanthen (SEN and SARKAR), i, 813.

Dinaphthoxyethyl ethers (CRETCHER, KOCH, and PITTENGER), i, 628.

$\alpha\beta$-Di-*α*-naphthoylethylene (CONANT and LUTZ), i, 683.

1:1-Dinaphthyl, 3:4:3′:4′-*tetra*hydroxy-, tetramethyl ether (STRAUS, BERNOULLY, and MAUTNER), i, 1155.
Dinaphthyls, *di*amino-, and *di*- and *tetra*-nitro- (CHUDOŽILOV), i, 903.
Di-α-naphthylarsine *tri*chloride and oxide (MATSUMIYA and NAKAL), i, 1339.
Di-α-naphthylarsinic acid (MATSUMIYA and NAKAL), i, 1339.
Di-α-naphthylmethane series, closure of the fluorene ring in (MAGIDSON), i, 384.
Di-α-naphthylmethylarsine(MATSUMIYA and NAKAL), i, 1339.
2:5-Di-α-naphthyl-1:3:4-thiodiazole (ISHIKAWA), i, 1149.
Dinorcamphocyclohexanedione, properties and constitution of (WEDEKIND), i, 685.
Dioctadecylacetic acid (ADAM and DYER), i, 354.
Dioctadecylmalonic acid (ADAM and DYER), i, 354.
Diopside, crystal structure of (WYCKOFF and MERWIN), ii, 485.
from Saulera, crystallography of (LUCIANO), ii, 1037.
Diosmetin, and its derivatives (OESTERLE and WANDER), i, 1439.
Diosmin (OESTERLE and WANDER), i, 1439.
Dioximes (PONZIO), i, 139; (AVOGADRO and TAVOLA), i, 1040; (PONZIO and RUGGERI), i, 1041; (PONZIO), i, 1075.
Dioxindole, 5:7-*di*iodo- (KALB and BERRER), i, 160.
Dioxy*di*hydroxydiacetoxydititanium (GIUA and MONATH), i, 531.
Dioxymethylene dibenzoate (STAUDINGER and LÜTHY), i, 361.
Di*cyclo*pentadienes, ozonides of (STAUDINGER), i, 898.
Dipeptides, reduction of (ABDERHALDEN and SCHWAB), i, 991.
isomerism of *N*-carbalkoxy derivatives of (LEUCHS and SANDER), i, 1248.
Diphenazineoxazine, and chloro- (KEHRMANN and BENER), i, 443.
***iso*Diphenetidine**, preparation of (WHISTON), i, 156.
9:12-Diphenetyl-Δ$^{9:11}$-diphensuccindadienes (BRAND and KREY), i, 904.
9:12-Diphenetyldiphensuccindandiols (BRAND and KREY), i, 904.
9:12-Diphenetyldiphensuccindanes (BRAND and KREY), i, 904.
9:12-Diphenetyl-Δ^{10}-diphensuccindenes (BRAND and KREY), i, 904.
Diphenic acid, preparation of (CHARRIER and BERETTA), i, 34.
Diphenic acid, derivatives of, with local anæsthetic properties (ROBERTS and JOHNSON), i, 816.
Diphenolisatin, diacyl derivatives of (HOFFMANN, LA ROCHE & Co.), i, 66.
9:9-Diphenoxy-9:10-dihydroacridine hydrochloride (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
***PP′*-Diphenoxy-*PP′*-dioxotetrahydrotetrazdiphosphinium** (AUTENRIETH and BÖLLI), i, 1469.
9:9-Diphenoxy-7-ethoxy-9:10-dihydroacridine hydrochloride, and 3-nitro- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
Di-β-phenoxyethyl ether (CRETCHER, KOCH, and PITTENGER), i, 627.
9:9′-Diphenoxy-10-keto-9:10-dihydrophenanthrene (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
***p*-Diphenoxymethylbenzene** (v. BRAUN and REICH), i, 1405.
Di-*m*- and -*p*-phenoxymethylbenzylamines (v. BRAUN and REICH), i, 1405.
Diphenoxymethyltoluene (SOMMELET), i, 803.
Diphenoxyphosphorylanilide (AUTENRIETH and HEFNER), i, 1376.
***PP′*-Diphenoxy-*PP′*-*di*thiotetrazdiphosphinium** (AUTENRIETH and MEYER), i, 990.
Diphensuccinda-9:12-dione, oxidation of (BRAND and LOEHR), i, 683.
Diphensuccinda-9:12-dione, 2:6-*di*amino-, and its hydrochloride and 2:6-*di*nitro- (BRAND and LOEHR), i, 684.
Diphensuccindene series (BRAND and LOEHR), i, 683, 684.
Diphenyl, action of benzoyl peroxide on (GELISSEN and HERMANS), i, 663.
ether, cryoscopy of (DURAND and ROUGÉ), ii, 759.
o-amino-, and its benzoyl derivative (TURNER and SHEPPARD), i, 705.
ethers, amino-, chloro-, chloroamino-, and chloronitro-, and their derivatives (ROBERTS and TURNER), i, 1340.
ethylene ether, 2:4:2′:4′-*tetra*-amino- and -nitro- (DOSIOS and TSATSAS), i, 655.
di-2:4:6-*tri*- and -2:3:4:6-*tetra*-bromo- (KOHN and FINK), i, 134.
methylene ether (BAEKELAND and BENDER), i, 690.
phosphorus nitride (ROSSET), i, 600.
*di*sulphide, *s*-*di*amino-, *iso*butyryl derivative (NAIK and PATEL), i, 121.

Diphenyl *tri*sulphide, 4:4′-*di*amino-, and its hydrochloride (HODGSON and WILSON), i, 532.
tri- and *tetra*-sulphides (LECHER and HOLSCHNEIDER), i, 391.
di-*p*-toluenesulphonate of (GILMAN, BEABER, and MYERS), i, 1057.
p-tolyl thiophosphate (AUTENRIETH and MEYER), i, 807.
Diphenyl, 3-amino-4-hydroxy-, and its derivatives, and *di*bromo-, and *di*bromonitro- (RAIFORD and COLBERT), i, 808.
2:6-*di*hydroxy-, and its derivatives (KUBOTA, FUJIMURA, and AKASHI), i, 809.
p-hydroxylamino-, and *p*-nitroso- (VORLÄNDER), i, 1258.
Diphenyl-4′-acenaphthylmethane (LORRIMAN), i, 673.
Diphenyl-4′-acenaphthylmethane-2-carboxylic acid, and its methyl ester (LORRIMAN), i, 672.
Diphenylacetaldehyde, formation of, from β-amino-αα-diphenylethan-α-ol (THOMAS and BETTZIECHE), i, 257.
Diphenylacetolactone, *o*-hydroxy-, tautomerism of (LÖWENBEIN and FOLBERTH), i, 546.
enolates of (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
2:6-Diphenyl-4-*o*-acetoxyphenylpyrylium *per*chlorate (DILTHEY and FLORET), i, 56.
α-Diphenylacetyl-β-acetylphenylhydrazide (VAN ALPHEN), i, 81.
Diphenylacetyl-2:4:6-*tri*bromoaniline (VAN ALPHEN), i, 83.
β-Diphenylacetyl-*p*-bromophenylhydrazide (VAN ALPHEN), i, 82.
β-Diphenylacetylnitrophenylhydrazides (VAN ALPHEN), i, 82.
α-Diphenylacetylphenylhydrazide, and its derivatives (VAN ALPHEN), i, 81.
β-Diphenylacetyltolylhydrazides (VAN ALPHEN), i, 82.
Diphenylamine as indicator for vanadium (FURMAN), ii, 442.
reactions of (MARQUEYROL and MURAOUR), i, 387.
Diphenylamine, 2:4-*di*amino-, 2-benzoyl derivative (BATTEGAY and VÉCHOT), i, 1467.
2-bromo-4:6-*di*nitro- (SANÉ and JOSHI), i, 134.
*hexa*nitro-, compound of pyridine and (DESVERGNES), i, 1056.
2:4-*di*nitro-5-amino-, and its acetyl derivative (KEHRMANN and STANOYÉVITCH), i, 1331.
Diphenylamine, 2:6 *di*nitro-4-amino-, and its derivatives (LINDEMANN and WESSEL), i, 1099.
o-nitro-*p*′-nitroso- (CHARRIER and BERETTA), i, 21.
Diphenylamine-4-sulphonic acid, 2-amino-4′-hydroxy-, and 2-nitro-4′-hydroxy- (BATTEGAY and VÉCHOT), i, 1468.
4:8-Diphenylaminoanthrarufin-*o*:*o*′-dicarboxylic acid, and 1:5-*di*amino- (BADDILEY, TATUM, and BRITISH DYESTUFFS CORPORATION, LTD.), i, 414.
Diphenyl-*p*-aminobenzylamine, and its derivatives (DESAI), i, 387.
Diphenyl-βγ-*di*amino-*n*-butanes, stereoisomeric (MORGAN and SKINNER), i, 1192.
2:4-Diphenylamino-6-*p*-hydroxynaphthyl-1:3:5-triazine (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 441.
***op*-Diphenylaminophenylbenztriazole**, *op*-*di*nitro- (ELBS), i, 165.
4:5-Diphenyl-2-*m*-aminophenylglyoxaline, and its derivatives (TRÖGER and THOMAS), i, 979.
4:6-Diphenyl-1-*p*-aminophenyl-2-*p*-hydroxyphenylpyridinium chloride hydrochloride (DILTHEY and SCHAEFER), i, 154.
4:6-Diphenyl-2-*m*-aminophenylpyridine, and its salts (DILTHEY and RADMACHER), i, 1441.
2:6-Diphenyl-4-*m*-aminophenylpyrylium hydroxide, and its salts (DILTHEY and RADMACHER), i, 1442.
2:6-Diphenyl-1-aminophenyl-4-quinopyridans, and their salts and derivatives (DILTHEY and SCHAEFER), i, 153.
4:6-Diphenyl-2-anisylpyrylium salts (DILTHEY and RADMACHER), i, 1442.
Diphenylarsinic acid (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319.
Diphenyl-*p*′-azobenzene, *p*-amino-, and its derivatives, and *p*-nitro- (VORLÄNDER), i, 1258.
Diphenylazodiacetylsuccinic acid, *p*-amino-, acetyl derivative (BÜLOW and BAUR), i, 1327.
Diphenylbenzidine, preparation of (MARQUEYROL and MURAOUR), i, 387.
Diphenylbenzylamine hydrochloride, and *p*-amino- (DESAI), i, 387.
αδ-Diphenyl-β-benzylbutan-β-ol, γ-amino- (THOMAS and BETTZIECHE), i, 251.
αα-Diphenyl-β-benzylethyl alcohol, *d*-β-amino- (MCKENZIE and WILLS), i, 396.

Diphenylbenzylmethylarsonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 496.

Diphenyl-3-benzyloxy-β-naphthylcarbinol, and its chloride (GOMBERG and MCGILL), i, 1270.

Diphenyl-3-benzyloxy-β-naphthylmethyl (GOMBERG and MCGILL), i, 1270.

αγ-Diphenyl-β-benzylpropan-β-ol, γ-amino- (THOMAS and BETTZIECHE), i, 250.

Diphenylbisazobisdiacetylsuccinic acid, ethyl ester (BÜLOW and BAUR), i, 1327.

1-*p*-Diphenylbis-(5-methylpyrazole)-3:4-dicarboxylic acid, and its salts and ethyl ester (BÜLOW and BAUR), i, 1327.

2:6-Diphenyl-1-bromophenyl-4-piperidone, 3:5-*di*bromo- (PETRENKO-KRITSCHENKO and BUTMI DE KAZMAN), i, 1094.

αα-Diphenylbutane, *pp'-di*hydroxy- (BAEKELAND and BENDER), i, 689.

αα-Diphenyl-α-butylene oxide (LÉVY and LAGRAVE), i, 679.

αβ-Diphenylcarbamide, α-chloro*di*nitro-, and α-*di*nitro- (KNIPHORST), i, 907.
s-di-4-chloro-3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.

***s*-Diphenylcarbamide-4:4'-diarsinic acid** (KING and MURCH), i, 320.

Diphenylcarbazide, compounds of, with metals (FEIGL and LEDERER), i, 170.

Diphenyl-*o*-carboxylic acid, hydrogenation of (RANEDO and LÉON), i, 665.

Diphenyl-2-carboxylic acid, 4-hydroxy- (COURTOT and GEOFFROY), i, 927.

3:4-Diphenylcoumarins, 7-hydroxy-, and *di*hydroxy-, and their acetyl derivatives (BARGELLINI), i, 1442.

αβ-Diphenyl-ββ-di-*p*-anisylethyl alcohol (TIFFENEAU and ORÉKHOV), i, 680.

αδ-Diphenyl-βγ-dibenzyl-βγ-dimethylbutane (TROTMAN), i, 383.

Diphenyl-4:3:4':3'-dicarboxylicsulphinide (HARDING), i, 670.

Diphenyl-4:4'-dicarboxy-3:3'-sulphimide. See Diphenyl-4:3:4':3'-dicarboxylicsulphinide.

Diphenyl-4:4'-di-diphenamic acid (SHIMOMURA), i, 982.

Diphenyldiethylarsonium bromide and iodide (STEINKOPF and BESSARITSCH), i, 496.

5:5-Diphenyl-5:10-dihydro-3-acridone, 7-amino-, 7:9-*di*amino-, 1-amino-7-hydroxy-, and 7-hydroxy-, and their derivatives (KEHRMANN and TSCHUI), i, 430.

1:4-Diphenyldihydronaphthalene, 1:4-*di*hydroxy- (FRANSSEN), i, 1146.

Diphenyldimethylammonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 495.

Diphenyldimethylarsonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 496.

3:3'-Diphenyl-4:4'-dimethyl-3:3'-dicoumaranyl, 2:2'-*di*hydroxy- (LÖWENBEIN and FOLBERTH), i, 552.

Diphenyldimethylethenylamidinium salts (FISCHER, MÜLLER, and VILSMEIER), i, 440.

1:3-Diphenyldimethylhydrazidouracil (LEVENE), i, 979.

***NN'*-Diphenyl-7:7'-dimethylindigotin**, potassium derivative (KUNZ and STÜHLINGER), i, 1319.

Diphenyldimethyltruxones (DE FAZI), i, 269.

3:6-Diphenyl-1:4-dioxane, and 3:6-*di*bromo-, and their picrates (LEWIS, NIERENSTEIN, and RICH), i, 935.

Diphenyl-4'-diphenamic acid, 4-amino- (SHIMOMURA), i, 982.

9:12-Diphenyldiphensuccindane (BRAND and MÜHL), i, 903.

9:12-Diphenyl-Δ^{10}-diphensuccindene (BRAND and MÜHL), i, 903.

Diphenyldi*iso*propyltetrazine (GOODWIN and BAILEY), i, 843.

Diphenyl-4:4'-disuccinamic acid (SHIMOMURA), i, 982.

Diphenylenedianisylethylene (SCHÖNBERG, ROSENBACH, KRÜLL, and OSTWALD), i, 1300.

Diphenylenedi-*p*-ethoxyphenylethylene (SCHÖNBERG, ROSENBACH, KRÜLL, and OSTWALD), i, 1301.

Diphenylene-ethane, αβ-*di*nitro- (WIELAND and KRAUSE), i, 902.

Diphenylene-ethylene. See Dibenzofulvene.

Diphenylene*di*thiocarbamide (AUTENRIETH and HEFNER), i, 1376.

***s*-Diphenylethane** (*dibenzyl*), *di*thiocyano- (SÖDERBÄCK), i, 899.

αα-Diphenylethan-α-ol, β-amino-, conversion of, into diphenylacetaldehyde, and its benzoyl derivative (THOMAS and BETTZIECHE), i, 257.

Diphenylethylamine hydrochloride (ELBS), i, 163.

β-Diphenylethylamine, and its derivatives (RUPE and GISIGER), i, 1095.

ββ-Diphenylethylamine, β-hydroxy-, action of nitrous acid on (ORÉKHOV and ROGER), i, 261.

Di(β-phenylethylamino)methane, and its diacetyl derivative (SHORT), i, 387.

s-**Diphenylethylene**, *di*thiocyano- (SÖDERBÄCK), i, 899.
as-**Diphenylethylene**, autoxidation of (STAUDINGER), i, 898.
Di-β-phenylethylmethylamine, and its picrate (WIELAND and DRAGENDORFF), i, 1090.
2:6-Di-β-phenylethylpiperidine (SHAW), i, 68.
Diphenylformamidine, condensation of, with phenols (SHOESMITH and HALDANE), i, 39.
2:5-Diphenylfuran, 3:4-*di*chloro- (CONANT and LUTZ), i, 682.
2:5-Diphenylfuran-3:4-dicarboxylic acid, anil and imide of (SEKA), i, 1298.
α-Diphenylglyoxime, absorption spectra of (PURVIS), ii, 627.
βδ-Diphenyl-α-heptylsemicarbazide (MAZOUREVITCH), i, 1247.
6:6-Diphenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylic acid, ethyl ester (INGOLD and WEAVER), i, 581.
Di-ζ-phenyl-Δ$^{\alpha\gamma\epsilon}$-hexatrienyl ketone, and its derivatives (VORLÄNDER, FISCHER, and KUNZE), i, 1069.
Diphenylhydantoins, *di-p*-hydroxy- (COGHILL and JOHNSON; COGHILL), i, 583.
Diphenylhydrazidouridine (LEVENE), i, 979.
1:3-Diphenylhydrindene (ZIEGLER, GRABBE, and ULRICH), i, 132.
Diphenyl-3-hydroxy-β-naphthylmethyl, and its *per*oxide (GOMBERG and MCGILL), i, 1270.
2:6-Diphenyl-4-*o*-hydroxyphenylpyridine, and its hydrochloride (DILTHEY and FLORET), i, 56.
2:6-Diphenyl-4-*o*-hydroxyphenylpyrylium salts (DILTHEY and FLORET), i, 56.
4:6-Diphenyl-2-hydroxyphenylpyrylium hydroxide, and its salts (DILTHEY and RADMACHER), i, 1442.
NN'-**Diphenylindigotin**, copper and iron derivatives (KUNZ and STÜHLINGER), i, 1318.
5:6-(2:3-Diphenylindolo)(6:7)-quinoline, and its salts (ARMIT and ROBINSON), i, 1172.
1:1-Diphenyl-2-keto-1:2-dihydrothionaphthen (BISTRZYCKI and RISI), i, 1426.
Diphenylmethane, 4:4'-*di*amino-, isomerism of, and its derivatives (BUTLER and ADAMS), i, 1458.
*di*bromo*tri*hydroxy-derivatives, and their benzoyl derivatives (KOHN and JAWETZ), i, 135; (KOHN and WIESEN), i, 540.
Diphenylmethane, *o*-hydroxy-. See *o*-Benzylphenol.
2:4-*di*hydroxy- (SHARP & DOHME and DOHME), i, 541.
Diphenylmethane series (SOMMELET), i, 247.
coloured salts of (MADELUNG), i, 1459.
Diphenylmethane-4'-azonaphthionic acid, 4-hydroxy-, sodium salt (BUTLER and ADAMS), i, 1458.
Diphenylmethane-4:4'-bisazo-β-naphthol (BUTLER and ADAMS), i, 1458.
Diphenylmethane-2:2'-dicarboxylic acid, brucine salts, and 4-nitro- (BUTLER and ADAMS), i, 1459.
Diphenylmethanedimethyldihydrazine, use of, in preparation of sugars (v. BRAUN and BAYER), i, 1382.
Diphenyl-3-methoxy-β-naphthylmethyl, and its *per*oxide (GOMBERG and MCGILL), i, 1270.
2:6-Diphenyl-4-*o*-methoxyphenylpyridine (DILTHEY and FLORET), i, 56.
2:6-Diphenyl-4-*o*-methoxyphenylpyrylium salts (DILTHEY and FLORET), i, 56.
Diphenylmethylallylarsonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 496.
Diphenylmethylcarbazine. See Diphenylmethyldihydroacridine.
2:3-Diphenyl-3-methylcoumaran-2-ol (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
5:5-Diphenyl-10-methyldihydroacridine, and its nitro derivatives (KEHRMANN and TSCHUI), i, 431.
Diphenylmethylethylarsonium bromide (STEINKOPF and BESSARITSCH), i, 496.
3:4-Diphenyl-5-methyl-Δ^2-*cyclo*penten-1-one, and its dibromide (RYAN and LENNON), i, 1282.
N-**Diphenylmethylphenanthraphenfluorindinium** chloride (KEHRMANN and SCHEDLER), i, 442.
dl-**1:4-Diphenyl-2-methylpiperazine**, resolution of, and the *d*-camphorsulphonate of the *l*-compound (KIPPING and POPE), i, 22.
αγ-Diphenyl-β-methylpropane (TROTMAN), i, 383.
1:3-Diphenyl-5-methylpyrazole-4-carboxylic acid, hydroxy- and nitro- (MINUNNI, LAZZARINI, and D'URSO), i, 1176.
1-Diphenyl-5-methylpyrazole-3:4-dicarboxylic acid, 1-*p*-amino-, and its acetyl derivative, and its salts and ethyl ester (BÜLOW and BAUR), i, 1327.

1:4-Diphenylnaphthalene (FRANSSEN), i, 1146.
2:3-Diphenyl-α-naphthaquinone (WEISS and SONNENSCHEIN), i, 938.
2:3-Diphenyl-αβ-naphthaquinoxaline, 7-amino- (FINZI), i, 701.
2:3-Diphenyl-α-naphthol, and its acetyl derivative (WEISS and SONNENSCHEIN), i, 938.
2:4-Diphenyl-α-naphthol, and its acetyl derivative (FRANSSEN), i, 1147.
Diphenyl-α-naphthylcarbinol, anilide of (DILTHEY), i, 653.
Diphenyl-1′-naphthylcarbinol-4′:5′-dicarboxylic acid, and its anhydride (LORRIMAN), i, 673.
αβ-Diphenyl-β-naphthylethylamine, β-hydroxy- (MCKENZIE and DENNLER), i, 26.
Diphenyl-1′-naphthylmethane-2:4′:5′-tricarboxylic acid, and its anhydride (LORRIMAN), i, 672.
Diphenyl-α-naphthylmethyl acetate (SCHOEPFLE), i, 811.
bromide and methyl ether (DILTHEY), i, 652.
Diphenyl-α-naphthylmethylamine (SCHOEPFLE), i, 811.
and its salts (DILTHEY), i, 652.
Diphenyl-*p*-nitrobenzylamine (DESAI), i, 387.
4:5-Diphenyl-2-*m*-nitrophenylglyoxaline (TRÖGER and THOMAS), i, 979.
2:6-Diphenyl-1-*m*-nitrophenyl-4-*p*-hydroxyphenylpyridinium bromide (DILTHEY and SCHAEFER), i, 153.
3:5-Diphenyl-1-*p*-nitrophenylpyrazoline (v. AUWERS and KREUDER), i, 1455.
4:6-Diphenyl-3-*p*-nitrophenylpyridine, 2-bromo- and 2-hydroxy- (ALLEN), i, 964.
Diphenyl-*m*-nitrophenylpyridines, and their salts and derivatives (DILTHEY and RADMACHER), i, 1441.
Diphenyl-*m*-nitrophenylpyrylium hydroxides, and their salts (DILTHEY and RADMACHER), i, 1441.
Diphenylnitrosoamine, action of acids on (MARQUEYROL and MURAOUR), i, 387.
2:3-Diphenyloxazolidine (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1064.
Di-ε-phenyl-Δ$^{\beta\delta}$-pentadienyl*cyclo*hexanone (VORLÄNDER, FISCHER, and KUNZE), i, 1069.
N-Diphenylphenanthraphenaflavindine (KEHRMANN and SCHEDLER), i, 442.
Diphenylphenylacetylenylcarbinol. See Triphenylpropargyl alcohol.
Diphenyl-*p*-phenylenediamine, *di*bromo-*tetra*nitro- (SANÉ and JOSHI), i, 134.
Diphenyl-4′-phthalamic acid, 4-amino- (SHIMOMURA), i, 981.
Diphenylphthalide, *op-di*hydroxy-. See *iso*Phenolphthalein.
αγ-Diphenylpropan-αβ-dione, derivatives of (DUFRAISSE and MOUREU), i, 937.
αα-Diphenylpropan-α-ol, β-amino-, and its hydrochloride (THOMAS and BETTZIECHE), i, 250.
αδ-Diphenylpropan-α-ol, resolution and rotation of, and its salts and esters (HEWITT and KENYON), i, 915.
αβ-Diphenylpropionylglycine, ethyl ester (GRANÄCHER), i, 594.
αα′-Diphenyl-*n*-propyl alcohol, β-amino- (MCKENZIE and WILLS), i, 395.
***dl*-Diphenylpropylenediamine, resolution of, and its derivatives** (KIPPING and POPE), i, 22.
αα-Diphenyl-α-propylene oxide (LÉVY and LAGRAVE), i, 679.
5-Diphenyl*iso*propylidenehydrazine, β-2:4-*di*nitro- (NEBER, HARTUNG, and RUOPP), i, 1073.
Di-γ-phenylpropylmalonic acid, and its salts and esters (LEUCHS and SANDER), i, 1432.
1:4-Diphenyl-2-*iso*propyl-semicarbazide and -thiosemicarbazide (GOODWIN and BAILEY), i, 843.
Diphenylpyrazole methiodides (v. AUWERS and SCHMIDT), i, 586.
3:5-Diphenylpyrazoline, acetyl derivative (FREUDENBERG and STOLL), i, 70.
2:5-Diphenylpyrrole-3:4-dicarboxylic acid, and its salts and anhydride (SEKA), i, 1298.
Diphenylpyrrolidine, and its derivatives (RUPE and GISIGER), i, 1096.
Diphenylpyrroline, and its salts and derivatives (RUPE and GISIGER), i, 1096.
2:6-Diphenylpyrone *di*bromide (ARNDT, NACHTWEY, and PUSCH), i, 1308.
derivatives of (ARNDT, SCHOLZ, and NACHTWEY), i, 58.
2:6-Diphenylpyrone, 4-thio- (ARNDT, SCHOLZ, and NACHTWEY), i, 58.
1:4-Diphenylsemicarbazide, 4-2′:4′-*di*nitro- (KNIPHORST), i, 907.
Diphenylstibine oxide, *di*amino-, diacetyl derivative, and its salts (CHEMISCHE FABRIK VON HEYDEN and SCHMIDT), i, 87.
Diphenylstibinyl chloride (CHEMISCHE FABRIK VON HEYDEN and SCHMIDT), i, 87.

Diphenylstyrylcarbinol (STRAUS and EHRENSTEIN), i, 534.
Diphenylstyrylmethane, and its derivatives (ZIEGLER, RICHTER, and SCHNELL), i, 915.
Diphenylsuccinic acid, *m*-nitro-, and its nitrile (BRAND and LOEHR), i, 684.
Diphenylsuccinic acids, isomerism of (MADINAVEITIA and RIBAS), i, 671.
α- and β-Diphenylsuccinic acids, sodium salts, surface tension of solutions of (RIBAS), ii, 647.
Diphenylsulphone, *mm'-di*nitro-, electrolytic reduction of (LACROIX), i, 156.
3:3'-Diphenyl-3'':5'':3''':5'''-tetramethyl-3:3'-dicoumaranyl, 2:2'-*di*hydroxy- (LÖWENBEIN and FOLBERTH), i, 552.
***s*-Di-2-phenyl-1:2:3:4-tetrazolyl-5-carbamide** (STOLLÉ and ORTH), i, 1464.
***s*-Diphenylthiocarbamide**, *p:p'-di*amino-, *di*hydrochloride (CHRISTIANSEN and NORTON), i, 654.
Di-β-phenylthioldiethyl ether (CRETCHER, KOCH, and PITTENGER), i, 628.
5:7-Diphenylthiolphenthiazine, 5:7-*di-o*-amino-, and its derivatives (HODGSON), i, 596.
Diphenylthiophosphorhydrazide, and its benzylidene derivative (AUTENRIETH and MEYER), i, 990.
2:6-Diphenylthiopyranones, and their derivatives (ARNDT, NACHTWEY, and PUSCH), i, 1307.
2:6-Diphenyl-1-thiopyrone, and its salts and derivatives (ARNDT, NACHTWEY, and PUSCH), i, 1308.
2:6-Diphenyl*di*thiopyrone, and its oxime, and 3-chloro- (ARNDT, NACHTWEY, and PUSCH), i, 1312.
Diphenyl-*p*-tolylacethydroxamic acid, and its acetyl derivative (HURD and BROWNSTEIN), i, 661.
2:5-Diphenyl-3-*o*-tolyl-1-*p*-anisyl-1:2:3:6-tetrahydro-1:3:4-triazine (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
Diphenyl-*p*-tolylmethylcarbimide (HURD and BROWNSTEIN), i, 661.
Diphenyl-*p*-tolylmethylurethane (HURD and BROWNSTEIN), i, 661.
1:5-Diphenyl-1:2:4-triazole, 3-thiol- (FROMM and TRUKA), i, 704.
Diphenyl-*p*-trimethylammonium salts, and *p'*-nitro- (VORLÄNDER), i, 1257.
Diphenyltruxone (DE FAZI), i, 270.
Diphenylyl-*o*-arsenious chloride and oxide (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319.
***oo'*-Diphenylylenearsinic acid** (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319.
***oo'*-Diphenylylenechloroarsine** (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319.
***oo'*-Diphenylyleneiodoarsine** (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319.
***oo'*-Diphenylylenemethylarsine**, and its methiodide (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), i, 319.
2:3-Diphenylyl-αβ-naphthaquinoxaline, 7-amino- (FINZI), i, 701.
Diphospho-*l*-glyceric acid, and its barium salts (GREENWALD), i, 712.
4:4'-Diphthalimidodiphenylmethane, 3:3'-*di*nitro- (BUTLER and ADAMS), i, 1458.
Diphtheria, toxin and anatoxin of (RAMON), i, 339.
Dipicolinic acid, phenyl ester (MEYER), i, 836.
9:10-Dipiperidino-9:10-dihydroanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
2:6-Dipiperonyl*cyclo*hexanone (GARLAND and REID), i, 1281.
***m*-Diplosal**. See 3-Benzoyloxybenzoic acid, *m*-hydroxy-.
1:4-Dipropionylpiperazine, *di-α*-bromo- (ABDERHALDEN and ROSSNER), i, 975.
Di-β-propoxyethyl ether (CRETCHER and PITTENGER), i, 228.
2:5-Dipropylacetophenone, and its oxime (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
Di-*n*-propylallylsulphonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 496.
Dipropylammonium iodides (STEINKOPF and BESSARITSCH), i, 497.
***p*-Dipropylbenzene** (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
Dipropyldiallylammonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 495.
Di*iso*propylidenegalactosylamine, and its derivatives (FREUDENBERG and DOSER), i, 366.
Di*iso*propylidenemannosylamine, and its derivatives (FREUDENBERG and WOLF), i, 367.
Di*iso*propylidenemannosyldimethylamine (FREUDENBERG and WOLF), i, 368.
Di*iso*propylidenequinamide (KARRER, WIDMER, and RISO), i, 673.
1:2-Dipropylindazolium iodide (v. AUWERS and PFUHL), i, 1101.
Dipropyl*di*thiocarbamic acid, salts of (WHITBY and MATHESON), i, 644.
4:4'-Dipyridyl, 2:2'-*di*amino- (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 301.

4:4′-Dipyridylium dialkyl halides, molecular compounds of (EMMERT and ROH), i, 587.
Dipyrocatecholboric acid, and its salts (MEULENHOFF), i, 541.
Dipyrocatecholboric acid, *di*-4-chloro-, and its salts (BÖESEKEN and MIJS), i, 911.
Dipyrogallolboric acid, and its salts (MEULENHOFF), i, 541.
Dipyruvic ureide (DAVIDSON), i, 583; (DAVIDSON and JOHNSON), i, 584.
Dipyrylenes (ARNDT, SCHOLZ, and NACHTWEY), i, 57.
2:2′-Diquinolyl, homologues of (CONOLLY), i, 1329.
Disaccharides, synthesis and oxidation of (WREDE and ZIMMERMANN), i, 1384.
Disaccharide-glucoside, synthesis of a (HELFERICH and BECKER), i, 9.
Disaccharins (CHOUFOER), i, 896.
Di*iso*safrole, *hexa*chloro- (PUXEDDU), i, 1266.
Disalicylidene*cyclo*pentanone (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 268.
Disease, infectious, effect of adsorption compounds on (BERING), i, 858.
Disinfectants, phenol coefficient of (SCHNEIDER), i, 1006.
Dispersion formula for monatomic gases (HERZFELD and WOLF), ii, 182.
electrical, of liquids (COFMAN), ii, 1060.
rotatory (LIFSCHITZ), ii, 264.
density and absorption spectra of homologous compounds (KRETHLOW), ii, 1029.
of organic compounds (LOWRY and RICHARDS), ii, 265; (LOWRY and CUTTER), ii, 356; (CUTTER, BURGESS, and LOWRY), ii, 743; (RICHARDS and LOWRY), ii, 632, 934.
anomalous (BÜRKI), ii, 33; (HJALMAR and SIEGBAHN), ii, 92.
photometer. See Photometer.
Dispersoids, effect of added substances on the life of (V. WEIMARN), ii, 969.
Dissociation constants of dibasic acids (PAUL), ii, 116.
influence of valency direction on (SPIERS and THORPE), ii, 395.
of organic acids (AUERBACH and SMOLCZYK), ii, 118.
Distillation apparatus (PATTERSON), ii, 151; (WIGGERS), ii, 320; (JOHN and FISCHL), ii, 897.
for corrosive liquids (SATTLER and MORTIMER), ii, 589.
flask for corrosive liquids (BROWN), ii, 897.
Distillation apparatus, fractionating column (MYERS and JONES), ii, 428.
for mercury (WETZEL), ii, 589.
vacuum (ŠVÉDA), ii, 428.
Claisen vacuum (PETERS), ii, 589.
2:4-Distyrylbenzopyrylium chloride, 4′:4″:7-*tri*hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.
Distyrylchloroarsine, *αα′-di*chloro- (HUNT and TURNER), i, 844.
Distyryl ketone (*dibenzylideneacetone*), additive compounds of *α*-naphthol and resorcinol with (PFEIFFER, GOEBEL, and ANGERN), i, 271.
di- and *tetra*-bromides (PETRENKO-KRITSCHENKO and BUTMI DE KAZMAN), i, 1095.
Distyryl ketone, *m*-amino-, *per*chlorates of (PFEIFFER), i, 410.
di-p-hydroxy-, salts of (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 267.
Distyryl ketones (STRAUS and HEYN), i, 1430.
Distyryl ketones, *o*-hydroxy-, reactions of ethyl acetoacetate with (HEILBRON, FORSTER, and WHITWORTH), i, 1284.
2:6-Distyrylpyridine, and its derivatives (SHAW), i, 68.
Disuccinylbenzidine (SHIMOMURA), i, 982.
Di-4′-sulphobenzenedis-4-azodiphenyl-*βγ-di*amino-*n*-butanes, and their salts (MORGAN and SKINNER), i, 1192.
Disulphonamido-*p*-toluic acids (CHOUFOER), i, 896.
Disulphosalicylic acid, theobromine salt (KNOLL & Co.), i, 828.
Disulphoxides, constitution of (MILLER and SMILES), i, 391; (GILMAN, SMITH, and PARKER), i, 656.
syntheses of (GIBSON, MILLER, and SMILES), i, 1137.
Ditellurodiacetic acid (MORGAN and DREW), i, 530.
Ditelluromethane (MORGAN and DREW), i, 531.
Diterpenes (KONDAKOV and SAPRIKIN), i, 1163, 1292.
Di-1:1′-tetrahydrodinaphthyl, 1:1′-*di*hydroxy- (SCHROETER, ZADEK, and HOFFMANN), i, 677.
3:3′-Ditetrahydroindazyl, and its picrate (V. AUWERS, BAHR, and FRESE), i, 311.
Ditetrahydronaphthoylbenzenedicarboxylic acid (PHILIPPI, SEKA, and FUNKE), i, 556.
Dithiomolybdates. See under Molybdenum.
Dithymolisatin, oxidation of, in alkaline solution (CÂNDEA), i, 298.

Di-*p*-toluenylazosulphime. See 2:5-Di-*p*-tolyl-1:3:4-thiodiazole.
Ditoluidino-1:4-naphthaquinones (FRIES and BILLIG), i, 940.
***o*:*o*′-Ditoluoylbenzils** (BRAND, LUDWIG, and BERLIN), i, 904.
4:6-Di-*p*-toluoyl-1:3-dimethylbenzene (DE DIESBACH and STREBEL), i, 1436.
αβ-Ditoluoylethane, α-amino-, and *di*chloro derivatives (CONANT and LUTZ), i, 682.
αβ-Ditoluoylethylene, α-amino-, and αβ-*di*-4- and -6-chloro- (CONANT and LUTZ), i, 682.
1:8-Ditoluoylnaphthalene (MASON), i, 33.
3:9-Ditoluoylperylenes, 4:10-*di*chloro- (ZINKE, FUNKE, MATSCHER, WOLFBAUER, and LORBER), i, 1436.
Ditolyl. See Dimethyldiphenyl.
Ditolyl carbonates, 3:3′-*di*bromo-, and 3:3′-*di*nitro- (GRIFFITH), i, 135.
2:2′-*di*sulphoxide, 4:4′-*di*amino-, acetyl derivative (BERE and SMILES), i, 22.
Ditolylamines, *di*nitro- and *hexa*nitro-derivatives (BRADY, HEWETSON, and KLEIN), i, 16.
βγ-Di-*p*-tolylaminobutanes, *di*- and *tetra*-nitro- (MORGAN and HICKINBOTTOM), i, 156.
9:10-Di-*o*-tolyldihydroanthracene, 9:10-*di*hydroxy- (BRAND, LUDWIG, and BERLIN), i, 905.
3:6-Ditolyl-4:5-dimethylhexahydro-1:2-diazine (JASPERS), i, 936.
9:12-Ditolyl-$\Delta^{9:11}$-diphensuccindadienes (BRAND, LUDWIG, and BERLIN), i, 904.
9:12-Di-*m*-tolyldiphensuccindan-9:12-diol (BRAND, LUDWIG, and BERLIN), i, 904.
9:12-Ditolyldiphensuccindanes (BRAND and MÜHL), i, 903.
9:12-Ditolyl-Δ^{10}-diphensuccindenes (BRAND and MÜHL), i, 903.
Di-*o*-tolylhydrazo*dithio*dicarbonamide, derivatives of (FROMM and SZENDRÖ), i, 985.
2:7-Di-*p*-tolylideneaminophenanthraquinone (SIRCAR and GUPTA), i, 984.
Di-*p*-tolylmethane (SOMMELET), i, 803.
Ditolylnaphthalide (MASON), i, 33.
Di-*p*-tolyl-α-naphthylmethyl chloride and methyl ether (DILTHEY), i, 653.
2:3-Di-*p*-tolyloxazolidine (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1064.
***PP*′-Di-*p*-tolyloxy-*PP*′-dioxotetrahydrotetrazdiphosphinium** (AUTENRIETH and BÖLLI), i, 1469.
9:9-Di-*p*-tolyloxy-7-ethoxy-9:10-dihydroacridine, 3-amino- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
Di-*p*-tolyloxythiophosphoryl amide and chloride (AUTENRIETH and MEYER), i, 807.
Di-*o*-tolylphthalide (WEISS and KOREZYN), i, 560.
2:5-Di-*p*-tolyl-1:3:4-thiodiazole (ISHIKAWA), i, 1149.
3:6-Di(3′:4′:5′-trimethoxybenzyl)-2:5-diketopiperazine (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
3:6-Di(3′:4′:5′-trimethoxybenzylidene)-2:5-diketopiperazine (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
αβ-Di-(2:4:6-trimethylbenzoyl)-ethane, αβ-*di*bromo- (CONANT and LUTZ), i, 682.
Di-ααγ-triphenylallyl ether (ZIEGLER, GRABBE, and ULRICH), i, 132.
Ditriphenylmethylcarbamide (HELFERICH, MOOG, and JÜNGER), i, 791.
3:6-Di[triphenylmethyl]-1:4-dioxane, and 3:6-*di*chloro-, and their picrates (LEWIS, NIERENSTEIN, and RICH), i, 936.
Diuracil-4:4′-indigotin (DAVIDSON and BAUDISCH), i, 1188.
Diuresis, loss of bases in (HENDRIX and CALVIN), i, 1350.
Di*iso*valeryl, and its phenylhydrazone (TISTCHENKO), i, 776.
***s*-Divalerylhydrazine** (NAIK and PATEL), i, 121.
Divarinol, synthesis of (MAUTHNER), i, 25.
Divinylarsenious oxide and sulphide, ββ-*di*chloro- (LEWIS and STIEGLER), i, 1470.
Divinylarsine, bromo and chlorobromo derivatives (LEWIS and STIEGLER), i, 1470.
Divinyldimethylarsonium iodide, ββ-*di*chloro- (LEWIS and STIEGLER), i, 1470.
Divinylethylarsine, ββ-*di*chloro- (LEWIS and STIEGLER), i, 1470.
Divinylmethylarsine, ββ-*di*chloro- (LEWIS and STIEGLER), i, 1470.
Divinylmethylethylarsonium iodide, ββ-*di*chloro- (LEWIS and STIEGLER), i, 1470.
Divinyl-α-naphthylarsine, ββ-*di*chloro- (LEWIS and STIEGLER), i, 1470.
Dixanthyls, substituted (CONANT and SLOAN), i, 955.
Dixanthylen, preparation of, from xanthion (SCHÖNBERG and KRÜLL), i, 149.
Dixanthylhydrazone-glyoxylic acid (FOSSE and HIEULLE), i, 1130.

Dixylenol, derivatives of (FICHTER and MEYER), i, 381.
Di-*p*-xylyl 2:2′-*di*sulphide, 6:6′-*di*nitro- (CHOUFOER), i, 896.
Dixylyldihydroanthracenes, 9:10-*di*hydroxy- (BRAND, LUDWIG, and BERLIN), i, 905.
9:12-Di-3′:4′-xylyl-Δ$^{9:11}$-diphensuccindadiene (BRAND, LUDWIG, and BERLIN), i, 905.
9:12-Di-3′:4′-xylyldiphensuccindan-9:12-diol (BRAND, LUDWIG, and BERLIN), i, 905.
Dodecahydrodecacyclene (DZIEWOŃSKI and SUSZKO), i, 242.
Dodecaindene, iodo- (STOBBE and FÄRBER), i, 20.
Dodecamethylpentastannane (KRAUS and GREER), i, 1394.
Dodecaoxymethylene diacetate (STAUDINGER and LÜTHY), i, 361.
***n*-Dodecoylglycine**, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
Döppler effect (KREFFT), ii, 3, 78.
Dogs, blood of. See Blood.
Dog-fish. See *Acanthias vulgaris*.
Dolomite, crystal structure of (WYCKOFF and MERWIN), ii, 94.
hydrogen sulphide in (NENADKEVITSCH; VERNADSKI), ii, 997.
Driers for fatty oils (EIBNER and PALLAUF), i, 777.
Drugs, action of, on blood (ETS), i, 734.
undissociated, action of (KEESER), i, 101.
Drying, effect of, on composition of solids (SMITS), ii, 268.
on inner equilibria (SMITS), ii, 532.
intensive, effect of, on internal change (SMITS), ii, 116.
Duane effect (WOO; JAUNCEY), ii, 368.
Duckweeds, growth of, in mineral nutrient solutions (SAEGER), i, 755.
Dulcin. See *p*-Phenetylcarbamide.
"**Dulcitol**" as a sugar substitute (UGLOW), i, 1356.
Dumontite (SCHOEP), ii, 64.
***n*-Duotriacontanedicarboxylic acid**, and its ethyl ester (FAIRWEATHER), i, 1237.
Dussertite (BARTHOUX), ii, 235.
Dyads, tautomerism of (INGOLD), i, 779; (GRIFFITHS and INGOLD), i, 1190.
Dyes. See Colouring matters.
Dyeing (RUGGLI and FISCHLI), ii, 194.
theory of (ROSSI and BASINI), ii, 286.
of wool (SPEAKMAN), ii, 515.
Dynad, definition of (HERZOG and WEISENBERG), ii, 942.
***photo*Dypnopinacolins** (DELACRE), i, 681.

E.

Earth, composition of the crust of the (CLARKE and WASHINGTON), ii, 63; (WASHINGTON), ii, 234, 591; (VERNADSKI), ii, 996.
Earths, rare (DRIGGS and HOPKINS), ii, 463; (THOMPSON and KREMERS), ii, 580; (KREMERS and BEUKER), ii, 581; (KREMERS), ii, 588.
structure of (SWINNE), ii, 922.
properties and atomic structure of (v. HEVESY), ii, 938.
phosphorence of, in alkaline-earth phosphors (TOMASCHEK), ii, 12.
potentials of (NEUMANN and RICHTER), ii, 797.
magnetic properties of (CABRERA), ii, 358.
magnetic susceptibility of (MEYER), ii, 173.
magnetism of (HUND), ii, 1038.
paramagnetism of (CABRERA), ii, 618.
magnetisation numbers of (MEYER), ii, 944.
periodic position of (FRIEND), ii, 363.
solubilities of salts of (WILLIAMS, FOGG, and JAMES), ii, 504.
in alkaline earth phosphors (TOMASCHEK), ii, 354.
double carbonates of guanidine and (CANNERI), i, 524.
isomorphism of molybdates of, with those of lead and the alkaline earths (ZAMBONINI and LEVI), ii, 1133.
isomorphism of thallium compounds with those of (ZAMBONINI and CAROBBI), ii, 272.
double salts of alkali metals with (CAROBBI; ZAMBONINI and CAGLIOTI), ii, 315.
double sulphates of the alkali metals and (ZAMBONINI and CAROBBI; ZAMBONINI and CAGLIOTI), ii, 222.
complex sulphites and thiosulphites of (CANNERI and FERNANDES), ii, 888.
of the cerium group, chromates of (ZAMBONINI and CAROBBI), ii, 700.
electrometric precipitation of hydroxides of (BRITTON), ii, 1204.
separation of (PRANDTL), ii, 439; (KENDALL and CLARKE), ii, 977.
separation of, from uranium (CANNERI and FERNANDES), ii, 71.
Ebullioscopic apparatus (SWIENTOSLAWSKI and ROMER), ii, 319.
Ebullioscopy in mixed solvents (CARROLL, ROLLEFSON, and MATHEWS), ii, 858.

Ecgonine, acyl derivatives, and their aromatic esters (GRAY), i, 829.
Echinacea angustifolia, oil from (BISCHOFF), i, 760.
Echinococcal fluid (FLÖSSNER), i, 329.
Echitamine, and its salts and derivatives (GOODSON and GOODSON), i, 1166.
Efflorescence, capillarity and evaporation (SCHULTZE), ii, 287.
Eggs, antiscorbutic properties of (HAUGE and CARRICK), i, 1021.
hen's, chemical changes in, during incubation (MURRAY), i, 1353.
effect of calcium carbonate in diet on (BUCKNER, MARTIN, and PETER), i, 1497.
transference of calcium from shells of, during incubation (BUCKNER, MARTIN, and PETER), i, 1497.
changes in the nitrogen of, in incubation (AGGAZZOTTI), i, 457.
Egg-white as nitrogenous diet for rats (BOAS), i, 211.
Egg-yolk, fractionation of (RAKUZIN and PEKARSKAYA), i, 607.
***n*-Eicosoic acid** from Rambutan tallow (MORGAN and HOLMES), i, 777.
mixtures of stearic acid and (MORGAN and BOWEN), i, 114.
Eicosylamine hydrochloride (ADAM and DYER), i, 354.
Eicosylcarbamide (ADAM and DYER), i, 354.
Eka-cæsium (LORING and DRUCE), ii, 1124.
Eka-iodine (LORING and DRUCE), ii, 1124.
α-Elæostearic acid from China wood oil, constitution of (BÖESEKEN and RAVENSWAAY), i, 1129.
α- and β-Elæostearic acids, structure of, and glyceryl ester of the latter (BÖESEKEN and RAVENSWAAY), i, 507.
Elaidic acid, metallic salts (KLIMONE, v. MOLTINI, and BENEDIK), i, 506.
Elastic modulus of metals (WIDDER), ii, 1043.
Elasticity, relation between atomic concentration and (LASAREV), ii, 1134.
of colloidal solutions (SZEGVARI), ii, 111; (FREUNDLICH and SCHALEK), ii, 112.
Electrets, permanent (EGUCHI), ii, 462.
Electric arc, formation of compounds of metallic salts in (PECZALSKI and MOKRZYCKI), ii, 814.
with zinc anode, reduction with (STOCK, BRANDT, and FISCHER), ii, 570.
low voltage (BÄR), ii, 254.
Electric arc, low voltage, in potassium and sodium vapours (NEWMAN), ii, 450.
metallic, Stark effect in (NAGAOKA and SUGIURA), ii, 171.
rotating, between carbon electrodes (PAUTHENIER), ii, 725.
charge on microscopic particles (SEXL; DERIEUX), ii, 832.
discharge through gases, radiation in (THOMSON), ii, 461.
at low pressure (BANERJI), ii, 921.
in mixtures of inert gases (GÜNTHER-SCHULZE), ii, 341.
deficit of condensed substances obtained by (YOVITCHITCH), ii, 406.
corona, decomposition of carbon monoxide in (CRESPI and LUNT), ii, 1178.
equilibrium of carbon oxides in (WENDT and FARNSWORTH), ii, 1158.
creepage corona, active hydrogen in (ANDEREGG and HERR), ii, 1180.
electrodeless, in gases (LASAREV), ii, 1107.
glow, chemical reactions in (GÜNTHER-SCHULZE), ii, 553.
spectrophotometric studies of (SEELIGER and LINDOW), ii, 739.
streamer (LANGMUIR, FOUND, and DITTMER), ii, 341.
striated, light emission from (SEELIGER and ÔKUBO), ii, 78.
vacuum arc, processes in (GÜNTHER-SCHULZE), ii, 341, 342.
moment of dipolar molecules (EBERT), ii, 262.
Electrical conductivity, measurement of (LORENZ and KLAUER), ii, 541.
theory of (REDLICH; DAVIES), ii, 541.
determination of, in non-aqueous solutions (WALDEN, ULICH, and LAUN), ii, 208; (WALDEN and ULICH), ii, 209.
apparatus for direct reading of (TÖDT), ii, 898.
of alloys (BORELIUS), ii, 749.
of fused alloys (KREMANN, KIENZL, and MARKL; KREMANN, MÜLLER, and KIENZL; KREMANN, MÜLLER, and ORTNER), ii, 132.
of fused chlorides (BILTZ and KLEMM), ii, 127.
of chlorides in fused antimony trichloride (KLEMENSIEWICZ), ii, 40.
of metallic colloids (ANDRÉ), ii, 976.

Electrical conductivity of crystal hydrates (JAKUBSOHN and RABINOVITSCH), ii, 847.
of electrolytes (SCARPA), ii, 128; (DAVIES), ii, 871.
of strong electrolytes at infinite dilution (FERGUSON and VOGEL), ii, 1163.
of heated gases (GHOSH), ii, 461.
in hydrogen sulphide solutions (QUAM and WILKINSON), ii, 542.
of metals (SIMON), ii, 94.
and their place in the periodic system (EPSTEIN), ii, 623.
of salt vapours in flames (KALANDYK), ii, 208.
of solid salts at high temperatures (VAILLANT), ii, 40, 165.
of salts in methyl alcohol (FRAZER and HARTLEY), ii, 1163.
of aqueous solutions, effect of temperature on (WIEN), ii, 931.
of very dilute solutions (REMY), ii, 299.
of solid solutions (CUY), ii, 378.
use of, in quantitative biochemical analysis (DEMJANOVSKI), i, 1113.
heating apparatus, laboratory (ATEN), ii, 588.
double layer and polarisation (CLARK), ii, 673.
double refraction of gases (LYON), ii, 266.
of organic liquids (BECKER), ii, 755.
resistance, apparatus for measuring (ULICH), ii, 671.
of metals and alloys (WILLIAMS), ii, 753.
of wires, influence of occluded gases on (SEXL), ii, 642.
Electrification at liquid–gas interfaces (GILBERT and SHAW), ii, 795.
by friction between solids and gases (PERUCCA), ii, 1028.
Electrochemical reactions, periodic (HEDGES and MYERS), ii, 680.
Electrochemistry of non-aqueous solutions (MÜLLER, PINTER, and PRETT), ii, 882.
Electrodes, phenomena at, in electrolysis (CROWTHER and STEPHENSON), ii, 1167.
potentials of (HEYROVSKÝ), ii, 211, 404; (GERKE), ii, 403.
in relation to free energy of solvation (HEYROVSKÝ), ii, 544, 672; (KONTNÍKOVÁ and SHIKATA), ii, 672.
comparison of potential scales and (BIRCHER), ii, 711.
and polarisation (HOLLER), ii, 793.
Electrodes, vessel for use with solutions of different densities in (DAWSON), ii, 978.
for measurement of bioelectric potentials (LUND), ii, 897.
for hydrogen-ion concentration measurements (PARKER), ii, 899.
antimony, potential of, and its use in determining free acid (KOLTHOFF and HARTONG), ii, 325.
barium and strontium amalgam (DANNER), ii, 42.
chlorine and hydrogen, influence of high concentrations of hydrochloric acid and sodium chloride on (WILKE and KIENIGER), ii, 790.
copper oxide, Becquerel effect on (VAN DIJCK), ii, 1083.
gas, measurements with (WÖHLISCH), ii, 301.
glass (GROSS and HALPERN), ii, 405; (HOROVITZ), ii, 673.
use of, in biochemistry (KERRIDGE), i, 1201.
hydrogen (BAUMBERGER), ii, 236; (BEANS and HAMMETT), ii, 694; (VLÈS and VELLINGER), ii, 817.
potential of, in dilute hydrochloric acid (MICHAELIS and MIZUTANI), ii, 130.
for use in solid media (RADSIMOWSKA), i, 338.
hydrogen and oxygen, titration of dibasic acids and dextrose with (BRITTON), ii, 977.
mercurous chloride (EWING), ii, 571; (SCHOLLENBERGER), ii, 711; (PARKER and DANNERTH), ii, 712.
·1*N* and 3·5*N*, potential difference between (GJALDBAEK), ii, 1066.
mercury, mercurous chloride, potentials of (SCATCHARD), ii, 398.
micro-, for hydrogen ions (BODINE and FINK), i, 1201.
non-polarisable, for physiological experiments (STEVENS and KARRER), ii, 1194.
platinum, influence of light and *X*-rays on anodically polarised (GRUBE and BAUMEISTER), ii, 46.
and its alloys, action of, in electrometric analysis (VAN NAME and FENWICK), ii, 594.
polarised, effect of alternating currents on (GLASSTONE; ISGARISCHEV and BERKMANN), ii, 548.
porous, for oxidation or reduction (KNOBEL), ii, 1092.
quinhydrone (SCHAEFER and SCHMIDT), i, 611.
potential of, in methyl alcohol (EBERT), i, 230.

Electrodes, quinhydrone, thermodynamics of (SCHREINER), ii, 978.
measurement of hydrogen-ion concentration with (MISLOWITZER), i, 1483; (KOLTHOFF), ii, 671; (O'SULLIVAN), ii, 822.
use of, for hydrogen-ion determinations in soils (BRIOUX and PIEN), i, 1227.
determination of hydrogen ions in blood-serum with (CULLEN and BIILMANN), i, 1201.
electrometric analysis with (NIKLAS and HOCK), ii, 595.
silver, silver chloride, potential of (SCATCHARD), ii, 398.
solid, electrochemical reduction of (FISCHBECK), ii, 1166.
Electro-dialysis (FREUNDLICH and LOEB), i, 96; (DHÉRÉ), i, 199; (PAULI), ii, 319.
Electro-endosmosis (FAIRBROTHER and MASTIN), ii, 47, 302; (FAIRBROTHER), ii, 129.
through mammalian serous membranes (MUDD), i, 468, 1355.
Electro-kinetic phenomena (LABES), ii, 796.
potentials (FREUNDLICH and ETTISCH), ii, 873.
Electrolysers, diaphragm, and circulation of the alkali chlorides (GIORDANI), ii, 550, 551.
Electrolysis, electrode phenomena in (CROWTHER and STEPHENSON), ii, 1167.
streams of gas bubbles in (COEHN), ii, 1165.
of equimolar mixtures (SAXON), ii, 984.
in liquid ammonia, sulphur dioxide, and phosphorus oxychloride (CADY and TAFT), ii, 1073.
of fused chlorides, anode effect in (HEPPENSTALL and SHUTT), ii, 45.
with gas cathodes (GÜNTHER-SCHULZE), ii, 549.
at mercury dropping cathodes (HEYROVSKÝ), ii, 43, 133.
of molten alloys (KREMANN and GRUBER-REHENBURG), ii, 678; (KREMANN and BENDA; KREMANN and BAUKOVAC; KREMANN and DELLACHER), ii, 679.
Electrolytes, definition of (BLUM), ii, 402.
Debye theory of (GROSS and HALPERN), ii, 866.
absorption of light by solutions of (V. HALBAN), ii, 1083.
electrical conductivity of (DAVIES), ii, 871.
Electrolytes, conductivity and ionisation of (SCARPA), ii, 128.
potential difference between metals and (GUYOT), ii, 402.
transport of (MESTREZAT and GARREAU), ii, 543.
thermo-electricity of (THIELE), ii, 545.
specific heat of (ZWICKY), ii, 1138.
thermodynamics of solutions of (HARNED), ii, 977.
dielectric constants of solutions of (WALDEN, ULICH, and WERNER), ii, 773; (ULICH), ii, 964.
freezing points of dilute solutions of (HOVORKA and RODEBUSH), ii, 772.
adsorption of, by charcoal (KOLTHOFF), ii, 383.
coagulation of colloids by (GHOSH and DHAR), ii, 511; (RABINOVITSCH), ii, 778.
activity of (SCATCHARD), ii, 397, 398.
threads of (MANEGOLD), ii, 873.
in the organism (KRAUS, ZONDEK, ARNOLDI, and WOLLHEIM), i, 198.
binary, dissociation of (SEMENTSCHENKO), ii, 117.
colloidal. See Colloidal electrolytes.
solid, migration of ions in (LE BLANC and KRÖGER), ii, 41, 977; (TUBANDT and REINHOLD), ii, 300.
strong, theories of (VAN LAAR), ii, 152.
theory of aqueous solutions of (HÜCKEL), ii, 513.
equivalent conductivity of (FERGUSON and VOGEL), ii, 1163.
dilution laws and distribution coefficients for (GROSS and HALPERN), ii, 117.
interionic attraction in (PIKE and NONHEBEL), ii, 1061.
activity of (SCATCHARD), ii, 971.
anomalous behaviour of (FRIVOLD), ii, 396.
weak, ionisation of, in aqueous-alcoholic solutions (MIZUTANI), ii, 867.
dissociation of, in aqueous-alcoholic solutions (MICHAELIS and MIZUTANI), ii, 793.
Electrolytic dissociation (V. HALBAN), ii, 511; (HANTZSCH), ii, 512.
of dibasic acids (LARSSON), ii, 294.
of weak electrolytes in aqueous-alcoholic solutions (MICHAELIS and MIZUTANI), ii, 793.
of polyatomic salts (SASAKI), ii, 512.
gas. See Gas.
ions, theory of (LORENZ and KLAUER), ii, 541.

Electrolytic polarisation (GLASSTONE), ii, 979.
solution tension (HEYROVSKÝ), ii, 793.
Electromotive force (BUTLER), ii, 42.
theory of (DENINA), ii, 41.
of cells with liquid junctions (MICHAELIS and FUJITA), ii, 131.
See also Potential.
Electrons, theory of (REISSNER), ii, 349.
theories of emission of (REICHINSTEIN), i, 345.
emission of, by Röntgen rays (SEITZ), ii, 168.
at transition and melting points (GOETZ), ii, 459.
photo-emission of (BURT), ii, 617; (AUGER and PERRIN), ii, 618.
thermionic emission of (v. RASCHEVSKY), ii, 920.
and light-quantum (MILLIKAN), ii, 624.
deflexion of, by radiation (HULBURT and BREIT), ii, 252.
reflection of, in gases (BAERWALD), ii, 731.
ionisation by collision of (FOWLER), ii, 7.
heat of evaporation of (WEIGLE), ii, 253.
orbits of (HOYT), ii, 252.
statics of phenomena involving (ROLLA and PICCARDI), ii, 1018, 1105.
equilibria between atoms, radiation, and (DIRAC), ii, 6.
mechanics of (SCHAPOSCHNIKOV and FEDOROV), ii, 1105.
equation of motion of (PAGE), ii, 80.
vaporisation of (v. RASCHEVSKY), ii, 731.
diffusion of, against an electric field (COMPTON and ECKART), ii, 253.
divisibility of (MILLIKAN), ii, 832.
variation of mass of, with velocity (TRICKER), ii, 1021.
bombardment of metal surfaces by (FARNSWORTH), ii, 169.
displacement of, in organic compounds (LUCAS and JAMESON), i, 2.
free, motion of, in the field of plane electromagnetic waves (FRENKEL), ii, 477.
moving, magnetic field of (GUÉRY), ii, 252.
thermionic, distribution of velocities between (GERMER; DAVISSON), ii, 730.
Electrophoresis, influence of light on (BAUM and FRIEDERICH), ii, 220.
Element of atomic number zero and atomic weight unity (LORING), ii, 842.
Elements, structure of (BEDREAG), ii, 363.
artificial disintegration of (RUTHERFORD and CHADWICK), ii, 83.
colloidal. See Colloidal elements.
light, mass spectra of (COSTA), ii, 1021.
two new, of atomic numbers 43 and 75 (NODDACK, TACKE, and BERG), ii, 939.
of atomic numbers 75 and 93 (DRUCE), ii, 1124.
radioactive. See Radioactive elements.
rare, detection of (NOYES and BRAY), ii, 242.
quantitative determination of, in mixtures and compounds, by means of Röntgen rays (GLOCKER and FROHNMAYER), ii, 270.
Elemi resin, Manila, β-amyrin from (ROLLETT and SCHMIDT), i, 945.
Emanation capacity and surface variation of precipitates (HAHN), ii, 177.
Emetics, arsenical (DEBUCQUET), i, 1090.
Emetine, derivatives of (KELLER and BERNHARD), i, 1086.
Emodic acid, derivatives of (EDER and HAUSER), i, 562.
Emodin from *Frangula*, and its derivatives (EDER and HAUSER), i, 562, 563.
Emulsifiers, polar (HOLMES and WILLIAMS), ii, 1156.
Emulsin, hydrolysis and synthesis of glucosides by (JOSEPHSON), i, 1359, 1360.
primeverosidase and primeverase from (BRIDEL), i, 1438.
hydrolysis of salicin by (BERTRAND and COMPTON), i, 738.
action of, on polymethylated sugars (KUHN and SCHLUBACH), i, 863.
Emulsions (SEIFRIZ), ii, 663, 779, 864.
wedge theory of (HARKINS and BEEMAN), ii, 1154.
size of particles in (KRAEMER and STAMM), ii, 202; (STAMM and SVEDBERG), ii, 774; (STAMM), ii, 1153.
crystallisation of (FREUNDLICH and OPPENHEIMER), ii, 203.
soap films in (RIEMAN and VAN DER MEULEN), ii, 1148.
photographic. See Photographic.
reversible, viscosity of (JOSHI), ii, 776.
Enchelys, effect of cholesterol and oxycholesterol on growth of (ROBERTSON), i, 1119.
Energy, null point (BENNEWITZ), ii, 97.

Enneamminediaquotrihydroxydioltrichromium thiosulphate. See under Chromium.
Enols, synthesis of (WIELAND and DORRER), i, 779.
ferric chloride reaction and bromine addition of (KAUFMANN and RICHTER), i, 231.
Enolates, action of acyl or alkyl halides on (SCHEIBLER, MARBENKEL, and BASSANOV), i, 918.
action of carbon monoxide on (SCHEIBLER and SCHMIDT), i, 917.
Enterokinase (WILLSTÄTTER and WALDSCHMIDT-LEITZ), i, 741.
activation of pancreatic juice by (SETH), i, 202.
Entropy, definition of (SCHRÖDINGER; PLANCK), ii, 951.
calculation of (WEBB), ii, 867.
of condensed gases at absolute zero (EUCKEN and FRIED), ii, 97.
of ideal gases (v. HAUER), ii, 495; (DE KOLOSOVSKI), ii, 496.
of supercooled liquids at absolute zero (PAULING and TOLMAN), ii, 952.
Enzyme, Schardinger's, separation of, from milk (HOPKINS and DIXON), i, 1506.
Enzymes, preparation of (DE TONI), i, 200.
electrolysis of (MAIGNON), i, 1116.
dialysis of (WALTER), i, 1357.
temperature coefficients of activity of (COOK), i, 1358.
action of (v. EULER), i, 863.
action of accelerators for (JACOBY and ROSENFELD), i, 1010.
combination of auxoureases with (ROSENFELD), i, 336.
influence of light and iodides on (PINCUSSEN), i, 468; (PINCUSSEN and KLISSIUNIS), i, 469.
carbohydrate, of starch-free monocotyledons (CHAPMAN), i, 215.
of gum (FOWLER and MALANDKAR), i, 1437.
oxidising (ONSLOW and ROBINSON), i, 1010.
pancreatic (WILLSTÄTTER, WALDSCHMIDT-LEITZ, and HESSE), i, 736; (WILLSTÄTTER and WALDSCHMIDT-LEITZ; WILLSTÄTTER and PERSIEL), i, 741; (WILLSTÄTTER, HAUROWITZ, and PETROU), i, 742.
hydrolysis of esters by (RONA and SPEIDEL), i, 103.
of plants, specific action of (BLAGOVESCHENSKI and SOSSIEDOV), i, 1007; (BLAGOVESCHENSKI and BIELOZEVSKI), i, 1009.
Enzymes, protective, production of, in the organism (FRANZEN), i, 1007.
proteolytic, constitution and mode of action of (HUGOUNENQ and LOISELEUR), i, 1507.
nephelometry of (RONA and KLEINMANN), i, 1507.
of the skin (WOHLGEMUTH and KLOPSTOCK), i, 203.
Enzymes. See also:—
Amylase.
Arginase.
Auxourease.
Carboligase.
Carboxylase.
Catalase.
Co-zymase.
Diastase.
Emulsin.
Enterokinase.
Erepsin.
Gelatinase.
Gentiobiase.
Hexophosphatase.
Hydrogenase.
Hydroxynitrilase.
Invertase.
Laccase.
Linamarase.
Lipase.
Methylglyoxalase.
Nucleotidase.
Pepsin.
Peptase.
Peptidase.
Perhydridase.
Peroxydase.
Phosphatase.
Phosphatese.
Primeverase.
Primeverosidase.
Reductase.
Rennin.
Succinodehydrogenase.
Sulphatase.
Taka-diastase.
Taka-esterase.
Taka-rennin.
Trypsin.
Urease.
Xanthine oxydase.
Enzyme action (NOYES and FALK), i, 471; (FALK, NOYES, and SUGIURA), i, 471, 1360; (ARMSTRONG), i, 1009.
electromagnetic nature of (DITMAN), ii, 51.
effect of hydrogen-ion concentration on (BROWNLEE), i, 1007.
kinetics of (BRIGGS and HALDANE), i, 736.

Enzyme action, application of the mass action law to (HEDIN), i, 1212.
Ephedrine, action of (CHEN and SCHMIDT), i, 194.
ψ-Ephedrine, synthesis of (SPÄTH), i, 291; (SPÄTH and KOLLER), i, 1086.
***d*- and *l*-Epicatechins**, and their pentamethyl ethers (FREUDENBERG, FIKENTSCHER, HARDER, and SCHMIDT), i, 1165.
Epipactis palustris, loroglossin in (CHARAUX and DELAUNEY), i, 874.
Equation of state and molecular attraction (JÄRVINEN), ii, 865.
in relation to laws of thermodynamics (KOLTSCHIN), ii, 1061.
thermodynamic deductions for adsorbed substances (VOLMER), ii, 539.
for gases (HERZ), ii, 496.
with molecular association (LEDUC), ii, 376.
Gibbs', method of testing (FRUMKIN), ii, 856.
Rydberg-Ritz, constants of (JONES), ii, 2.
Volmer's, for adsorbed molecules (KAR), ii, 1045.
van der Waals' (BERGER), ii, 376; (VAN LAAR), ii, 495, 647.
Equilibria at high temperatures (PUSHIN and GREBENSHCHIKOV), ii, 38.
in binary organic systems (KITRAN), ii, 533.
effect of substitution on, in binary systems (KREMANN and DRAZIL), ii, 649; (KREMANN, ZECHNER, and WEBER; KREMANN, ZECHNER, and DRAZIL), ii, 650.
in ternary systems, graphic representation of (URAZOV), ii, 788.
of isomerides, influence of solvent on (VIXSEBOXSE), ii, 396.
at membranes (HÜCKEL), ii, 528, 668.
of liquids separated by a membrane (SCHREINEMAKERS), ii, 399.
in systems with semi-permeable membranes (SCHREINEMAKERS), ii, 538, 869, 975, 1062, 1063; (KAMEYAMA), ii, 1062.
in fused salts (JELLINEK and WOLFF), ii, 974; (JELLINEK), ii, 1160.
in-, uni-, and multi-variant (SCHREINEMAKERS), ii, 124, 402, 975.
Equilibrium, diagrams of (KURNAKOV), ii, 868.
Haber's, equation for (GILLESPIE), ii, 294.
Lewis' principle of (LEONTOVICZ), ii, 926.
Equilibrium constants in gaseous and liquid phases (SWIENTOSLAWSKI), ii, 204.
Erbium nitride (FRIEDERICH), ii, 374; (FRIEDERICH and SITTIG), ii, 420.
Erepsin, hydrolysis of peptides by (LEVENE and SIMMS), i, 473.
pancreatic (WALDSCHMIDT-LEITZ and HARTENECK), i, 1360.
Ergotinine, detection of (MAREEUW), ii, 1010.
Erucic acid, calcium salt (KLIMONE, v. MOLTINI, and BENEDIK), i, 506.
Erythrocyanic acid, and its salts (WIELAND), i, 1050.
Eserethole, *tri*nitro- (STEDMAN and BARGER), i, 293.
Eserine (*physostigmine*) (STEDMAN and BARGER), i, 292.
constitution of (SPÄTH and BRUNNER), i, 574.
tautomerism of, and its derivatives (POLONOVSKI and POLONOVSKI), i, 151.
detection of, colorimetrically (EKKERT), ii, 247.
Esters, preparation of (WAHL; KAILAN and RAUPENSTRAUCH), i, 880.
formation of, from aldehydes (CHILD and ADKINS), i, 632.
catalytic formation of (PEARCE and ALVARADO), ii, 381.
velocity of formation of (PETRENKO-KRITSCHENKO, BOGATSKY, and LUBMAN), ii, 556.
liquid-crystalline properties of acids, salts, and (VORLÄNDER), i, 267.
velocity of decomposition of (KARLSSON), ii, 877.
influence of the base on the velocity of saponification of, in methyl alcohol–water mixtures (JONES, MCCOMBIE, and SCARBOROUGH), ii, 137.
additive compounds of acids and (KENDALL and BOOGE; KENDALL and KING), ii, 972.
of dibasic acids, velocity of saponification of (BRÖNSTED and DELBANCO), ii, 684.
of strong acids, hydrolysis of (OLIVIER and BERGER), ii, 802.
aromatic, synthesis of (SODERMANN and JOHNSON), i, 814.
reaction of sodium with (BLICKE), i, 662.
Esterification (BHIDE and SUDBOROUGH), i, 1127.
viscosity and surface tension during (CAUQUIL), ii, 964.
Ethane, dielectric constant of (SMITH and ZAHN), ii, 1118.
Ethane, *hexa*bromo-, preparation of, electrolytically (DUSSOL), i, 350.
*s-di*bromo*di*thiocyano- and *tri*bromothiocyano- (SÖDERBÄCK), i, 899.

Ethane, *αβ-di*chloro-, action of sulphuric acid and its anhydride on (LEPOUSE), i, 784.
*tetra*chloro-, solubility of mixtures of naphthalene and (COHEN, DE MEESTER, and MOESVELD), ii, 190, 852.
halogen derivatives, reactivities of, with various reagents (PETRENKO-KRITSCHENKO, TALMUD, BUTMI-DE-KATZMAN, and GANDELMAN), ii, 802.
Ethanetetracarboxylic acid, potassium and sodium salts, and amino-, potassium salt (PHILIPPI, SEKA, HAGER, and LANDAU), i, 512.
Ethers, preparation of (SENDERENS), i, 113; (WUYTS), i, 501.
reaction of, with oxalic acid (WASER and SANDER), i, 536.
halogen-substituted, preparation of (FORAN), i, 774.
imino-aryl (CHAPMAN), i, 1400.
Etheserolene picrate (STEDMAN and BARGER), i, 293.
Ethoxide, sodium, action of nitric oxide on (HESS), i, 58; (TRAUBE), i, 110.
additive compounds of esters and (ADICKES), i, 1378.
Ethoxyacethydroxamic acid, and its potassium salt and derivatives (JONES and POWERS), i, 14.
2-Ethoxyacridine, 9-amino-, and its acetyl derivative (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 429.
7-Ethoxyacridines, *di*amino-, and chloroamino- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
4-Ethoxyallylbenzene, 3-hydroxy-, and its derivatives, preparation of, from safrole (KAFUKU), i, 1413.
β-*p*-Ethoxyanilinobutaldehyde diethylacetal (MASON), i, 834.
4-α-*p*-Ethoxyanilinoethylideneaminoantipyrine (WEIL), i, 157.
4-α-*p*-Ethoxyanilinoethylideneaminobenzoic acid, ethyl ester (WEIL), i, 157.
β-Ethoxybenzoic acids, *p*-bromo-, *p*-chloro-, *p*-iodo-, and *p*-hydroxy-, and their esters (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1423.
1:Ethoxy-2:3-benzoxazine (GRIFFITHS and INGOLD), i, 1190.
β-Ethoxybenzoyl chloride, *p*-chloro- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1423.
2-Ethoxybenzoylbenzoic acids (BRAND and KREY), i, 904.
5-Ethoxy-2-*iso*butyloxazole (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
γ-Ethoxybutyronitrile (BRECKPOT), i, 14.
α-Ethoxy-αβ-dibenzoylethylene (CONANT and LUTZ), i, 682.
5-Ethoxy-2:4-dimethyloxazole, and its picrate (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
4-Ethoxy-2:6-dimethylpyridine, 3-amino- and 3-nitro-, and their derivatives (COLLIE and BISHOP), i, 974.
5-Ethoxy-1:3-dimethyl-3-vinylindolin-2-one, and its picrate (STEDMAN and BAYER), i, 293.
7-Ethoxy-9:9-diphenoxy-9:10-dihydroacridine, 3-amino-, and its hydrochloride (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
α-Ethoxy-α-ethylbutyramide (NEWBERY), i, 376.
5-Ethoxy-3-ethyl-4:5-dihydrouric acid, 4-hydroxy- (BILTZ and PEUKERT), i, 1463.
2-Ethoxy-1-*cyclo*hexanol (KÖTZ and HOFFMANN), i, 910.
2-Ethoxy-1-*cyclo*hexanone (KÖTZ and HOFFMANN), i, 910.
2-Ethoxy-Δ^1-*cyclo*hexene, 1-cyano- (v. AUWERS, BAHR, and FRESE), i, 312.
7-Ethoxy-9-hydroxyethylaminoacridine, 3-amino-, and its hydrochloride (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
Ethoxylutidine. See Ethoxy-2:6-dimethylpyridine.
Ethoxymalonic acid, dissociation constant of (FAIRWEATHER), i, 631.
8-Ethoxy-2-*p*-methoxyphenylbenzopyrylium salts, 3-hydroxy- (RIDGWAY and ROBINSON), i, 55.
2-Ethoxy-5-methylacetophenone, and its derivatives (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
***m*- and *p*-Ethoxymethylbenzonitriles** (v. BRAUN and REICH), i, 1405.
Ethoxymethylbenzyl alcohols (v. BRAUN and REICH), i, 1405.
Ethoxymethylbenzyl bromides (v. BRAUN and REICH), i, 1405.
***m*- and *p*-Ethoxymethylbenzylamines**, and their salts (v. BRAUN and REICH), i, 1405.
Ethoxymethylcarbimide (JONES and POWERS), i, 14.
Ethoxymethylenemalonoguanidic acid ethyl ester (MITTER and PALIT), 1320.
ω-Ethoxymethylfurfuryl-bis-(3-acetyl-2:4-dimethylpyrryl)methane (FISCHER and HEYSE), i, 78.

ω-Ethoxymethylfurfuryl-bis-(3-carbethoxy-2:4-dimethylpyrrylmethane (Fischer and Heyse), i, 78.
m- and *p*-Ethoxymethylphenylacetonitriles (v. Braun and Reich), i, 1405.
β-Ethoxymethylphenylethylamines, and their salts (v. Braun and Reich), i, 1405.
5-Ethoxy-2-methyl-4-*iso*propyloxazole, and its picrate (Karrer, Miyamichi, Storm, and Widmer), i, 594.
4-Ethoxy-2-methylpyridine-6-carboxylic acid, and nitro-, and their derivatives (Collie and Bishop), i, 974.
3-Ethoxy-2-methylquinoline methiodide (Tröger and Dunker), i, 433.
N-Ethoxymethylsuccinimide (Cherbuliez and Sulzer), i, 1252.
Ethoxyoxalacetic acid, ethyl ester, thermal decomposition of (Watson), ii, 556.
8-Ethoxy-2-phenylbenzopyrylium ferrichloride, 3-chloro- (Ridgway and Robinson), i, 693.
3-*p*-Ethoxyphenylhydantoin (Coghill and Johnson), i, 582.
2-Ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylic acid, and its esters (Haerdi and Thorpe), i, 924.
1-*p*-Ethoxyphenylpyridinium salts (Vorländer), i, 1256.
1-*p*-Ethoxyphenyl-4-pyridone, and its *per*chlorate (Vorländer), i, 1257.
p-Ethoxyphenylthiohydantoic acid, potassium salt (Coghill and Johnson), i, 582.
Ethoxypicoline chloroplatinate (Collie and Bishop), i, 974.
4-Ethoxypropenylbenzene, 3-hydroxy-, and its derivatives, preparation of, from *iso*safrole (Kafuku), i, 1413.
β-Ethoxypropylbenzene, γ-bromo- (Schmidt, Bartholomé, and Asmas), i, 136.
4-Ethoxypropylbenzene, 3-hydroxy-, and its phenylurethane (Kafuku), i, 1413.
o-γ-Ethoxypropylbenzonitrile (v. Braun and Kaiser), i, 1414.
o-γ-Ethoxypropylbenzyl alcohol (v. Braun and Kaiser), i, 1414.
o-γ-Ethoxypropylbenzylamine, and its hydrochloride (v. Braun and Kaiser), i, 1414.
5-Ethoxy-2-*n*-propyl-4-*iso*butyloxazole (Karrer, Miyamichi, Storm, and Widmer), i, 594.
5-Ethoxy-4-*iso*propyl-2-*sec.*-butyloxazole (Karrer, Miyamichi, Storm, and Widmer), i, 594.
4-Ethoxypyridine, and its 2:6-dicarboxylic acid, and their salts (Collie and Bishop), i, 974.
2-Ethoxy-1:2:3:4-tetrahydronaphthalene (v. Braun and Kaiser), i, 1414.
5-Ethoxy-2-αββγ-tetramethyl*cyclo*pentyl-4-*iso*butyloxazole (Granacher), i, 594.
Ethyl alcohol, preparation of, by catalytic reduction of acetaldehyde (Negoshi), i, 1375.
by dehydration of rectified spirit with anhydrous calcium chloride (Sudborough and Ayyar), i, 1125.
formation of, by carbohydrate fermentation (Moskovits), i, 1511.
refractive index of (Bennett and Garratt), i, 498.
thermal properties of (Parks), ii, 491.
density and compressibility of solutions of (Richards and Chadwell), ii, 1049.
boiling points of mixtures of benzene, water, and (Barbaudy), ii, 766.
distillation of aqueous mixtures of (Öman and Gunnelius), ii, 953.
surface tension of (Ali), ii, 763.
equilibrium of *n*-butyl alcohol, water, and (Drouillon), ii, 651.
miscibility of *iso*butyl alcohol, water, and (Brun), ii, 769.
equilibrium of ethyl ether, water, and (Pease and Yung), ii, 37.
properties of mixtures of *iso*propyl alcohol and (Parks and Kelley), ii, 764.
apparatus for dehydration of (Guinot), i, 1229.
contraction of, on dilution (Foran), ii, 101.
effect of, in promoting swelling (Loebenstein), ii, 520.
polymerisation of, by heating with aluminium oxide and iron (Ipatiev and Kijukwin), i, 226.
catalytic dehydrogenation of, and its mixtures with amyl alcohol (Constable), ii, 881.
electrolytic chlorination of (Koidzumi), ii, 808.
catalysis by alumina of the reaction between ammonia and (Dorrell), ii, 1174.
effect and fate of, in the body (Southgate), i, 1503.
concentration in blood and excretion of, at high altitudes (Biehler), i, 1115.
tolerance of, in man (Hansen), i, 1503.
detection of ethyl phthalate in (Raleigh and Marie), ii, 605.
determination of (Astruc and Radet), ii, 443; (Martini and Nourisson), ii, 719; (Wimmer), ii, 1006.

Ethyl alcohol, determination of, volumetrically (JEROME and PEPIN), ii, 905.
determination of water in mixtures of ethyl ether, water, and (NEWMAN), ii, 156.
Ethyl alcohol, *tri*bromo-, behaviour of, in the body (ENDOH), i, 332.
β-bromo-β-nitro-, potassium salt, and β-chloro-β-bromo-β-nitro-, and chloronitro-, sodium salt (TRÉNEL and WILKENDORF), i, 112.
Ethyl orthocarbonate, hydrolysis of (SKRABAL and BALTADSCHIEVA), ii, 139.
β-benzoxy- and β-methoxy-ethyl ethers, β-chloro- (CRETCHER and PITTENGER), i, 228.
chloride, inhalation of (DAVIDSON), i, 1503.
determination of Avogadro's number from the diffusion of light by (DAURE), ii, 753.
Ethyl ether, density and compressibility of (RICHARDS and CHADWELL), ii, 1049.
viscosity of (CLARK), ii, 499.
mobilities of ions in (LOEB), ii, 832.
mutual solubilities of aqueous mixtures of (KABLUKOV and MALISCHEVA), ii, 768.
equilibrium of ethyl alcohol, water, and (PEASE and YUNG), ii, 37.
pharmacology of the oxidation products of (MITA), i, 195.
determination of water in mixtures of alcohol, water, and (NEWMAN), ii, 156.
Ethyl ether, ββ′-*di*chloro-, syntheses with (CRETCHER and PITTENGER), i, 228; (CRETCHER, KOCH, and PITTENGER), i, 627.
*octa*chloro- (GOLDSCHMIDT and SCHÜSSLER), i, 497.
Ethyl 3-hydroxy-5-methoxyphenyl ether, β-hydroxy-, and its phenylurethane (SONN and PATSCHKE), i, 282.
hypochlorite, and its reactions (TAYLOR, MCMILLAN, and GAMMAL), i, 501; (GOLDSCHMIDT, ENDRES, and DIRSCH), i, 502; (DURAND and NAVES), i, 1054, 1230.
p-methylaminophenyl sulphide, and its picrate (RIVIER and RICHARD), i, 1416.
sulphide, compounds of platinic chloride and (P. C. and K. C. B. RÂY), ii, 1121.
vinyl ether, β-chloro- (CRETCHER, KOCH, and PITTENGER), i, 628.
Ethylacetylurethane, β-chloro- and β-iodo- (CHINOIN FABRIK CHEMISCH-PHARMAZEUTISCHER PRODUKTE), i, 13.
Ethyl alkyl ketones, formation of, from vinylalkylcarbinols (DELABY and DUMOULIN), i, 632.
Ethylallylbarbituric acid (VOLWILER), i, 1174.
Ethylallyldi*iso*butylarsonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 496.
α-**Ethylallylbutyrophenone** (HALLER, BAUER, and RAMART), i, 261.
Ethylallylindazolium iodides (v. AUWERS and PFUHL), i, 1101.
9-**Ethylamino-7-ethoxyacridine**, 3-amino- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 430.
2-**Ethylamino-5-phenyl-1:3:4-thiodiazine** (BOSE), i, 1466.
2-**Ethylamino-*p*-toluic acid**, 3:5-*di*nitro- (GIUA and PETRONIO), i, 1397.
2-**Ethylamino-*p*-tolyl** hydrogen 4-thiosulphate, 5-amino- (HELLER), i, 315.
Ethylammonium chloroferrates (REMY and ROTHE), ii, 1089.
Ethylaniline, vapour pressure of (NELSON and WALES), ii, 494.
m-nitrobenzenesulphonamide (MARVEL, KINGSBURY, and SMITH), i, 245.
Ethylanthraquinones, fluoro- (QUAYLE and REID), i, 1289.
Ethylbenzene, *o*- and *p*-fluoro- (QUAYLE and REID), i, 1289.
Ethylbenzoyl-*o*-benzoic acids, chloro- and fluoro- (QUAYLE and REID), i, 1289.
4-**Ethyl-1-benzylglyoxaline**, 4-β-amino- (GERNGROSS), i, 441.
β-**Ethylbenzyltetrahydro*iso*quinoline**, *o*-amino-, and its derivatives (v. BRAUN and ZOBEL), i, 1456.
Ethyl-*p*-bromoaniline, *N*-hydroxy- (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1063.
β-**Ethylbutan-γ-ol**, δ-amino-, benzoyl derivative (THOMAS and BETTZIECHE), i, 250.
Ethylbutylals (ADAMS and ADKINS), i, 785.
Ethyl-*n*-butylhydroxylamines, and their hydrochlorides (NEUFFER and HOFFMAN), i, 891.
Ethyl-*n*-butylhydroxyurethanes (NEUFFER and HOFFMAN), i, 891.
α-**Ethylbutyronitrile**, α-bromo- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 377.

α-Ethylbutyrylcarbamide, α- and β-bromo-, action of alkali hydroxides on, and αβ-*di*bromo- (NEWBERY), i, 375.
ω′-Ethylcarbamide, ω-cyanoacetyl derivative (BILTZ and PEUKERT), i, 1462.
Ethylcarbonato-3-methyl-2-coumarilic acid (FRIES and NÖHREN), i, 954.
7-Ethylcarbonatocoumarin, and 3-bromo- (FRIES and NÖHREN), i, 954.
6-Ethylcarbonato-4-methylcoumarin (FRIES and NÖHREN), i, 954.
7-Ethylcarbonato-4-methylcoumarin, and 3-bromo- (FRIES and NÖHREN), i, 954.
β-Ethylcarbonatopropionic acid, ethyl ester and nitrile (CHAPMAN and STEPHEN), i, 669.
Ethyl-β-chloroethylmalonic acid, ethyl ester (VOORHEES and SKINNER), i, 837.
Ethyl-γ-chloropropylaniline (WOLFF), i, 428.
α-Ethylcrotonylcarbamide (NEWBERY), i, 375.
5-Ethyl-5-β-diethylaminoethylbarbituric acid, and its hydrochloride (VOORHEES and SKINNER), i, 837.
Ethyl-β-diethylaminoethylmalonic acid, ethyl ester (VOORHEES and SKINNER), i, 837.
Ethyldihydrochelerythrine (GADAMER and STICHEL), i, 287.
5-Ethyl-5-β-dimethylaminoethylbarbituric acid, and its hydrochloride (VOORHEES and SKINNER), i, 837.
Ethyl-β-dimethylaminoethylmalonic acid, ethyl ester (VOORHEES and SKINNER), i, 837.
4-Ethyl-1:6-dimethylmethylenedihydropyridine, and its derivatives (MUMM), i, 967.
4-Ethyl-1:6-dimethylpyridine-3:5-dicarboxylic acid, ethyl ester, methosulphate (MUMM), i, 964.
N-Ethyldiphenylamine-6-carboxylic acid, 2′-amino-, and its acetyl derivative and their silver salts, and 2′-nitro- (BURTON and GIBSON), i, 154.
Ethyldi-*n*-propylsulphonium iodide, and its compound with iodoform (STEINKOPF and BESSARITSCH), i, 496.
Ethylene, preparation of, and its dibromide (KESTING), i, 625.
dielectric constant of (SMITH and ZAHN), ii, 1118.
compressibility of (BATUECAS), ii, 497.
absorption of, by phosphoric acids (GILLIAN), i, 1373.
[illegible] of hydrogen bromide with (MAKIN and WRIGHT), ii, 214.
Ethylene, spontaneous combustion of, during preparation of ethylene dichloride (SHARMA), i, 109.
catalytic combination of hydrogen and, in presence of copper (PEASE and STEWART), ii, 691.
catalytic addition of halogen acids to (WIBAUT, DIEKMANN, and RUTGERS), i, 494.
as an anæsthetic (OBERHELMAN and DYNIEWICZ; LEAKE), i, 862; (DAVIDSON), i, 1503.
substituted derivatives, action of silicates on (LEBEDEV and FILONENKO), i, 225.
Ethylene, *di*bromonitro- (WIELAND and JUNG), i, 1374.
β-bromo-α-thiocyano-, and *s-di*thiocyano- (SÖDERBÄCK), i, 899.
*tetra*iodo-, preparation of, electrolytically (DUSSOL), i, 350.
Ethylenes, addition of azo compounds to (INGOLD and WEAVER), i, 580.
Ethylenes, *di*chloro-, ultra-violet absorption spectra of (ERRERA and HENRI), ii, 738.
Ethylenediamines, substituted, *N*-carboxylic esters of (HARTMANN and KÄGI), i, 1045.
Ethylene glycol, latent and specific heats of (PARKS and KELLEY), ii, 949.
Ethylene glycol, thio-, derivatives of (FROMM and JÖRG), i, 352.
*di*thio-, compounds of gold chloride with (RÂY,) ii, 184.
Ethylene oxide, Friedel and Crafts' synthesis with (SCHAARSCHMIDT, HERMANN, and SZEMZÖ), i, 1278.
action of aniline on (GABEL), i, 535.
pharmacological action of (STEHLE, BOURNE, and LOZINSKY), i, 333.
Ethylene oxides, substituted, isomerism of (TIFFENEAU, ORÉKHOV, and LÉVY), i, 544.
Ethylenic compounds, addition of iodine to (ANDRÉ and FRANÇOIS), i, 356.
isomeric, optical properties of (ERRERA and HENRI), ii, 1137.
aliphatic, rate of catalytic hydrogenation of (LEBEDEV, KOBLIANSKY, and YAKUBCHIK), i, 350.
aromatic, velocity of oxidation of (BÖESEKEN and BLUMBERGER), i, 240.
Ethylenic *per*oxides (FERNÁNDEZ), i, 769.
δ-Ethylhexenones, isomeric, and their semicarbazone (KON and LINSTEAD), i, 633.
1-Ethyl-2-*cyclo*hexyl*cyclo*hexane (GARLAND and REID), i, 1281.

1-Ethyl-2-*cyclo*hexyl*cyclo*hexanol (GARLAND and REID), i, 1281.
1-Ethyl-6-*cyclo*hexyl-Δ^1-*cyclo*hexene (GARLAND and REID), i, 1281.
1-Ethyl-2-*cyclo*hexylidene*cyclo*hexanol (GARLAND and REID), i, 1281.
1-Ethyl-6-*cyclo*hexylidene-Δ^1-*cyclo*hexene (GARLAND and REID), i, 1281.
Ethylideneaminosuccinic acid, *tri*chloro-, brucine salt (BERGMANN, EUSSLIN, and ZERVAS), i, 891.
Ethylideneaniline, bromonitro- (WIELAND and JUNG), i, 1374.
Ethylidenemalonic acid, ethyl ester, action of anilinophenylacetonitrile with (HIGGINBOTHAM, LAPWORTH, and SIMPSON), i, 35.
α-Ethylindole (VERLEY and BEDUWÉ), i, 578.
α-Ethylindole, 3-β-amino-, salts of (MAJIMA and HOSHINO), i, 1451.
3-β-amino-α-hydroxy-, synthesis of, and its picrate and acetyl derivatives, and 3-*p*-nitro-α-hydroxy-, acetyl derivative (MAJIMA and KOTAKE), i, 1450.
5-Ethylindolylhydantoin (ODDO), i, 298.
Ethylglycuronic acid, *tri*bromo- (ENDOH), i, 332.
γ-Ethyl-$\Delta^{\alpha\gamma}$-heptadiene (GRIGNARD and VESTERMAN), i, 514.
γ-Ethylheptane-βδ-diol (GRIGNARD and VESTERMAN), i, 513.
γ-Ethyl-Δ^{γ}-hepten-α-ol (GRIGNARD and VESTERMAN), i, 513.
β-Ethylhexaldehyde, γ-hydroxy-, preparation of (GRIGNARD and VESTERMAN), i, 513.
and its semicarbazone (GRIGNARD and DUBIEN), i, 111.
γ-Ethylhexan-δ-one, γ-hydroxy-, semicarbazone of (BRUYLANTS), i, 15.
2-Ethyl*cyclo*hexanone, 2-cyano-, and its derivatives (v. AUWERS, BAHR, and FRESE), i, 312.
β-Ethyl-Δ^{β}-hexenaldehyde (GRIGNARD and VESTERMAN), i, 513.
Ethylhydrobenzoins, optically active, dehydration of (MCKENZIE and ROGER), i, 25.
Ethylmaltoside, and its hepta-acetyl derivative (FREUDENBERG, v. HOCHSTETTER, and ENGELS), i, 635.
Ethylmercuric mercaptan (KOTEN and ADAMS), i, 236.
Ethylmercuric-2:4:6-*tri*nitrophenyl (KOTEN and ADAMS), i, 237.
ε-Ethylnonane (HESS and BAPPERT), i, 349.
δ-Ethyl-$\Delta^{\alpha\delta}$-octadiene (GRIGNARD and VESTERMAN), i, 514.
δ-Ethyloctane-γε-diol (GRIGNARD and VESTERMAN), i, 513.
δ-Ethyl-Δ^{δ}-octen-γ-ol (GRIGNARD and VESTERMAN), i, 514.
Ethyloleamide, *N*-amino- (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
γ-Ethylpentan-γ-ol, δ-amino-, benzoyl derivative (THOMAS and BETTZIECHE), i, 250.
β-Ethyl-Δα- and **-Δβ-pentenoic acids**, and their derivatives (KON and LINSTEAD), i, 506.
α-Ethyl-Δ^1-*cyclo*pentenylacetone, and its semicarbazone (KON and LINSTEAD), i, 633.
6-Ethylphenoxarsine, and its oxide (AESCHLIMANN), i, 706.
Ethylphenylacetic acids, amino-, and their derivatives (v. BRAUN and REICH), i, 1406.
2-Ethyl-3-phenyl*iso*indolinone, 3-hydroxy-2-β-bromo-, and its derivatives (KOHN and LAKNER), i, 1276.
Ethylphthalimide, β-bromo-, action of magnesium phenyl bromide on (KOHN and LAKNER), i, 1276.
Ethylpiperidinoethylcarbamic acid, phenyl ester, and its hydrochloride (HARTMANN and KÄGI), i, 1046.
Ethylpropylindazolium iodides (v. AUWERS and PFUHL), i, 1101.
2-Ethyl-1-propyl*cyclo*propane-1-glyoxylic acid, and its salts and oxime (FREJKA and BALAŠ), i, 669.
Ethylpyridine picrate (THOMS and BERGERHOFF), i, 575.
4-Ethylpyridine (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 431.
4-Ethylpyridine, 2-amino- (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 301.
1-Ethyl-2-pyridylnitroimine (TSCHITSCHIBABIN and MENSCHIKOV), i, 438.
2-Ethyl-4-quinazolone, 3-amino-, and its acetyl derivative (HELLER, GÖHRING, KLOSS, and KÖHLER), i, 1323.
Ethylstearamide, *N*-amino- (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
Ethylsulphonic acid, calcium salt (CHEMISCHE FABRIK VORM. SANDOZ), i, 1377.
2-Ethyl-1:2:3:4-tetrahydro*iso*quinoline, 2-β-hydroxy-, and its derivatives (SKITA and REITMEYER), i, 140.
α-Ethylthiocarbamides, αβ-hydroxy-, substituted, and their derivatives (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1063.

Ethyl*di*thiocarbomalic acids, and their salts (HOLMBERG), i, 1238.
α-Ethyl-αα′-thiodilactic acids, and their salts (AHLBERG), i, 885.
2-Ethylthiol-1:4-dimethylglyoxaline, and its salts (BURTLES, PYMAN, and ROYLANCE), i, 697.
2-Ethylthiol-1-phenylglyoxaline, and its picrate (BURTLES, PYMAN, and ROYLANCE), i, 697.
***o*-Ethylthiophenol**, and its salts and methyl ether (FRICKE and SPILKER), i, 249.
2-Ethylthiouracil xyloside and triacetylxyloside (LEVENE and SOBOTKA), i, 1464.
Ethyl-*m*-toluidine, 2:4- and 4:6-*di*nitro-, (GIUA and PETRONIO), i, 1397.
1-Ethyluracil, 6-amino-, 5:6-*di*amino-, and 5-nitroso-6-amino-, and its ammonium salt (BILTZ and PEUKERT), i, 1462.
1-Ethyluracil-5-ethylurethane, 6-amino- (BILTZ and PEUKERT), i, 1462.
Ethylurethane, β-chloro- and β-iodo- (CHINOIN FABRIK CHEMISCH-PHARMAZEUTISCHER PRODUKTE), i, 13.
*di*chloro- (MELDRUM and ALIMCHANDANI), i, 1273.
Ethylurethylane, *di*chloro- (MELDRUM and ALIMCHANDANI), i, 1273.
3-Ethyluric acid, derivatives of, and 8-thio- (BILTZ and PEUKERT), i, 1462.
3-Ethyl*iso*uric acid, 5(4)-chloro- (BILTZ and PEUKERT), i, 1463.
Ethylvinylcarbinol, resolution and rotation of, and its esters (KENYON and SNELLGROVE,), i, 771.
3-Ethylxanthine, and 8-chloro- (BILTZ and PEUKERT), i, 1463.
4-Ethyl-*o*-xylene, *tri*bromo- and *tri*nitro- (KRUBER), i, 1137.
4-Ethyl-*o*-xylenesulphonic acid, sodium salt and amide (KRUBER), i, 1138.
Ethyl-*p*-xylidine, *N*-hydroxy- (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1063.
Eucalyptus oil (PENFOLD and MORRISON), i, 688.
Sicilian (INVIDIATO), i, 688.
Eucalyptus piperita, oils from (PENFOLD and MORRISON), i, 688.
Eugenol, oxidation of, with ozone (VERLEY), i, 406.
derivatives of (THOMS and KEMP), i, 789.
iso-Eugenol, electrochemical oxidation of (FICHTER and CHRISTEN), i, [illegible].
Euphorbiaceæ, oil from species of [illegible], i, 760.
Evaporation, capillarity and efflorescence (SCHULTZE), ii, 287.
of liquids, kinetic theory of (MACLEOD), ii, 784.
Evaporation apparatus for bumping liquids (SCHMALFUSS and WERNER), ii, 590.
Excreta of rats, vitamin-*B* in (SALMON), i, 1516.
Expansion coefficient of liquids (SASLAWSKY), ii, 26.
Explosions, theory of waves of (JOUGUET), ii, 1169.
wave of maximum energy in the sound spectrum of (DUFOUR), ii, 183.
propagation of (LAFFITTE), ii, 135.
ionisation in propagation of (MALINOWSKI), ii, 182.
gaseous (BROWN, LESLIE, and HUNN), ii, 682.
of electrolytic gas, safety devices against (NORMANN), ii, 996.
of mixed gases (BERL and FISCHER), ii, 413; (WENDLANDT), ii, 801.
Explosives, theoretical force of (BURLOT; LE CHATELIER), ii, 558.
force and co-volume of (BURLOT), ii, 1170.
test for the stability of (POLLARD), ii, 803.
rates of explosion of (SMITH), ii, 804.
pressure developed by combustion of (BURLOT), ii, 1170.
equilibrium of gases in combustion of (YAMAGA), ii, 294.
determination of nitrogen in (MARQUEYROL, CHENEL, FRIEDERICH, FLORENTIN, KOEHLER, and LORIETTE), ii, 599.
Extraction, theory of (FRENC), ii, 506.
Extraction apparatus (PATTERSON), ii, 151.
for solids (SCHMALFUSS and WERNER), ii, 234; (STRUENSEE), ii, 996.
with heavy solvents (SCHMALFUSS and WERNER), ii, 897.
modified Soxhlet (KÖHLER), ii, 708.
Eye, chemical constitution of the lens of (LABBÉ and LAVAGNA), i, 724.
effect of magnesium on pressure in the (KANEKO), i, 333.

F.

Fæces, porphyrin of (PAPENDIECK), i, 98.
human, new porphyrin from (KÉMERI), i, 188.

Fæces, detection of bilirubin and urobilin in (ADLERSBERG and PORGES), i, 98.
determination of blood in (VAN ECK), i, 187.
determination of diastase in (FRANK and DOLESCHALL), i, 461.
determination of urobilin in (VAN SPENGLER; TERWEN), i, 1351.
determination of urobilinogen in (TERWEN), i, 1351.
Fagopyrum esculentum, water-soluble proteins of (SAWAMURA and SASAKI), i, 346.
Fats, Röntgen-ray structure of (TRILLAT), ii, 752.
chemistry of (MARGOSCHES, FRIEDMANN, and TSCHÖRNER), i, 629; (MARGOSCHES, FRIEDMANN, SCHEINOST, and TSCHÖRNER), i, 883.
spreading of lenses of, on water (CARY and RIDEAL), ii, 1046, 1047, 1048.
biochemistry of (BLOOR), i, 1346.
specific dynamic action of (MELLY and v. RÖTTH), i, 332.
autoxidation of (TSCHIRCH), i, 356.
oxidation of, by fungi (DERX), i, 1119.
influence of glutathione on oxidation of (HOPKINS), i, 1499.
animal, calorific value and analysis of (KRZYWANIK), i, 1496.
colloidal, interaction of colloidal lipoids with (EICHHOLTZ), i, 199.
human subcutaneous, fatty acid in (ECKSTEIN), i, 1203.
natural, fatty acid constituents of (ARMSTRONG, ALLAN, and MOORE), i, 353, 504.
in blood. See Blood.
determination of the acetyl value of (ANDRÉ), ii, 446.
determination of iodine-bromine numbers of (KÖPKE), ii, 246; (WINKLER), ii, 446, 1009.
determination of the iodine value of, by Winkler's method (SCHEFFLER), ii, 1008.
Fehling's solution (PÉGURIER), ii, 1208.
Fenchane-6-nitrosohydroxylamine, 6-cyano-, and its salts and derivatives (PASSERINI), i, 1290.
Fenchone cyanohydrin (PASSERINI), i, 1290.
α- and β-Fenchyl alcohols, and their esters, and their rotatory power (KENYON and PRISTON), i, 941.
Fermentation as a unimolecular reaction (AMBARD), ii, 1170.
action of iron salts in (HODEL and (NEUENSCHWANDER), i, 615.
in the organism, effect of quinine on (SMORODINCEV and ADOVA), i, 335.
Fermentation with zymase (JENSEN), i, 337.
alcoholic (LEBEDEV), i, 204; (KOSTYTSCHEV and FREY), i, 1214.
effect of radioactive substances on (KAYSER and DELAVAL), i, 1118.
action of ultra-violet light on (ROMOLO and REMO DE FAZI), i, 475.
relation of hydrogen-ion concentration to (HÄGGLUND and AUGUSTSON), i, 476.
bacterial (DE GRAAFF and LE FÈVRE), i, 478.
of carbohydrates by *Bacillus macerans* (MOSKOVITS), i, 1511.
lactic acid (VIRTANEN), i, 866.
in presence of mercuric chloride (LUMIÈRE), i, 108.
effect of insulin on (NOYES and ESTILL), i, 107.
Ferric hydroxide. See under Iron.
Ferric acid. See under Iron.
Ferricyanides, oxidation of iodides by (WAGNER), ii, 49.
Ferrite, crystalline structure of, in pearlite (BELAIEW), ii, 768.
Ferrocyanides, action of halogens on (DEL FRESNO), ii, 1192.
Ferromagnetism, theory of (MCKEEHAN), ii, 944.
Ferrous salts. See under Iron.
Fibres, vegetable, *d*-glycuronic acid in (SCHWALBE and FELDTMANN), i, 1238.
Fibrin, bromo- (VANDERVELDE), i, 707.
Fibrinogen, physical chemistry of (WÖHLISCH), i, 452.
precipitin reactions of (HEKTOEN and WELKER), i, 1487.
determination of (STARLINGER and HARTL), i, 716.
Ficus carica, enzymes in latex of (VISCO), i, 471.
Films, formation of, on water (CARY and RIDEAL), ii, 1046, 1047, 1048.
on water, structure of (ADAM), ii, 195.
between liquids (HARKINS and MCLAUGHLIN), ii, 771.
surface tension of, in relation to temperature (MARCELIN and DELAPLACE), ii, 772.
thin, molecular structure of (ADAM and DYER), ii, 32.
unimolecular, electrical properties of (FRUMKIN), ii, 873.
uni- and multi-molecular, on surfaces of liquids (HARKINS and MORGAN), ii, 1148.
Filters, air-binding of (BAYLIS), ii, 980.
light, for interferometry (FERGUSON), ii, 839.

Filters, glass, in qualitative analysis (HÜTTIG and NETTE), ii, 431.
Filter-paper, adsorption of acids by (MOKRUSCHIN), ii, 957.
Filter tube, Shimer (BINGHAM), ii, 432.
Filtration, effect of, on potential (RIETY), ii, 796.
Filtration apparatus, glass (PRAUSNITZ), ii, 996.
Fisetin, fluorescence of, in ultra-violet light (MEUNIER and BONNET), ii, 738.
Fisetinidin chloride trimethyl ether (PRATT and ROBINSON), i, 422.
Fish, arsenic in (COX), ii, 157.
blood-sugar in, under various conditions (MCCORMICK and MACLEOD), i, 856.
insulin from (MCCORMICK and NOBLE; MCCORMICK), i, 754.
marine, effect of hydrogen-ion concentration on oxygen consumption in (PEREIRA), i, 177.
Pacific Coast, analyses of (DILL), i, 855.
Flame, propagation of, in inflammable mixtures of gases (WHITE), ii, 48, 408, 553.
propagation of, in closed vessels (ELLIS and WHEELER), ii, 554.
photography of (ELLIS and ROBINSON), ii, 590.
effect of nitrogen dilution on speed of (ELLIS), ii, 135.
Flames, mobility of negative ions in (WATT), ii, 170.
monochromatic illuminator for (GORDON), ii, 588.
ozone in (v. WARTENBURG), ii, 147; (RIESENFELD), ii, 148.
chlor- and oxy-hydrogen, conductivity of salt vapours in (KALANDYK), ii, 208.
non-luminous, radiation from (HASLAM, LOVELL, and HUNNEMAN), ii, 475.
oxy-hydrogen, hydrogen peroxide in (RIESENFELD), ii, 148.
Flavan, 4:5:7:3′:4′-*penta*hydroxy-, and its acetyl derivative (NIERENSTEIN), i, 280.
Flavanols, influence of methoxy-substitution on the absorption spectra of (TASAKI), i, 1444.
Flavanone, 2′-chloro-, and *iso*nitroso- (RÖTHLISBERGER), i, 572.
Flavanones, bromothio- (ARNDT), i, 1309.
Flavone glucosides, absorption spectra of (TASAKI), i, 1445.
Flavones, 3-bromo-1-thio-, and thio- (ARNDT), i, 1309.
Flavone, 2′-chloro- (RÖTHLISBERGER), i, 571.
*di*thio- (ARNDT, NACHTWEY, and PUSCH), i, 1312.
Flavones, influence of methoxy-substitution on the absorption spectra of (TASAKI), i, 1444, 1445.
physiology and distribution of, in plants (KLEIN and WERNER), i, 870.
***iso*Flavone group**, syntheses in the (BAKER and ROBINSON), i, 1299.
Flavonol, 2′-chloro-, and its acetyl derivative (RÖTHLISBERGER), i, 571.
Flavouring materials in foods (BYLSMA), i, 1356.
Flavylium chloride, 3:5:7:3′-*tetra*hydroxy- (PRATT and ROBINSON), i, 826.
Flesh, pigments of (SCHUMM), i, 341, 721, 1347.
Flint, formation of, in chalk (LINCK and BECKER), ii, 820.
Flores primulæ, green colouring matter from (v. LINGELSHEIM), i, 601.
Florida earth, polymerisation of unsaturated compounds by means of (LEBEDEV and FILONENKO), i, 225.
Florideæ, pigments of (RODIO), i, 621.
Flowers, extraction of essential oils from (v. SODEN), i, 1123.
Fluoflavine, 3-*mono*- and 3:8-*di*-chloro- (KEHRMANN and BENER), i, 443.
Fluoran derivatives, structure of (DOMINIKIEWICZ), i, 53.
Fluorene, 2:7-*di*amino-, derivatives of (STOLLÉ and ADAM), i, 1469.
2:7:9:9-*tetra*hydroxy-, true nature of (COURTOT and GEOFFROY), i, 926.
Fluorenes, 9-amino-, stereoisomeric, and their derivatives (KUHN and JACOB), i, 1260, 1404.
Fluorenone hydrate, constitution of (KUHN and WASSERMANN), i, 1398.
Fluorenone, 2-hydroxy-, and 2:7-*di*hydroxy-, and its derivatives (COURTOT and GEOFFROY), i, 927.
Fluorenylamines, synthesis of (COURTOT and PETITCOLAS), i, 247.
Fluorenyl-α-naphthylamine (COURTOT and PETITCOLAS), i, 248.
Fluorenyl-*p*-nitroaniline (COURTOT and PETITCOLAS), i, 248.
Fluorenyl-*p*-tolylamine (COURTOT and PETITCOLAS), i, 248.
Fluoresceïn, phosphorescence of (BATSCHA), ii, 181.
halogen derivatives, absorption and stability to hydrogen ions of (HOLMES), i, 255.
determination of, spectro-photometrically (FABRE), ii, 1212.
Fluoresceins (DUTT and THORPE), i, 140.

Fluorescence (PERRIN and CHOUCROUN), ii, 55; (BAYLÉ, FABRE, and GEORGE), ii, 260.
theory of diminution of (PREDVODITELEV), ii, 738.
and chemical change (CHAKRAVARTI and DHAR), ii, 629.
of colouring matters, extinction of (VAVILOV), ii, 474.
and phosphorescence (LEVSCHIN), ii, 629.
polarisation of (LEVSCHIN), ii, 13, 1117; (VAVILOV), ii, 739; (WEIGERT and KÄPPLER), ii, 1026.
of liquids (ASTERBLUM), ii, 1026.
of organic compounds (MOIR), ii, 261.
as a test of purity (BAYLÉ and FABRE), ii, 604.
of photographic developers (A. and L. LUMIÈRE and SEYEWETZ), i, 1060.
of solids (GYEMANT), ii, 13.
polarised, theory of (PERRIN), ii, 353.
resonance (STUART; HANLE), ii, 629.
Fluorescent substances, absorption of light by (PIENKOVSKI and JABLONSKI), ii, 1031.
Fluorescin, detection of hydrocyanic acid with (STAMM), ii, 76.
Fluorides. See under Fluorine.
Fluorindines, and their salts (KEHRMANN and SCHEDLER), i, 441.
Fluorine, potential of (NEUMANN and RICHTER), ii, 1164.
Hydrofluoric acid, ionisation potential of (GLOCKLER), ii, 1105.
freezing point of (ANTHONY and HUDLESTON), ii, 644.
determination of (WAETZEL), ii, 433.
Fluorides, effect of, in diet on the teeth of rats (MCCOLLUM, SIMMONDS, BECKER, and BUNTING), i, 861.
determination of, electrometrically (TREADWELL), ii, 1197.
Fluorine detection and determination:—
detection and determination of (MEYER and SCHULZ), ii, 598.
Fluorite, effect of heating on the cathode luminescence of (WICK and GLEASON), ii, 262.
Fluorocyclene, and its bromo and nitro derivatives (DZIEWOŃSKI and SUSZKO), i, 649.
Fluorocyclenetetrasulphonic acid, *di*-hydroxy-, and its salts (DZIEWOŃSKI and SUSZKO), i, 650.
α-9-Fluoryldimethylcarbamide (KUHN and JACOB), i, 1261.
Foaming power, relation between surface tension and (OSTWALD and STEINER), ii, 771.
Fœtus, calcium in the growing (SCHMITZ), i, 456.
rôle of calcium and potassium in development of the (MENDELÉEV and GLOSSE), i, 456.
Foods, perfumes and flavourings in (BYLSMA), i, 1356.
marine, iodine in (TRESSLER and WELLS), i, 183.
Foodstuffs, specific dynamic action of (MIYAZAKI and ABELIN; ABELIN), i, 332.
effect of treatment of, on value for growth (MILLER and YATES), i, 108.
iodine in (v. FELLENBERG), i, 347.
Formaldehyde (*methanal*; *formalin*), formation of, by action of ultra-violet light on carbon dioxide and water (PORTER and RAMSPERGER), ii, 573.
preparation of, with lead carbonate containing radium-Ω (STOLFI), ii, 1111.
heat of formation of (v. WARTENBERG and LERNER-STEINBERG), ii, 745.
vapour pressure and chemical constant of (MALI and GHOSH), i, 116.
vapour pressure of aqueous solutions of (BLAIR and LEDBURY), ii, 400.
effect of inorganic substances on polymerisation of (K. and W. F. SHORT), i, 232.
catalytic decomposition of (E. and F. MÜLLER), ii, 414.
electrolytic oxidation of (DEL FRESNO), ii, 267.
kinetics of the oxidation reduction of (v. EULER and LÖVGREN), ii, 981.
oxidation of *p*-phenylenediamine with hydrogen peroxide and (LÄTT), i, 1457.
condensations of (SCHMALFUSS and KALLE), i, 116.
condensation of, with *p*-aminoacetophenone (GRABOWSKA and WEIL), i, 260.
compounds of glycine with (BERGMANN and ENSSLIN), i, 1046.
action of, on methyluracils (SCHMEDES), i, 435.
action of, on proteins of serum (HENLEY), i, 716.
detection of (GHIGLIOTTO), ii, 445.
determination of (SCHULEK), ii, 606; (ROMEO), ii, 1009.

Formazylbenzene, *di*bromo- (CHATTAWAY and WALKER), i, 930.
Formic acid, oxidation of, by hydrogen peroxide (HATCHER and HOLDEN), ii, 684.
action of, on sesquiterpenes (ROBERTSON, KERR, and HENDERSON), i, 1293.
calcium salt, crystal structure of (YARDLEY), ii, 430.
chromous salts (TRAUBE, BURMEISTER, and STAHN), ii, 990.
sodium salt, reduction of mercuric bromide by (BOURION and PICARD), ii, 685.
alkoxymethyl esters (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
*iso*bornyl ester (PARISELLE), ii, 742.
methyl ester, pyrogenic decomposition of (MULLER and PEYTRAL), i, 353; (PEYTRAL), i, 777.
determination of, in blood and urine (DE EDS), i, 713.
Formic acid, chloro-, esters of (OESPER, BROKER, and COOK), i, 1408.
cyano-, ethyl ester, action of magnesium ethyl bromide on (BRUYLANTS), i, 15.
methyl ester, action of, on magnesium organic compounds (FINGER and GAUL), i, 1431.
α-Formiminoacetoacetic acid, ethyl ester hydrochloride (WIELAND and DORER), i, 779.
Formyltrimethylarsonium bromide, action of, on the nervous system (HUNT and RENSHAW), i, 861.
Fourmarierite, constitution of (SCHOEP), ii, 236.
Foyaite (MOLENGRAAFF and HALL), ii, 64.
Fractionation apparatus, Fischer vacuum (SATTLER), ii, 708.
Free-space numbers (LORENZ and HERZ), ii, 185.
Freezing points of binary mixtures (ANDREWS, KOHMAN, and JOHNSTON), ii, 852.
of dilute solutions of electrolytes (HOVORKA and RODEBUSH), ii, 772.
Friction, internal, of aqueous solutions, effect of temperature on (WIEN), ii, 931.
internal relative (HERZ and WEGNER), ii, 482.
Friedel and Crafts reaction with aldehydes and ethylene oxide (SCHAARSCHMIDT; HERMANN and SZEMZI), i, 1278.
[illegible] of. See Heart.
[illegible] of. See Metabolism.
[illegible] of. See Nerves.
Fruits, constituents of (TUTIN), i, 1028.
effect of storage on the anti-scurvy value of (DELF), i, 484.
lead salts of acids from (AUERBACH and WEBER), i, 1130.
Fruit juices, detection of lactic acid in (BORNTRÄGER), ii, 1007.
Fulgides, halochromism of (DIETZEL and NATON), i, 1067.
Fulminic acid (WIELAND), i, 1048.
Fumaric acid, formation of, from maleic acid (TERRY and EICHELBERGER), i, 780.
crystal structure of (YARDLEY), ii, 1126.
halogenation of (TERRY and EICHELBERGER), i, 631.
oxidation of, to tartaric acid (MILAS and TERRY), i, 780.
sodium salt, surface tension of solutions of (RIBAS), ii, 647.
Fungi, staling of cultures of (PRATT), i, 106.
calcium requirements of algæ and (LOEW), i, 1218.
colouring matters of (KÖGL and POSTOWSKY), i, 50, 1033, 1439; (KÖGL and v. TAEUFFENBACH), i, 1440.
ammonium acetate as source of nitrogen for (BACH), i, 216.
oxidation of fats by (DERX), i, 1119.
excretion of urea by (IVANOV), i, 344, 746.
higher (GUTH), i, 1247.
Furfuraldehyde, molecular association of (GETMAN), ii, 511.
condensation of, with aliphatic aldehydes (IVANOV), i, 421.
Furfuraldoxime *N*-phenyl ether (BAMBERGER), i, 142.
Furfuroic acid, furfuryl ester (ZANETTI), i, 953.
Furfuryl alcohol, esters of (ZANETTI), i, 567.
Furfuryl bromide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
Furfurylbenzylmethylamine, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
α-Furfurylideneacetaldehyde, and its derivatives (IVANOV), i, 421.
Furfurylideneaminoacetic acid, barium salt (BERGMANN, ENSSLIN, and ZERVAS), i, 891.
α-Furfurylidenebutaldehyde, and its derivatives (IVANOV), i, 421.
α-Furfurylideneheptaldehyde, and its derivatives (IVANOV), i, 421.
2-Furfurylidene-6-*cyclo*hexylidene*cyclo*hexanone (GARLAND and REID), i, 1281.

α-Furfurylidenepropaldehyde, and its derivatives (IVANOV), i, 421.
α-Furfurylidenevaleraldehyde, and its derivatives (IVANOV), i, 421.
Furnace, micro-, for high magnifications (ROBERTS and STADNICHENKO), ii, 707.
Furoxane, *di*cyano- (WIELAND), i, 1050.
Furyl-*n*-butylcarbinol (PIERCE and ADAMS), i, 824.
4-Furyl-1:6-dimethylmethylenedihydropyridine, and its salts and derivatives (MUMM), i, 965.
4-Furyl-1:6-dimethylpyridine-3:5-dicarboxylic acid, ethyl ester, methosulphate (MUMM), i, 964.
4-Furyl-1:6-dimethyl-α-pyridone (MUMM), i, 966.
Furyltrichloromethylcarbinol (HOWARD), i, 557.
4-Furyl-1:2:6-trimethyldihydropyridine-3:5-dicarboxylic acids, ethyl esters (MUMM), i, 966.
Fusain, oxidation of (TIDESWELL and WHEELER), i, 373.
Fusarium, development of pigment in species of (SIDERIS), i, 1363.
Fusarium cromyophthoron, effect of hydrogen-ion concentration on the pectinase in (SIDERIS), i, 1117.
Fusarium lini, growth of (ANDERSON), i, 1522.

G.

*iso*Gadoleic acid, and its silver salt (HASHIMOTO), i, 1234.
Galactosamic acid, and its phenylhydrazide (FREUDENBERG and DOSER), i, 367.
Galactose, fermentation of, by yeast (v. EULER and NILSSON), i, 866; (v. EULER and LÖVGREN), i, 1214; (ABDERHALDEN), i, 1362.
metabolism of. See Metabolism.
*iso*propylidene ether (LEVENE and MEYER), i, 1043.
Galactosemonodiphenylmethanedimethyldihydrazone (v. BRAUN and BAYER), i, 1383.
Galactosidoglucose (SCHLUBACH and RAUCHENBERGER), i, 888.
Galanginidin chloride 3-methyl ether (MALKIN and ROBINSON), i, 827.
iodide (PRATT and ROBINSON), i, 826.
Galangin 3-methyl ether, and its diacetyl derivative (KALFF and ROBINSON), i, 423.
trimethyl ether (TASAKI), i, 1444.
Galegine, and its salts (MÜLLER), i, 1520.
Gallium (FRICKE and BLENCKE) ii, 417.
spark spectrum of (WEINBERG), ii, 249; (CARROLL), ii, 1101.
hydroxide (FRICKE), ii, 578.
Gallium separation:—
separation of (SWIFT), ii, 71.
separation of, from aluminium and iron (FRICKE), ii, 717.
Gallotannin (NIERENSTEIN, SPIERS, and HATCHER), i, 692.
action of yeast on (NIERENSTEIN, SPIERS, and HADLEY), i, 951.
Gamboge suspensions, specific volume of (COUTTS), ii, 290.
Gardenia turgida, *d*-mannitol from (FORSTER and RAO), i, 1295.
Gas, electrolytic, safety devices against explosions of (NORMANN), ii, 996.
Gases, electrical double refraction of (LYON), ii, 266.
reflection of electrons in (BAERWALD), ii, 731.
diamagnetism of (GLASER), ii, 82.
dispersion formula for (HERZFELD and WOLF), ii, 182, 478.
electric discharge through (THOMSON), ii, 461; (BANERJI), ii, 921.
electrodeless discharge in (LASAREV), ii, 1107.
apparatus for studying passage of sparks through (JOLIBOIS), ii, 1194.
electrification by friction between solids and (PERUCCA), ii, 1028.
ionisation in (LANGMUIR and JONES), ii, 169.
by impacts (COMPTON and VAN VOORHIS; TUVE; TATE; WALDIE), ii, 1106.
by slow-moving electrons (JESSE), ii, 919.
by α-particles (GURNEY), ii, 256.
ionisation and vapour pressure of (BECKER), ii, 342.
mobility of ions in (LOEB), ii, 461; (WAHLIN), ii, 615.
liberation of ions in reactions between (BREWER), ii, 919.
critical potentials of (DYMOND), ii, 6, 253.
potential at interfaces of liquids with (FRUMKIN), ii, 873.
attachment of electrons to molecules of (BAILEY), ii, 1019.
molecular heats of, at low temperatures (GIACOMINI), ii, 757.
specific heat of (BRINKWORTH), ii, 373.
thermodynamic temperature of (WERTHEIMER), ii, 784.
thermal study of systems of (PICCARDI), ii, 540.

Gases, kinetic theory of (DE KOLOSOVSKI), ii, 531.
in relation to the quantum theory (SCHIDLOF), ii, 843.
equations for (LEDUC), ii, 376; (HERZ), ii, 496.
mass-action law for (GILLESPIE), ii, 532.
quantum methods applied to (PLANCK; EINSTEIN), ii, 495.
compressibility of (BATUECAS; BATUECAS, MAVERICK, and SCHLATTER), ii, 497.
apparatus for measuring (HOWARTH and BURT), ii, 818.
effect of molecular attraction on the pressure of (MAASS and MORRISON), ii, 500.
pressure and radiation in relation to intermolecular forces in (STEWART), ii, 1112.
equilibrium pressure of hydrates of (TAMMANN and KRIGE), ii, 869.
temperature and pressure variations in (MANDELL and WEST), ii, 99.
sudden cooling of, in a quartz tube (STAUDINGER and KREIS), ii, 316.
critical pressure of, under varying specific heat (WALKER), ii, 100.
cryoscopy of solutions of, in various solvents (GARELLI), ii, 1151.
density and diffusion of (BARUS), ii, 25.
viscosity of, at low temperatures (GÜNTHER), ii, 100.
interfacial properties of, in contact with liquids (GILBERT and SHAW), ii, 795.
movements of small bubbles of, in water (McTAGGART), ii, 509.
determination of solubility of, in liquids (MANCHOT), ii, 233.
supersaturation of, in liquids (KENRICK, WISMER, and WYATT), ii, 105; (WYATT), ii, 504.
absorption coefficients for electrons in (BRODE), ii, 617.
adsorption of (URBAIN; MUNRO and JOHNSON; RAY), ii, 191; (RUFF and HOHLFELD), ii, 192.
equation for (BANGHAM and SEVER), ii, 507.
influence of rate of flow on (LORENZ and WIEDBRAUCK), ii, 507.
by cellulose nitrate (COSTA), ii, 956.
by graphite (LOWRY and MORGAN), ii, 1051.
by liquids (LEWIS and WHITMAN), ii, 106.
by titania (BISCHOFF and ADKINS), ii, 563.
by [illegible] (WHITMAN and DAVIS; ii, 106.
Gases, catalysis of, with metals of the platinum group (DUPARC, WENGER, and URFER), ii, 1177.
combustion of, with air (WHITE), ii, 48.
at high pressures (BONE, NEWITT, and TOWNEND), ii, 800.
electrification in (DICKINSON), ii, 740.
electrical ignition of (MORGAN), ii, 553.
influence of vapours on the inflammability of mixtures of air and (JORISSEN and MEUWISSEN), ii, 307; (JORISSEN and VAN DER VALK), ii, 874; (JORISSEN and ONGKIEHONG), ii, 875.
explosion of (BROWN, LESLIE, and HUNN), ii, 682.
apparatus for preparation of constant mixtures of air and (YANT and FREY), ii, 897.
circulation pump for (MENZIES, COLLINS, and TYSON), ii, 818.
complex, band spectra of crystals and of (KAHLER), ii, 626.
condensed, entropy of, at absolute zero (EUCKEN and FRIED), ii, 97.
degraded, theory of (BENNEWITZ), ii, 97.
diatomic, molecular heat and thermal conductivity of (SCHREINER), ii, 97.
heated, electrical conductivity of (GHOSH), ii, 461.
ideal, quantum theory of (EINSTEIN), ii, 624.
entropy of (v. HAUER), ii, 495; (DE KOLOSOVSKI), ii, 496.
inert, cathode fall, current density, and dark space in mixtures of (GÜNTHER-SCHULZE), ii, 341.
calculation of atomic frequencies of (NARBUTT), ii, 948.
rarity of (ASTON), ii, 18.
inflammable, propagation of flame in mixtures of air and (WHITE), ii, 408.
mixed, action of radiation on (SENFTLEBEN), ii, 883.
mobility of ions in (LOEB and ASHLEY), ii, 7.
adsorption and evolution of, from charcoal (LORENZ and WIEDBRAUCK), ii, 382.
effect of infra-red radiation on combustion of (DAVID), ii, 980.
ignition of (WHEELER), ii, 408; (WHITE), ii, 553.
explosion of (BERL and FISCHER), ii, 413; (WENDLANDT), ii, 135, 801.

Gases, mixed, separation of, by diffusion (LORENZ and MAGNUS), ii, 501.
thermal separation of (ELLIOTT and MASSON), ii, 763.
monatomic, chemical constants of (SIMON), ii, 98.
perfect, definition of (CLARK), ii, 495.
rare, in the atmosphere (JEFFREYS), ii, 83.
from volcanoes (PIUTTI and BOGGIO-LERA), ii, 1092.
excitation and ionisation potentials of (HERTZ and KLOPPERS), ii, 342.
ionisation and resonance potentials of (HERTZ and KLOPPERS), ii, 730.
relationship of pseudo- and non-electrolytes to (CARLSOHN), ii, 1044.
determination of, by combustion with cupric oxide (SVÉDA), ii, 432.
Gas absorption apparatus (PATTERSON), ii, 151.
Geissler bulbs (ODDO), ii, 431.
pipette (JONES), ii, 431.
Gas analysis, absorption of oxygen in (FIESER), ii, 238.
by combustion with copper oxide (SVÉDA), ii, 154.
automatic (LÖWENSTEIN), ii, 154.
Gas analysis apparatus (MURRAY), ii, 593; (CHAMBERLAIN and NEWITT), ii, 710.
burette for electrochemical processes (JOFINOV), ii, 898.
burette for micro-analysis (CHRISTIANSEN), ii, 593.
multiple (DIRKEN), ii, 154.
for determining oxygen and carbon dioxide in respiratory exchange (HAGEDORN), i, 177.
Gas circulation apparatus (PEARSON and THOMAS), ii, 1194.
Gas interferometer, Haber-Löwe, calibration of (WERNER), ii, 1091.
Gastric juice, action of, on chlorophyll (KORTSCHAGIN), i, 200.
determination of the free acid of (SAHLI), i, 458.
determination of pepsin in (ROSTOCK), i, 1009; (BOAS; HIRSCH-MAMROTH and RINDFLEISCH), i, 1213.
Gastropods, intestines of. See Intestines.
Gaucher's disease, kerasin in (LIEB), i, 189.
Gay-Lussac's law applied to liquid films (MARCELIN; DELAPLACE), ii, 772.
Gehlenite, constitution of (GOSSNER), ii, 821.
Gein, extraction and properties of (HÉRISSEY and CHEYMOL), i, 487.
sugars from (HÉRISSEY and CHEYMOL), i, 1383.
Gels, character and electrical properties of (MICHAUD), ii, 292.
velocity of hydrogen ions in (ISGARISCHEV and POMERANZEVA), ii, 300.
kinetics of swelling and shrinking of (LIEPATOV), ii, 685, 968.
replacement of (LINDGREN), ii, 392.
adsorption and osmosis in (TOMITA), ii, 202.
effect of hydrogen-ion concentration on adsorption of colouring matters by (MARKER and GORDON), ii, 31.
rhythmic precipitation in (FISCHER), ii, 853.
microtome for cutting sections of (FRICKE), ii, 965.
deformed, effect of drying on (HATSCHEK), ii, 667.
dyed, birefringency and dichroism in (NEUBERT), ii, 201.
Gelatin (KINGSTON and SCHRYVER), i, 89; (KNAGGS and SCHRYVER; MANNING), i, 90; (HORNE), i, 91.
optical activity of (KRAEMER and FANSELOW), ii, 1057.
ultra-violet absorption spectrum of (BAKER and DAVIDSON), ii, 838.
rotatory power of (VLÈS and VELLINGER), ii, 292.
effect of hydrogen-ion concentration on (BOGUE and O'CONNELL), ii, 744.
photographically active (SHEPPARD), ii, 966.
second isoelectric point of (KRAEMER), ii, 519.
density and hydration of (SVEDBERG), ii, 202.
swelling of, in carbamide (CHODAT), ii, 521.
effect of hydrogen-ion concentration on (OSTWALD, KUHN, and BÖHME), ii, 777.
elasticity of (SCARTH), ii, 862.
electro-ultrafiltration of (BECHHOLD and ROSENBERG), ii, 668.
surface tension of (JOHLIN), ii, 388; (JOHNSTON and PEARD), ii, 659; (DE CARO), ii, 857.
distribution of hydrogen ions between water and (SHUKOV and STSCHOUKAREV), ii, 386.
influence of, on transport numbers (SCATCHARD), ii, 41.
gels, elasticity of (POOLE; SAUER and KINKEL), ii, 519.

Gelatin gels, formation of Liesegang's rings in (SCOTT-BLAIR), ii, 519.
action of sodium aminoacetate and tungstate on, in test tubes (STUCKERT), ii, 1061.
solutions, plasticity and structure of (SHEPPARD; BOGUE), ii, 1058.
influence of neutral salts on (STIASNY and GUPTA), i, 707; ii, 392; (STIASNY, GUPTA, and TRESSER), ii, 393; (STIASNY), ii, 524; (CSAPÓ), ii, 1157.
action of bile salts on (STUCKERT), ii, 392.
protective action of, on gold sols (TARTAR and LORAH), ii, 864.
action of ferric hydroxide sols on aqueous solutions of (WINTGEN and MEYER), ii, 524.
precipitation of, by tannin (SMORODINCEV and ADOVA), i, 847.
titration curve of (ATKIN and DOUGLAS), ii, 113.
sensitisation of Congo-red by (ETTISCH and RUNGE), ii, 864.
Gelatinase, formation of, by *Proteus* (CLARK and MERRILL), i, 1511.
Geneserine hydriodide (POLONOVSKI and POLONOVSKI), i, 960.
ψ-Geneserolimethine hydrochloride (POLONOVSKI and POLONOVSKI), i, 293.
ψ-Geneseroline (POLONOVSKI and POLONOVSKI), i, 293.
Gentiacaulin, hydrolysis of (BRIDEL), i, 336.
Gentiobiase (KARRER and STAUB), i, 336.
Geodia gigas, constituents of (ACKERMANN, HOLTZ, and REINWEIN), i, 720.
Geraniol, hydrogenation of (GRIGNARD and ESCOURROU), i, 772.
Germane. See Germanium hydride.
Germanibenzoic acid. See Phenylgermanoic acid.
Germanite, analysis of (KRIESEL), ii, 153.
Germanium (DENNIS and HANCE), i, 798; (COREY, LAUBENGAYER, and DENNIS), ii, 493; (DENNIS and LAUBENGAYER), ii, 888.
spectrum of (LUNT), ii, 611.
ultra-violet spark spectrum of (IRETON), ii, 453.
Germanium hydride, physical properties of (COREY, LAUBENGAYER, and DENNIS), ii, 493.
vapour pressure of (SCHENCK and IMKER), ii, 279.
pharmacology of (PANETH and JOACHIMOGLU), i, 197.
dioxide, allotropy of (MÜLLER and BLANK), ii, 145.
Germanium organic compounds, aromatic (MORGAN and DREW), i, 1197.
tetra-alkyls and -aryls, and tetraethoxide (TABERN, ORNDORFF, and DENNIS), i, 1108.
tetraethyl (DENNIS and HANCE), i, 798.
Germanium determination:—
determination of (JOHNSON and DENNIS), ii, 442.
Germicides, properties of, in relation to structure (ISHIWARA), i, 750.
determination of power of (COOPER, WOODHOUSE, and FORSTNER), i, 749.
Geum urbanum, extraction of gein from (HÉRISSEY and CHEYMOL), i, 487.
Gitogenin in digitalis leaves (WINDAUS and BRUNKEN), i, 873.
Gitonin, and its degradation products (WINDAUS and LINSERT), i, 1438.
Gitoxigenin, and its derivatives (WINDAUS and SCHWARTE), i, 1295.
Gitoxin from digitalis leaves (WINDAUS and SCHWARTE), i, 1295.
Glands, physiology of (ASHER and TAKAHASHI), i, 331.
sexual, influence of, on metabolism (KORENCHEVSKY and CARR), i, 1513.
Glands. See also Prostate, Salivary, Thymus, and Thyroid glands.
Glass, structure of (SELJAKOV, STRUTINSKI, and KRASNIKOV), ii, 849.
constitution and properties of (TURNER), ii, 1144; (ECKERT; TOOL and HILL; TAMMANN), ii, 1145.
physico-chemical composition of (BARY), ii, 380.
transparency of, in the infra-red (LIANA), ii, 357.
allotropy of (LE CHATELIER), ii, 190.
viscosity of (STOTT, IRVINE, and TURNER), ii, 503; (STOTT), ii, 1146.
influence of composition on (ENGLISH), ii, 954.
viscosity and allotropy of (LE CHATELIER), ii, 280.
fusibility and viscosity of (LACRENIER and GILARD), ii, 379.
vapour pressure of the volatile constituents of (BORN), ii, 785.
sorption of ammonia and carbon dioxide by (BANGHAM and BURT), ii, 284.
adsorption of colouring matters by (SCHELTE), ii, 286.
adsorption of water on (MCHAFFIE and LENHER), ii, 854.
adsorption of water and vapours by (D'HUART; BANGHAM and BURT), ii, 657.

Glass, effect of chemicals on (KLAMER), ii, 427.
blue, substitute for (MEYER), ii, 601.
germanium (DENNIS and LAUBENGAYER), ii, 888.
molten, surface tension of (LACRENIER and GILARD), ii, 387.
silicate, physical properties of (TURNER), ii, 767.
soda–lime–silica, *X*-ray diffraction of (WYCKOFF and MOREY), ii, 1146.
Gliadin (TROENSEGAARD and FISCHER), i, 848.
isoelectric point of (TAGUE), ii, 391.
from wheat, preparation and properties of (DILL and ALSBERG), i, 1478.
Globulins, physical chemistry of (ADOLF), ii, 199.
heat changes of (ADOLF), ii, 520.
increase in, in blood, from decomposition of hæmoglobin (REYMANN), i, 1345.
Glucal, change of, to deoxyglucose, in rabbits (KONDO), i, 99.
Gluconic acid, formation of, by moulds (BUTKEWITSCH), i, 341.
p-toluenesulphonylhydrazide (FREUDENBERG and BLÜMMEL), i, 52.
Glucoproteins, carbohydrate group in (IZUMI), i, 848.
Glucosamine, configuration of (KARRER, SCHNIDER, and SMIRNOV), i, 418.
β-Glucosan from cellulose (VENN), i, 887.
Glucosans (KERB and KERB-ETZDORF), i, 233.
***d*-Glucose**. See Dextrose.
β-Glucose, mutarotation of (LUNDSGAARD and HOLBØLL), i, 1494.
α- and β-Glucosephosphoric acids, barium salts (KOMATSU and NODZU), i, 515.
Glucoside, $C_{21}H_{36}O_{12}$, from *Helianthus annuus* (SANDO), i, 1026.
Glucosides (CRAIK and MACBETH), i, 1296.
enzymic hydrolysis of (JOSEPHSON), i, 1359, 1360.
synthesis of alkyl derivatives of (PACSU), i, 515.
standardisation of, affecting the heart (LENDLE), i, 1501.
Glucosides. See also:—
Acaciin.
Amygdalin.
Arbutin.
Asperuloside.
Datiscin.
Diosmin.
Gein.
Gitogenin.
Gitonin.
Gitoxin.
Glucosides. See also:—
Helicin.
Irisin.
Loroglossin.
β-Methylglucoside.
Rhamnicoside.
Salicin.
6(?)-[β-*d*-Glucosido]-α-methyl-*d*-glucoside (HELFERICH and BECKER), i, 11.
Glue, velocity of swelling of (LIEPATOV), ii, 968.
electro-ultrafiltration of (BECHHOLD and ROSENBERG), ii, 668.
Glutaconic acids (GOSS, INGOLD, and THORPE), i, 549.
Glutardialdoxime, preparation of (SHAW), i, 299.
Glutarylfluorescein (DUTT and THORPE), i, 141.
Glutarylrhodamine (DUTT and THORPE), i, 142.
Glutathione (TUNNICLIFFE), i, 752; (HOPKINS), i, 1499.
synthesis of (STEWART and TUNNICLIFFE), i, 795.
effect of traces of iron on oxidation of (HARRISON), i, 13.
in mammalian blood (HOLDEN), i, 1484.
as an arsenic receptor in mammals (VOEGTLIN, DYER, and LEONARD), i, 861.
Glutelin from cotton seed (JONES and CSONKA), i, 1225.
Gluten, constituents of (DILL), i, 622.
Gluten, bromo- (VANDEVELDE), i, 91.
Glutenin, isoelectric point of (TAGUE), ii, 391.
Glyceraldehyde, oxidation of, in presence of phosphates (WIND), ii, 1174.
***l*-Glyceric acid**, effect of substitution on rotation of (GREENWALD), i, 712.
Glycerol, preparation of, by fermentation (TOMODA), i, 227.
heat of solution of (DE KOLOSOVSKI), ii, 540.
and its aqueous solutions, freezing points of (LANE), ii, 971.
dielectric constant and absorption coefficient of (BOCK), ii, 355.
vapour pressure of aqueous solutions of (IYER and USHER), ii, 501.
and its mixtures with sodium chloride (CARR, TOWNSEND, and BADGER), ii, 767.
purification of (KAILAN and OBIGI), i, 501.
assimilation of, by oxygenated yeast (MARIAN), i, 105.
acetylenic derivatives of (LESPIEAU), i, 1375.
metabolism of. See Metabolism.

Glycerol, detection of, colorimetrically (KOLTHOFF), ii, 161.
Glycine, possible synthesis of, in the body (SWANSON), i, 465.
relation between taste and concentration of solutions of (HEIDUSCHKA and KOMM), i, 1389.
compounds of formaldehyde with (BERGMANN and ENSSLIN), i, 1046.
Glycine-*p*-allyloxyanilide (KARRER, DIECHMANN, and HAEBLER), i, 243.
Glycine anhydride, oxidation of, by hydrogen peroxide (LÜDTKE), i, 837.
diacetyl and dibenzoyl derivatives (ABDERHALDEN and KOMM), i, 175.
Glycogen (LING, NANJI, and PATON), i, 1011.
molecular weight of (FEARON), i, 12.
heat of combustion of (MEIER and MEYERHOF), ii, 92.
effect of sugar administration on formation of (GIGON), i, 192.
hexose from fermentation of (v. EULER and NILSSON), i, 1496.
hydrolysis of, by salivary diastase (PAECHTNER), i, 738.
content of, in liver (FRANK and FÖRSTER), i, 1503.
decomposition of, in muscle (WEBER), i, 1004.
determination of small quantities of (DE JONGH and PLANELLES), i, 325.
Glycol, $C_{29}H_{60}O_2$, and its derivatives, from American cotton wax (FARGHER and PROBERT), i, 879.
Glycols, synthesis of, from atrolactinic acid (ROGER), i, 659.
wandering of acyl groups in (BETTZIECHE), i, 1147.
reaction of, with acetone (HERMANS), ii, 50.
Glycolysis (NEGELEIN), i, 856.
measurement of (WARBURG), i, 321.
in vitro (MORGULIS and BARKUS; JOHN), i, 1344.
effect of insulin on (NITZESCU and CADARIU), i, 1352.
Glycosuria. See Diabetes.
Glycuronic acid in plants (PALLADIN and LEVTSCHENKO), i, 1369.
d-**Glycuronic acid** (EHRLICH and REHORST), i, 1379.
in vegetable fibres (SCHWALBE and FELDTMANN), i, 1238.
d-**Glycuronolactone**, structure and rotation of (HUDSON), i, 515.
Glycyl-*dl*-serine, hydrochloride and anhydrides of (BERGMANN and MIEKELEY), i, 235.
Glycyltriphenylmethylaminoacetic acid, and its sodium salt and ethyl ester (HELFERICH, MOOG, and JÜNGER), i, 792.
Glycyrrhizin, reactions of (BERTOLO), ii, 1212.
Glyoxaline (*iminazole*), excretion of, in urine (HUNTER), i, 459.
Glyoxalines, methylation of (FORSYTH and PYMAN), i, 699.
metabolism of. See Metabolism.
determination of, colorimetrically (HUNTER), ii, 332.
Glyoxaline compounds, crystallography of (GREENWOOD), ii, 1037.
Glyoxaline-4:5-dicarboxylic acid, dissociation constants of (PAULY), i, 1327.
salts of (LEHMSTEDT), i, 1103.
l-**Glyoxalinelactic acid**, fate of, in the animal body (KONISHI and TANI), i, 731.
Glyoxalinepropionic acid, fate of, in the animal body (KONISHI and TANI), i, 731.
Glyoxime dimethyl ether, *di*amino-, and its tetra-acetyl derivative (AVOGADRO and TAVOLA), i, 1041.
Glyoximes, hydroxy- (PONZIO), i, 8.
Glyoxylic acid, isomeric hydrazones of (BUSCH and v. BEUST), i, 400.
colour reaction of, with Schryver's reaction (FOSSE and HIEULLE), ii, 162.
identification of, by its reaction with hydrazine and xanthhydrol (FOSSE and HIEULLE), i, 1130.
Goats, protein substitutes in diet of (PAASCH), i, 1498.
bile of. See Bile.
blood of. See Blood.
thyroid of. See Thyroid.
Goitre, relation between iodine content of environment and (v. FELLENBERG), i, 329.
Gold obtained from mercury, atomic weight of (HÖNIGSCHMID and ZINTL), ii, 924.
formation of, from mercury (KAUL), ii, 177; (NAGAOKA), ii, 835, 1111; (STAMMREICH), ii, 1208.
arc spectrum of (LOWERY), ii, 4.
series spectrum of (MCLENNAN and MCLAY), ii, 913.
spark spectrum of (L. and E. BLOCH), ii, 829.
ultra-violet absorption spectrum of (ZUMSTEIN), ii, 453.
X-ray absorption coefficient of (WARBURTON and RICHTMYER), ii, 1103.
photo-electric sensitivity of (SUHRMANN), ii, 831.
physical state and catalytic activity of (SMITH), ii, 1072.

Gold, catalysis of hydriodic acid on the surface of (HINSHELWOOD and PRICHARD), ii, 981.
anodic oxidation of (JIRSA and JELINEK), ii, 54, 141.
anodic solution of, in hydrochloric acid (ALLMAND and PURI), ii, 302.
behaviour of, with fused silicates (JANDER), ii, 416.
colloidal, preparation of (ZSIGMONDY and HÜCKEL), ii, 775; (HADEN), ii, 895.
effect of proteins on (ZSIGMONDY and JOËL), ii, 35; (KREBS), ii, 1155.
films, emission of electrons from, exposed to Röntgen rays (SIMONS), ii, 81.
sols (v. WEIMARN), ii, 196; (GALECKI), ii, 516.
mobility of particles in (THIESSEN), ii, 1157.
protective action of gelatin on (TARTAR and LORAH), ii, 864.
action of proteins on (REINDERS), ii, 1059.
action of salts on (KERMACK and VOGE), ii, 523.
protective action of soaps on (PAPACONSTANTINOU), ii, 393, 526.
"explosive," nature of (RASCHIG), ii, 144.
Gold alloys with cadmium (SALDAU), ii, 872.
with copper (SEDSTRÖM), ii, 104.
gold–copper compound in (STERNER-RAINER), ii, 651.
with palladium, structure of (HOLGERSSON and SEDSTRÖM), ii, 20.
with zinc (SALDAU), ii, 205.
Röntgen-ray analysis of (WESTGREN and PHRAGMÉN), ii, 746.
Gold salts, toxic action of, on protoplasm (VOEGTLIN, JOHNSON, and DYER), i, 1116.
trypanocidal action of (LEVADITI, GIRARD, and NICOLAU), i, 1117.
Gold amidine and iminochloride (RASCHIG), ii, 144.
selenides (MOSER and ATYNSKI), ii, 584.
Auric chloride, preparation of (PETIT), ii, 1089.
dissociation of (PETIT), ii, 668.
compound of carbon monoxide and (MANCHOT and GALL), ii, 1182.
compounds of, with mercaptans (RÂY), ii, 184.
telluride (BRUKL), ii, 895.
Aurous halides, ammoniates of (BILTZ and WEIN), ii, 1182.
Gold:—
Chloroauric acid, compounds of acid amides with (FRICKE and RUSCHHAUPT), ii, 894.
Gold detection and determination:—
detection of (STEIGMANN), ii, 719.
detection of, spectrographically (JOLIBOIS and BOSSUET), ii, 1208.
determination of, electrometrically (ZINTL and RAUCH), ii, 1005.
Gonepteryx rhamni, dye from the wing of (WIELAND and SCHÖPF), i, 1464.
Goose, catalytic hydrolysis of proteins from the feathers of (SADIKOV), i, 175.
Goppelsroeder's reaction (SCHANTL), ii, 440.
Gossypic acid, gossypyl ester (FARGHER and HIGGINBOTHAM), i, 880.
Granite, weathering of, under peat (BLANCK and RIESER), ii, 820.
Grapes, American, effect of seasons on constituents of the juice of (CALDWELL), i, 1368.
Concord, non-volatile acids of (NELSON), i, 762.
Grape fruit, insulin-like substances in (FISHER and MCKINLEY), i, 1016.
Graphite, structure of (BERNAL), ii, 17.
crystal structure of wurtzite and (BECKENKAMP), ii, 271.
heats of combustion of (ROTH and NAESER), ii, 1140.
melting point and vaporisation of (RYSCHKEVITSCH), ii, 276, 374; (FAJANS), ii, 277.
adsorption of gases by (LOWRY and MORGAN), ii, 1053.
"activated," sorption of oxygen by (BANGHAM and STAFFORD), ii, 655.
"**Graphites**" (CIUSA), ii, 1083.
Grass, Appa. See *Ageratum conyzoides*.
inchi. See *Cymbopogon cæsius*.
Grignard reaction, mechanism of (RHEINBOLDT and ROLEFF), i, 6.
in presence of water (SCHMALFUSS and WETZEL), i, 395.
Grignard reagents, constitution of (MEISENHEIMER), i, 527.
luminescence spectra of (DUFFORD, NIGHTINGALE, and CALVERT), ii, 89, 474.
action of aldehydes on (MARSHALL), i, 1428.
action of, on amino-acids (THOMAS and BETTZIECHE), i, 250, 251, 257; (BETTZIECHE), i, 251, 1147.
detection of, colorimetrically (GILMAN and SCHULZE), ii, 1011.
Growth, effect of ultra-violet light on, of rats (HUME and SMITH), i, 211.
effect of radium emanation on, of rats (CHICK and TAZELAAR), i, 211.

Growth, factors promoting (v. EULER, WIDELL, and ERIKSON; v. EULER and WIDELL), i, 869; (v. EULER and ERIKSON), i, 1220.
influence of fluorides and iodides on (MAZÉ), i, 870.
on a vitamin-rich diet, action of ions on (TSUKAMOTO), i, 210.
Guaiacol, melting point of (PUSHIN), ii, 277.
Guaiacol, 4-amino-, acetyl derivative, acetate, and benzoyl derivative (KEHRMANN and HOEHN), i, 561.
Guanidine (PELLIZZARI), i, 1047.
and its methyl derivatives, distinction between (MARSTON), i, 1047.
double carbonates of rare earth metals and (CANNERI), i, 524.
Guanidine, nitro-, isomeric forms of (DAVIS, ASHDOWN, and COUCH), i, 644.
Guanidines, alkylated (LECHER, GRAF, and GNÄDINGER), i, 1392.
methylated, pharmacological action of (v. GRAEVENITZ), i, 734.
determination of, in urine (SHARPE), i, 722.
Guanidine bases, detection of, colorimetrically (TIEGS), i, 97.
determination of, colorimetrically (MARSTON), i, 97.
Guanidoacetic acid, cyano-, and its salts and derivatives (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 595.
Guanylic acid, salts of (IZUMI), i, 174.
brucine and strychnine salts (PEISER), i, 1477.
d-**Gulose**, preparation of, by oxidation of *d*-sorbitol (TALEN), i, 1382.
Gums, enzymes of (FOWLER and MALANDKAR), i, 1437.
Gum arabic, replacement of blood by solutions of (UEKI), i, 177.
Gum benzoin sols, action of salts on (KERMACK and VOGE), ii, 523.
Gypsum, lattice constants of calcite and (HJALMAR and SIEGBAHN), ii, 92.
solubility of (COLSON), ii, 37.

H.

iso-**Hæmagglutinin**, physical chemistry of (WÖHLISCH and SCHÜTZ), i, 717.
Hæmatin, natural pigments resembling (SCHUMM), i, 854.
Hæmatite, crystal structure of (PAULING and HENDRICKS), ii, 368.
transformation of magnetite into (WELO and BAUDISCH), ii, 845.
Hæmatoidin, identity of bilirubin and (RICH and BUMSTEAD), i, 1475.
Hæmatoporphyrin, fluorescence of (FABRE), ii, 1116.
metallic derivatives, absorption spectra of (HILL), i, 994.
fluorescence of (DHÉRÉ, SCHNEIDER, and VAN DER BOM), ii, 88.
detection of, in urine (POLICARD and LEULIER), i, 1351.
Hæmin, formation of porphyrin from (KÜSTER and HUTTENLOCHER), i, 845.
esterification of (ZALESKI and LINDENFELD), i, 89.
derivatives of (KÜSTER and HEESS), i, 992.
Hæmin, hydroxy- (HAMSIK), i, 1476.
Hæmochromogen (ANSON and MIRSKY), i, 1475.
carbon monoxide dissociation curve of (ANSON and MIRSKY), i, 456.
Hæmocyanin (STEDMAN and STEDMAN), i, 1199.
Hæmoglobin, osmotic pressure of (WILSON), ii, 292; (ADAIR), ii, 965.
ionic nature of (TAYLOR), i, 93.
surface tension of (JOHLIN), ii, 857.
kinetics of reactions of (HARTRIDGE and ROUGHTON), ii, 557.
parent substance of (MARCHLEWSKI), i, 604.
oxidation-reduction of (NEILL), i, 868, 993.
influence of tension of oxygen on oxidation of (NEILL and HASTINGS), i, 709.
oxygen-combining capacity of (MASUDA), i, 604.
oxygen dissociation curve of (ADAIR), i, 851.
and its derivatives, hydrolysis of starch by (BIEDERMANN and JERNAKOFF), i, 11.
formation of bilirubin from (RICH), i, 711; (RICH and BUMSTEAD), i, 1482.
formation of porphyrin from (SCHUMM), i, 88.
action of digestive enzymes on the iron of (LINTZEL; BARKAN), i, 1482.
ultra-violet absorption spectra of derivatives of (FRIEDLI), ii, 179.
nitric oxide compound of (ANSON and MIRSKY), i, 1475.
non-protein component of (ANSON and MIRSKY), i, 1475, 1476.
storage and excretion of, in the organism (SHIMURA), i, 1342.
reactions of (ADAIR), i, 849, 850, 851.
determination of (NEWHAM, WILTSHIRE, and SCHARFF), i, 711.

Hæmoglobin, determination of, colorimetrically (KÄMMERER and SCHAULIN), i, 851.
use of acetylene in determination of (MILLER), i, 1112.
Hæmoglobinometer, new (BÜRKER), i, 177.
Hæmoleucolysin from the pancreas (BELFANTI), i, 326.
Hæmolysis, effect of blood serum and of sugars on (KENNEDY), i, 717.
specific (KLOPSTOCK), i, 1345.
Hæmolysis, colloidal theory of (HERRMANN and ROHNER), i, 1202.
conductivity of red blood corpuscles during (PONDER and TAYLOR), i, 1202.
Hæmometer, Sahli's, standard solution for (KOUMANS), i, 851.
Hæmoporphyrin, conversion of into mesoporphyrin and ætioporphyrin (FISCHER and MÜLLER), i, 845.
Hafnium, discovery and properties of (v. HEVESY), ii, 708.
atomic weight of (HÖNIGSCHMID and ZINTL), ii, 255, 347; (v. HEVESY), ii, 255.
preparation of (VAN ARKEL and DE BOER), ii, 1193.
content of, in zirconium ores (v. HEVESY and JANTZEN), ii, 430.
Hafnium double fluorides, solubility of (v. HEVESY, CHRISTIANSEN, and BERGLUND), ii, 505.
oxide, density of (v. HEVESY and BERGLUND), ii, 25.
in tungsten filaments (VAN LIEMPT), ii, 233.
phosphate (v. HEVESY and KIMURA), ii, 1085.
solubility of zirconium phosphate and (v. HEVESY and KIMURA), ii, 1147.
Hafnium separation:—
separation of, and its arc spectrum (BARDET and TOUSSAINT), ii, 826.
separation of, from cerium, thorium, and titanium (MOSER and LESSING), ii, 718.
separation of zirconium and (NAAMLOOZE VENOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN), ii, 62, 63; (DE BOER and VAN ARKEL), ii, 243; (v. HEVESY and MADSEN), ii, 425; (MARQUIS, P. and G. URBAIN), ii, 699.
Hair, hydrolysis of (MERRILL), i, 92; (HOFFMAN), i, 1480.
substance giving the nitroprusside reaction in (KAYE), i, 180.
Halides, action of water on (SIDGWICK), ii, 102.
Halides of elements of the fourth group, melting points of (HANTZSCH and CARLSOHN), ii, 1043.
inorganic, reduction of (RUFF and THOMAS), ii, 1157.
organic, structure of, and their reactions with inorganic iodides (CONANT and HUSSEY), i, 493; (CONANT, KIRNER, and HUSSEY), i, 494.
Hall coefficient, relation of, to thermoelectric power (HEAPS), ii, 1135.
Hall effect in crystals (LENZ), ii, 920.
Halochromic salts, electrochemistry of, in relation to free radicals (CONANT, SMALL, and TAYLOR), ii, 874.
Halogens, photochemistry of (BERTHOUD and BELLENOT), ii, 141.
spectra of (STEUBING), ii, 452.
ultra-violet emission spectra of (LUDLAM and WEST), ii, 350.
action of light on air saturated with vapour of (JONES), ii, 984.
electron affinity of (LUDLAM), ii, 1018; (v. ANGERER and MÜLLER), ii, 1025.
lability of, in organic compounds (MACBETH and TRAILL), i, 628, 782.
reaction of saturated aliphatic ketones with (RICE and FRYLING), ii, 556.
reaction of potassium cyanide with (MÜLLER and SCHUCH), ii, 825.
determination of, in organic compounds (BUSCH), ii, 823.
ψ-Halogens (BIRCKENBACH and KELLERMANN), ii, 568.
Halogen compounds, partial dehalogenation of (MEREJKOVSKI), i, 878.
reaction of siloxen with (KAUTSKY and THIELE), ii, 698.
Halogen hydrides, structure and nature of (HANTZSCH), ii, 359; (v. WISNIEWSKI), ii, 361.
Halogen organic compounds, action of alkali disulphides and of sodium tetrasulphide on (THOMAS and RIDING), i, 113.
reactions of sodium arsenite with (GUTMANN), ii, 238.
Halogenation (DATTA and CHATTERJEE), i, 891.
Hamamelitannin, and its derivatives (FREUDENBERG and BLÜMMEL), i, 51.
Hay fever, analysis of blood in (RAMIREZ, ST. GEORGE, and MOSES), i, 999.
Heart, frog's, action of calcium and sodium ions on (HOLZLÖHNER), i, 1500.
action of potassium cyanide and copper on (FUJIMAKI), i, 333.

Heat, atomic, of solid aliphatic crystals (SALANT), ii, 1042.
latent, determination of (SMITH), ii, 756.
molecular, of gases, at low temperatures (GIACOMINI), ii, 757.
of diatomic gases at low temperatures (SCHREINER), ii, 97.
specific (WIESNER), ii, 275, 737.
at low temperatures (LANGE), ii, 96.
and viscosity (DE KOLOSOVSKI), ii, 870.
of electrolytes (ZWICKY), ii, 1138.
of gases (BRINKWORTH), ii, 373.
of liquids (GHOSH), ii, 275; (SCHULZE), ii, 491; (FOA), ii, 1138.
of binary mixed liquids (WILLIAMS and DANIELS), ii, 765.
of organic liquids (BUSSE), ii, 373.
of metals (BEHRENS and DRUCKER), ii, 24.
of solutions (DE KOLOSOVSKI), ii, 653, 791.
of aqueous solutions (RICHARDS and GUCKER), ii, 848.
Heat of combustion (JAEGER and v. STEINWEHR), ii, 126.
standard values for (VERKADE), ii, 871.
of members of homologous series (VERKADE, HARTMAN, and COOPS), ii, 364.
of organic compounds (VERKADE, COOPS, and HARTMAN), ii, 490.
in relation to valency of organic compounds (KHARASCH and SHER), ii, 636.
Heat of dilution and solution of salts (WÜST and LANGE), ii, 791, 976.
Heat of evaporation of electrons (WEIGLE), ii, 253.
Heat of formation of alloys (BILTZ and HOLVERSCHEIT), ii, 268.
of onium compounds (TSCHELINCEV), ii, 480.
Heat of fusion, latent (STRATTON and PARTINGTON), ii, 25.
Heat of hydration of alkali halides (LANGE), ii, 847.
Heat of mixture of condensed systems (VAN LAAR and LORENZ), ii, 870.
Heat of oxidation of pure metals (MOOSE and PARR), ii, 208.
Heat of reaction, incomplete (BÉRENGER and TIAN), ii, 791.
dissipation of (BORN and FRANCK), ii, 365.
Heat of solution (BÉRENGER and TIAN), ii, 790; (WÜST and LANGE), ii, 791.
Heat of solution, determination of (COHEN, MOESVELD, and HELDERMAN), ii, 402.
calorimeter for (COHEN, MOESVELD, and HELDERMAN), ii, 151.
solubility and lattice energy of salts (BUTLER), ii, 39.
of alkali halides (LANGE), ii, 847.
partial, relation between, and the deviation from Raoult's law (BUTLER), ii, 539.
Heat of vaporisation (BYK), ii, 97.
molecular (PRUD'HOMME), ii, 188; (NARBUTT), ii, 1140.
relation between surface tension and (PLÁCINTEANU), ii, 39.
of liquids in relation to the velocity of sound (IONESCU), ii, 644.
Hederagic acid, and its methyl esters (JACOBS), i, 948.
Hederagenic acid, methyl ester, and its derivatives (JACOBS), i, 948.
Hederagenin, structure of (VAN DER HAAR), i, 946.
and its derivatives (JACOBS), i, 948.
Hederagenolic acid, and its sodium salt (VAN DER HAAR), i, 946.
Hederagenone (VAN DER HAAR), i, 946.
Hederagenonic acid, and its salts and derivatives (VAN DER HAAR), i, 947.
Helianthin. See Methyl orange.
Helianthus annuus, anthocyanins in (SANDO), i, 1026.
green pigment of (OPARIN), i, 1517.
Helianthrone. See *meso*Benzdianthrone.
Helicin, hydrolysis of (JOSEPHSON), i, 1359.
Helicorubin, and its relation to hæmoglobin (ANSON and MIRSKY), i, 1476.
Helium in petroleum gases (CLAY), ii, 1195.
in vacuum tubes (RIDING and BALY), ii, 925.
atom, and molecule models of (ALLEN), ii, 349.
spectrum of (ORNSTEIN and BURGER), ii, 4; (BRUNETTI), ii, 249; (FOSTER), ii, 1099.
band spectrum of (CURTIS and LONG), ii, 722; (MERTON and PILLEY), ii, 1024.
structure of lines in spectrum of (HAM; GEHRCKE), ii, 1098.
Stark effect in (FOSTER), ii, 831.
Zeeman effect in (CURTIS and JEVONS), ii, 1103.
impacts of electrons in (GLOCKLER; DYMOND), ii, 617.
mobility of positive ions in (WAHLIN), ii, 170.

Helium, atomic field of (JONES), ii, 253.
life of metastable atoms of (KANNENSTINE; DEMPSTER), ii, 171.
rectilinear diameter of (MATHIAS, CROMMELIN, ONNES, and SWALLOW), ii, 468.
density of (BAXTER and STARKWEATHER), ii, 1045.
liquefaction of (MEISSNER), ii, 1135.
liquid, dielectric constant of (WOLFKE and ONNES), ii, 631.
experiments with (WOLTJER and ONNES), ii, 1038.
isotherms of (HOLBORN and OTTO), ii, 851.
diffusion of, through crystalline septa (PIUTTI and BOGGIO-LERA), ii, 500.
through glass (VAN VOORHIS), ii, 1143.
viscosity of (GÜNTHER), ii, 100.
metastable (ECKART), ii, 1104.
chemical activity of (BOOMER), ii, 925.
compounds of (BOOMER), ii, 144.
combination of mercury and (MANLEY), ii, 57; (LIND and BARDWELL), ii, 1181.
Hemicellulose, electrolysis of colloidal solutions of (LENOBLE), i, 793.
Hemicelluloses (PRINGSHEIM and GENIN), i, 214.
Hemipyocyanine, and its derivatives (WREDE and STRACK), i, 174.
Hemp-seed, vitamin-*E* in (SURE), i, 212.
Hens, digestion in (MANGOLD), i, 615.
chemistry of the oviduct of (BUCKNER, MARTIN, and PETER), i, 1347.
laying, calcium metabolism in (BUCKNER, MARTIN, and PETER), i, 190.
eggs. See Eggs.
Heparin, purification of, and its presence in blood (HOWELL), i, 1346.
***n*-Heptadecane**, 1-amino-2-hydroxy-, synthesis of (LEVENE and HALLER), i, 890.
Heptadecaoxymethylene diacetate (STAUDINGER and LÜTHY), i, 361.
Heptadecylcarbamide, β-hydroxy- (LEVENE and HALLER), i, 890.
Heptaethyl-β-ethylcellobioside (HESS and SALZMANN), i, 1383.
Heptamethyl-β-benzylcellobioside (HESS and SALZMANN), i, 1383.
αα′-Heptamethylene*dii*iminodi*iso*butyric acid, and its derivatives (SCHLESINGER), i, 1250.
αα′-Heptamethylene*dii*iminodiphenyldiacetic acid, and its derivatives (SCHLESINGER), i, 1250.
Heptanaphthene, action of aluminium chloride on (ZELINSKI and SMIRNOV), i, 1125.
Heptane, δ-amino-, oxalate (MAZOUREVITCH), i, 1241.
γδ-*di*chloro- (BOURGUEL), i, 770.
Heptanediols, and their di-*p*-nitrobenzoates (PIERCE and ADAMS), i, 824.
***cyclo*Heptane*spiro*-1-methoxy*cyclo*propane-1:2-dicarboxylic acid**, and its derivatives (BAKER), i, 1277.
Heptane-βγδ-triol (DELABY and MOREL), i, 773.
Heptan-β-one, δ-hydroxy- (GRIGNARD and DUBIEN), i, 111.
Heptaoxymethylene diacetate (STAUDINGER and LÜTHY), i, 361.
Δγ-Heptene (BOURGUEL), i, 770.
Δγ-Hepten-β-one, action of organomagnesium compounds on (GRIGNARD and DUBIEN), i, 111.
Δγ-Heptinene (BOURGUEL), i, 364.
Heptodilactone (BENNETT), i, 883.
2-*n*-Heptyl*cyclo*telluripentane-3:5-dione, 1:1-*di*chloride (MORGAN and TAYLOR), i, 634.
2-*n*-Heptyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), i, 634.
Hesperidine, occurrence of, in plants (OESTERLE and WANDER), i, 1438.
Heterocyclic compounds (SEKA), i, 57, 1298.
tautomerism of (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1328.
decomposition of (PETRENKO-KRITSCHENKO and BUTMI DE KAZMAN), i, 1094.
nuclear hydrogenation of, with colloidal platinum (SKITA), i, 140.
Heterositostanone, and its derivatives (WINDAUS and BRUNKEN), i, 394.
Hevea, constituents of latex of (SPOON), i, 621; (GORTER), i, 622.
Hevea brasiliensis, hydrogen-ion concentration in latex of (BOBILIOV), i, 622.
quebrachitol in latex of (CONTARDI), i, 277.
tannin from (ARISZ and SCHWEIZER), i, 873.
Hexachlororuthenic acid. See under Ruthenium.
Hexadecahydrodecacyclene (DZIEWOŃSKI and SUSZKO), i, 242.
Hexadecane, pyrogenic dissociation of (GAULT and HESSEL), i, 109.
Hexadecanedicarboxylic acid, ethyl hydrogen ester (FAIRWEATHER), i, 1237.
Hexadecene. See Cetene.
Hexahydrobenzoic acid, phenyl ester (BLICKE), i, 662.

Hexahydrocadalene, synthesis of (RUZICKA and CAPATO), i, 943.
Hexahydrodecacyclene (DZIEWOŃSKI and SUSZKO), i, 242.
Hexahydromandelic acid, and its derivatives, methyl esters of (FREUDENBERG and MARKERT), i, 1275.
alkyl esters, rotatory dispersion of (WOOD and COMLEY), ii, 264.
Hexahydromethylmorphimethines, and their derivatives (SPEYER and KOULEN), i, 61.
α- and β-Hexahydrotrianhydrostrophanthidins (JACOBS and COLLINS), i, 567.
Hexaicosihydrodecacyclene (DZIEWOŃSKI and SUSZKO), i, 242.
Hexametaphosphates. See under Phosphorus.
Hexamethylbenzene, formation of (BRINER, PLÜSS, and PAILLARD), i, 248.
Hexamethyldiethyltristannane (KRAUS and GREER), i, 1394.
Hexamethyldipyridyl-blue iodide (EMMERT, JUNGCK, and HAFFNER), i, 72.
2:2′:3:3′:5:5′-Hexamethyl-4:4′-dipyrrylmethane (FISCHER and NENITZESCU), i, 835.
Hexamethylenetetramine (*hexamethyleneamine*; *urotropine*) as a plant nutrient (E. and G. NICOLAS), i, 623.
as source of plant nitrogen (BIALOSUKNIA), i, 1366.
fate of, in the body (DE EDS), i, 461.
hydroferricyanide (CUMMING), i, 122.
additive compounds of stannic iodide and (SCAGLIARINI), i, 890.
Hexamethylguanidinium salts (LECHER, GRAF, and GNÄDINGER), i, 1393.
Hexamethylrottlerin, and its derivatives (DUTT), i, 1296.
Hexamethyltristannane, disodium derivative (KRAUS and GREER), i, 1394.
Hexamminecobaltictriaquodisulphitosulphatocobaltiate. See under Cobalt.
***n*-Hexane**, solubility of mixtures of liquid sulphur dioxide and (SEYER and GILL), ii, 504.
***cyclo*Hexane**, structure of, and benzene (RAMANATHAN), i, 1255.
physical constants of (NAGORNOV and ROTINJANC), ii, 646.
***cyclo*Hexane series**, physico-chemical properties of derivatives of (HERZ and BLOCH), ii, 98.
***cyclo*Hexane-1-acetic acid**, 1:2-*di*bromo-, ethyl ester (BAKER), i, 916.
***cyclo*Hexane-1-acetic-2-propionic acid**, and its dianilide (HÜCKEL and GOTH), i, 402.
***cyclo*Hexane-1:2-diacetic acid**, 1:2-*di*hydroxy-, lactone (BAKER), i, 916.
***cyclo*Hexane-1:3-dicarboxylic acids**, isomeric, and their optically active components (BÖESEKEN and PEEK), i, 1150.
β-*cyclo*Hexaneglutarylfluorescein (DUTT and THORPE), i, 141.
β-*cyclo*Hexaneglutarylrhodamine (DUTT and THORPE), i, 142.
***as-cyclo*Hexanesuccinylfluorescein** (DUTT and THORPE), i, 141.
***as-cyclo*Hexanesuccinylrhodamine** (DUTT and THORPE), i, 142.
***cyclo*Hexanesulphonic acid**, salts and derivatives of (KOLKER and LAPWORTH), i, 353.
***cyclo*Hexanol**, surface tension and vapour pressure of, and its mixtures (WEISSENBERGER and SCHUSTER), ii, 648.
***cyclo*Hexanol**, 1-amino-2-cyano- (v. AUWERS, BAHR, and FRESE), i, 312.
1-*cyclo*Hexanol-2-malonic acid, ethyl ester lactone (KÖTZ and HOFFMANN), i, 911.
***cyclo*Hexanone** 2-phenylsemicarbazone (GOODWIN and BAILEY), i, 318.
derivatives of (GARLAND and REID), i, 1280.
***cyclo*Hexanones**, cyano-, and their derivatives (v. AUWERS, BAHR, and FRESE), i, 310.
2:6-*di*bromo-, action of alkalis on (CUSMANO), i, 818.
***cyclo*Hexanoxide**, sodium (CAUQUIL), i, 657.
***d*-Hexan-αδε*ζ*-tetrol.** See Tetrahydro-ψ-glucal.
Hexaphenyldigermane (MORGAN and DREW), i, 1197.
***cyclo*Hexene**, catalytic hydrogenation of (ZELINSKI), i, 237.
nitrates of (HAINES and ADKINS), i, 801.
Δ¹-*cyclo*Hexene, 2-amino-1-cyano-, and its hydrochloride (v. AUWERS, BAHR, and FRESE), i, 312.
***cyclo*Hexenes**, catalytic decomposition of (ZELINSKI), i, 122.
Δ¹-*cyclo*Hexeneacetic acid, 2-bromo-, ethyl ester (BAKER), i, 916.
Δ¹-*cyclo*Hexene-1-acetic-2-malonic acid, and its ethyl ester (BAKER), i, 916.
Δ¹-*cyclo*Hexene-1:2-diacetic acid (BAKER), i, 917.
Δ¹-*cyclo*Hexene-4:5-dione, 1:2:3:3:6:6-*hexa*chloro-, and its hydrates (ELLER and LORENZ), i, 537.
***cyclo*Hexenols**, preparation and derivatives of (SENDERENS), i, 537.
***n*-Hexoic acid**, 3-hydroxybenzaldehyde 2-mercuric ester (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i 1154.

Hexoic acid, ϵ-bromo- (MARVEL, MACCORQUODALE, KENDALL, and LAZIER), i, 234.
ϵ-cyano- (v. AUWERS, BAHR, and FRESE), i, 312.
Hexonic acids, α-amino-, configuration of (LEVENE), i, 523.
Hexophosphatases in organs and body fluids (DEMUTH), i, 1497.
Hexoses, amino-, synthesis of, from galactose (FREUDENBERG and DOSER), i, 366.
α-amino-, configuration of (LEVENE), i, 523.
Hexosephosphates, formation of (NEUBERG and KOBEL), i, 476.
Hexosephosphoric acid, esters, in development of bone (MARTLAND and ROBISON), i, 201.
n-**Hexoylglycine**, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
*cyclo***Hexyl** chloromethyl ether (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
*cyclo***Hexylamine**, catalytic decomposition of (KOMATSU and TANAKA), i, 905.
n-**Hexylbenzene**, 2:4-*di*hydroxy- (SHARP & DOHME and DOHME), i, 541.
*p-cyclo***Hexylbenzoyl-***o*-**benzoic acid** (QUAYLE and REID), i, 1289.
*cyclo***Hexylbenzyl** ether (SCHORIGIN), i, 1404.
*cyclo***Hexylbutinenes** (BOURGUEL), i, 1, 770.
*cyclo***Hexylbutinoic acid** (BOURGUEL), i, 770.
γδ-**Hexylene oxide**, heat of combustion of (ZUBOV and SWIENTOSLAWSKI), ii, 364.
*cyclo***Hexylheptinoic acid** (BOURGUEL), i, 770.
*cyclo***Hexylhexinenes** (BOURGUEL), i, 1, 770.
*cyclo***Hexylhexinoic acid** (BOURGUEL), i, 770.
*cyclo***Hexylhydroxylamine** (VAVON and BERTON), i, 807.
*cyclo***Hexylideneazine**, action of hydrochloric acid on (PERKIN and PLANT), i, 842.
*cyclo***Hexylidenenitroanthranilic acids** (PERKIN and SEDGWICK), i, 64.
*cyclo***Hexylidene***cyclo***pentylideneazine** (PERKIN and PLANT), i, 843.
*cyclo***Hexylpentinenes** (BOURGUEL), i, 1, 770.
*cyclo***Hexylpentinoic acid** (BOURGUEL), i, 770.
γ-*cyclo***Hexylpropyl alcohol**, and its derivatives (WASER), i, 584.
2-*n*-**Hexyl***cyclo***telluripentane-3:5-dione** 1:1-*di*chloride (MORGAN and TAYLOR), i, 634.
2-*n*-**Hexyl***cyclo***telluropentane-3:5-dione** (MORGAN and TAYLOR), i, 634.
Hippuric acid, effect of diet on synthesis of (GRIFFITH), i, 1002.
effect of carbohydrate metabolism on synthesis of (WIDMARK and JENSEN-CARLEN), i, 331.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
Hippuric diethylamide (GRANÄCHER), i, 594.
Hippuryl chloride, action of diazomethane on (KARRER and WIDMER), i, 593.
Histamine, effect of injection of, on blood (HASHIMOTO), i, 1005.
influence of, on nitrogenous metabolism (IWATSURU), i, 1502.
detection of, microchemically (VAN ITALLIE and STEENHAUER), ii, 608.
Histidine in the animal organism (STEWART), i, 730.
degradation of, to *l*-aspartic acid (LANGENBECK), i, 306.
relation of, to creatine and purine metabolism (ROSE and COOK), i, 1003.
Holmium, atomic weight of (DRIGGS and HOPKINS), ii, 463.
Homatropine *N*-oxide, and its derivatives (POLONOVSKI and POLONOVSKI), i, 829.
Homoaspartimide (STOSIUS and PHILIPPI), i, 892.
Homobenz*iso***thiopyran**, and its derivatives (v. BRAUN, BAYER, and KAISER), i, 1446.
Homologous compounds, rotation dispersion, density, and absorption spectra of (KRETHLOW), ii, 1029.
n- and *iso*-**Homopilopic acids**, methylamides of (LANGENBECK), i, 151.
N-**Homopiperonyl-4:5-dimethoxyhomophthalamic acid**, and its methyl ester (HAWORTH, PERKIN, and PINK), i, 1169.
2-Homopiperonyl-6:7-dimethoxyhomophthalimide, and its dimethyl derivative (HAWORTH, PERKIN, and PINK), i, 1169.
2-Homopiperonyl-6:7-dimethoxy-1-*iso***quinolone**, 3-chloro- (HAWORTH, PERKIN, and PINK), i, 1169.
2-Homopiperonyl-4:4-dimethylhomophthalimide (HAWORTH, PERKIN, and PINK), i, 1168.
N-**Homopiperonylhomophthalamic acid**, and its amide and methyl ester (HAWORTH, PERKIN, and PINK), i, 1169.

2-Homopiperonylhomophthalimide (HAWORTH, PERKIN, and PINK), i, 1168.
3-Homopiperonyl-2-methylchromone, 7-hydroxy-, and its derivatives (BAKER and ROBINSON), i, 926.
2-Homopiperonyl-1-*iso*quinolone, 3-chloro- (HAWORTH, PERKIN, and PINK), i, 1168.
Homopiperonylresacetophenone (BAKER and ROBINSON), i, 925.
***as*-Homotetrahydro*iso*quinoline** methobromide (v. BRAUN and KAISER), i, 1414.
Homoveratroylhomopiperonylamine, 6′-bromo- (HAWORTH and PERKIN), i, 970.
3-Homoveratryl-2-methylchromone, 7-hydroxy-, and its acetyl derivative (BAKER and ROBINSON), i, 926.
Homoveratrylresacetophenone (BAKER and ROBINSON), i, 926.
Hops, bitter principles of (WÖLLMER), i, 690.
preservative principles of (WALKER), i, 1479.
resin acids of (WIELAND, SCHNEIDER, and MARTZ), i, 276; (WIELAND, MARTZ, and HOEK), i, 1422.
determination of humulone in (KLEIN), ii, 248.
Hormones, action of (GOTTSCHALK; ZONDEK and UCKO), i, 1513.
Horn, solubility of, in alkali sulphides (PULEVKA), i, 1341.
Horse, vitamins in flesh of (SCHEUNERT and HERMERSDÖRFER), i, 617.
Humic acids (ELLER, HELMRICH, KLEMM, HAUBOLD, and SCHÖPPACH), i, 521.
constitution of (BURIAN; ELLER), i, 372; (MARCUSSON), i, 793.
formation of, from cellulose, lignin, and wood (WEHMER), i, 521.
Humins, properties and reactions of (ELLER, HELMRICH, KLEMM, HAUBOLD, and SCHÖPPACH), i, 521.
Humulic acid, constitution of (WIELAND, MARTZ, and HOEK), i, 1422.
***iso*Humulic acid**, and its derivatives (WIELAND, SCHNEIDER, and MARTZ), i, 276.
Humulon, structure of (WIELAND, SCHNEIDER, and MARTZ), i, 276; (WIELAND, MARTZ, and HOEK), i, 1422.
Humuloquinone, semicarbazone of (WIELAND, SCHNEIDER, and MARTZ), i, 276.
Humus, nature of (WAKSMAN), i, 1528.
soils, foaming power and surface tension of (OSTWALD and STEINER), ii, 771.
Hydantoic acid, cyano- (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 596.
Hydantoins (COGHILL and JOHNSON), i, 582; (COGHILL, JOHNSON, and RENFREW; DAVIDSON), i, 583; (DAVIDSON and JOHNSON), i, 584; (DAVIDSON), i, 975.
substituted, preparation of (THOMPSON, BEDELL, and BUFFETT), i, 699.
Hydantoin-3-acetic acid, and 2-thio- (JOHNSON and RENFREW), i, 583.
Hydantoin-[$\Delta^{5:2'}$]-ψ-indoxyl (HILL and HENZE), i, 306.
Hydantoin-[$\Delta^{5:3'}$]-oxindole (HILL and HENZE), i, 305.
Hydnora americana. See *Prosopanche Burmeisteri*.
Hydrangea paniculata, composition of (KOMATSU and UEDA), i, 762.
Hydrargyrum salicylicum, constitution of (BOEDECKER and WUNSTORF), i, 1107.
Hydrastine, excretion of, in urine (BAYLE and FABRE), i, 609.
Hydrato*iso*cyanilic acid (WIELAND), i, 1049.
***r*-Hydratropic acid**, β-chloro-, resolution of (MCKENZIE and STRATHERN), i, 401.
Hydrazidoanthraquinones, acyl derivatives of (BATTEGAY and AMUAT), i, 169.
Hydrazine, oxidation of, and its sulphonic acids (RASCHIG), ii, 224.
action of, on cyanotetrazole (OLIVERI-MANDALÀ), i, 78.
action of, on dimethylpyrone (KIJNER), i, 1105.
sulphate, use of, in iodometry (CATTELAIN), ii, 1197.
and its salts, electrometric determination of (GILBERT), ii, 239.
Hydrazines, action of ketens on (VAN ALPHEN), i, 80.
action of, on semicarbazones (SUTHERLAND and WILSON), i, 42.
aromatic halogenated (VOTOČEK and JIRŮ), i, 317.
α-Hydrazino-β-aminoethane, and its salts (SOMMER, SCHULZ, and NASSAU), ii, 990.
2-Hydrazinoanthraquinone, 3-hydroxy- (TANAKA), i, 1106.
4-Hydrazinobenzoic acid, 3:5-*di*nitro-, ethyl ester (LINDEMANN and WESSEL), i, 1099.
2-Hydrazino-9:10-dihydroanthracene hydrochloride (SCHROETER, GLUSCHKE VAN HULLE, and GÖTZKY), i, 128.
2-Hydrazino-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazine (GUHA and DE), i, 600.

Hydrazobenzene hydroferricyanide (CUMMING), i, 122.
o-**Hydrazobenzyl**-*o*-**toluidine** (ELBS and GAUMER), i, 168.
Hydrazones, isomeric (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 40.
coloured sulphuric acid solutions of (CHATTAWAY, IRELAND, and WALKER), i, 1194.
o-**Hydrazotoluene** hydroferricyanide (CUMMING), i, 122.
Hydrides, non-metallic, structure of (GRIMM), ii, 1123.
volatile (PANETH and RABINOVITSCH), ii, 760.
"**Hydrindine**," identity of hydroxydihydro*iso*indigotin and (SANDER), i, 977.
1-Hydrindone, influence of substituents on formation of derivatives of, from β-phenylpropionic acids (SPEIGHT, STEVENSON, and THORPE), i, 32.
1-Hydrindones, 2-oximino-, action of phosphorus pentachloride on (HAWORTH and PINK), i, 929.
Hydrobenzoins, stereoisomeric, adsorption of, by charcoal (HERMANS), ii, 31.
dibenzoates of (MEERWEIN and SCHMIDT), i, 1240.
Hydrobromic acid. See under Bromine.
Hydrocarbon, $C_{10}H_{16}$, from *tert.*-amino-*iso*bornylane and nitrous acid (NAMETKIN, ABAKUMOWSKI, and SELIVANOV), i, 48.
$C_{10}H_{16}$, from lupanine (THOMS and BERGERHOFF), i, 575.
$C_{10}H_{18}$, from hydrogenation of $C_{10}H_{16}$ from *tert.*-amino*iso*bornylane (NAMETKIN, ABAKUMOWSKI, and SELIVANOV), i, 48.
$C_{11}H_{12}$, from 5-methylphenylene-1:3-diacetonitrile (v. BRAUN and ENGEL), i, 382.
$C_{15}H_{22}$, from reduction of humulic acid (WIELAND, SCHNEIDER, and MARTZ), i, 276.
$C_{18}H_{34}$, from abietic acid (VESTERBERG and BORGE), i, 252.
$C_{20}H_{32}$, from the action of metallic chlorides on pinene hydrochloride (KOMATSU and FUJIO), i, 564.
Hydrocarbons, preparation of (GILMAN and BEABER), i, 802.
X-ray investigation of (MÜLLER and SAVILLE), ii, 367.
action of bromine on (MERESHKOVSKI), i, 1033.
action of nitrogen peroxide on (SCHAARSCHMIDT,) ii, 227.
action of radium emanation on (MUND and KOCH), i, 625.
Hydrocarbons, halogen derivatives, ultra-red absorption spectra of (BONINO), ii, 838.
acetylenic, preparation of (BOURGUEL), i, 1, 770.
disubstituted, reaction of Grignard reagents with (GILMAN and SHUMAKER), i, 493.
aromatic, Tesla-luminescence spectra of (MCVICKER, MARSH, and STEWART), ii, 12.
photochemical oxidation of (SUDBOROUGH, WATSON, and NARAYANAN), i, 1136.
condensation of, with nitrosyl chlorine (SCHAARSCHMIDT and RAECK), i, 380.
polynuclear, spectrochemistry and structure of (v. AUWERS and KRAUL), i, 900.
benzenoid, optical constants of (EISENLOHR and SCHULZ), i, 17.
cyclic unsaturated, catalytic transformation of (ZELINSKI), i, 122, 146, 821.
ethylenic, action of iodine in chloroform on (BÖESEKEN and BLUMBERGER), i, 225.
combination of hydrogen sulphites with (KOLKER and LAPWORTH), i, 353.
higher, synthesis of, from lower hydrocarbons (LIND and BARDWELL), i, 493.
olefine, action of nitrogen tetroxide on (SCHAARSCHMIDT and HOFMEIER), i, 877.
paraffin, boiling point chart for (BAHLKE and WILSON), ii, 73.
cracking of (WILLIAMS-GARDNER), i, 1229.
polynuclear, Tesla-luminescence spectra of (MCVICKER, MARSH, and STEWART), ii, 630.
quaternary, preparation of (TROTMAN), i, 382.
unsaturated, photochemical combination of bromine with (PLOTNIKOV), ii, 985.
Hydrocarbons, chloro-, toxic action of (DOUGAL), i, 334.
Hydrocellulose (HESS), i, 519.
nitrates (ATSUKI), i, 120.
Hydrochloric acid. See under Chlorine.
Hydrocinnamic acid, electrolytic preparation of (NORRIS and CUMMINGS), i, 668.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
Hydrocupreidine hydrochloride (GIEMSA and BONATH), i, 291.

Hydrocupreidinesulphonic acid, and its sulphate (GIEMSA and BONATH), i, 291.
Hydrocupreine, salts of (GIEMSA and BONATH), i, 291.
Hydrocupreinesulphonic acid, and its salts (GIEMSA and BONATH), i, 291.
Hydrocyanic acid. See under Cyanogen.
Hydroferricyanic acid, preparation of, and its alkaloidal salts (CUMMING and BROWN), i, 572.
salts of, with organic bases (CUMMING), i, 122.
Hydroferricyanocarboxylic acid, salts of (PASCAL), i, 984.
Hydroferrocyanic acid, alkaloidal salts of (CUMMING and BROWN), i, 572.
copper salt, permeability of membranes of, to acids (COLLANDER), ii, 201.
coagulation of sols of (SEN), ii, 664; (SEN and MEHROTRA), ii, 665.
double salts of, with hydrazine and metals (RÂY and GUPTA), i, 377.
potassium salt, preparation of (DOMINIK), i, 526.
sensitiveness of, to light (BAUR), ii, 884.
use of, in analysis (LUFF), ii, 826.
salts of, with organic bases (CUMMING), i, 122.
Hydroferrocyanocarboxylic acid, salts of (PASCAL), i, 984.
Hydrofluoric acid. See under Fluorine.
Hydrogen, atomic weight of (MOLES), ii, 346.
atoms, structure of (REICHENBÄCHER), ii, 734.
electron orbits in (REICHENBÄCHER), ii, 624.
molecules, ionised, structure of (UREY), ii, 1105.
pure, preparation of (BAYERLE and TAMELE), ii, 233.
refractive index and electron velocity of (SCHÜLER and WOLF), ii, 1118.
spectrum of (DIEKE), ii, 450; (GEHRCKE and LAU), ii, 609; (SCHÜLER and WOLF), ii, 829; (VAN CITTERT), ii, 909.
Balmer lines in (HANOT), ii, 170; (JANICKI), ii, 449; (HANSEN), ii, 1097; (HAM; GEHRCKE), ii, 1098; (JOLOWICZ), ii, 1097.
Fulcher lines in spectrum of (CURTIS), ii, 351; (BURY), ii, 1113.
excitation of (BLACKETT and FRANCE), ii, 1097.
spectrohelio grams of (ROYDS), ii, 456.
band spectrum of (DIEKE), ii, 737.
Hydrogen, continuous spectrum of (CARST), ii, 333; (LAU), ii, 721.
infra-red emission spectrum of (PFUND), ii, 11.
secondary spectrum of (RICHARDSON and TANAKA), ii, 11, 469; (DUFFENDACK), ii, 333; (NICHOLSON), ii, 468, 721; (MCLENNAN and SHRUM), ii, 468; (DIEKE), ii, 625; (RICHARDSON), ii, 909, 1013; (TANAKA; SANDEMAN), ii, 909.
dry, effect of ultra-violet light on (BAKER and CARLTON), ii, 1180.
particles, photographic action of (BLAU), ii, 1111.
passage of canal rays through (DEMPSTER), ii, 1020.
Döppler effect in canal rays of (KREFFT), ii, 78.
Paschen-Back effect in (FALKENHAGEN), ii, 79.
stopping power of, for α-particles (FOWLER), ii, 834.
magnetic susceptibility of (GLASER), ii, 82, 642.
active (BONHOEFFER), ii, 52; (PANETH), ii, 57; (COPAUX, PERPEROT, and HOCART), ii, 587; (COLLINS), ii, 842; (BACH), ii, 885.
formation of, in the creepage corona discharge (ANDEREGG and HERR), ii, 1180.
by excited mercury atoms, and its reactions (MITCHELL), ii, 1077; (TAYLOR and MARSHALL), ii, 1078.
luminescence with (BONHOEFFER), ii, 839.
electronegative (VAN ARKEL and DE BOER), ii, 734.
electrical properties of (MCCALLUM and FOCKEN), ii, 641.
ionisation of (SMYTH), ii, 459; (LUNT), ii, 616.
by electron impact (HOGNESS and LUNN), ii, 839.
potentials for discharge of electrons in (RICHARDSON and TANAKA), ii, 13.
overvoltage of (HARKINS and ADAMS), ii, 301.
influence of colloids on cathodic overvoltage of (MARIE and LEJEUNE), ii, 115.
chemical constants of (SCHREINER), ii, 978.
specific heat of (PARTINGTON and HOWE), ii, 1041.
specific heats of air and (BRINKWORTH), ii, 372.
specific heat of molecules of (PREDVODITELEV), ii, 1041; (VAN VLECK), ii, 1138.

Hydrogen, isotherms of (HOLBORN and OTTO), ii, 851.
heat of adsorption of, on nickel (FORESTI), ii, 692.
heat of oxidation of, by manganese dioxide (FRAZER and GREIDER), ii, 1064.
mass of particles of (STETTER), ii, 1021.
liquid and solid, dielectric constants of (WOLFKE and ONNES), ii, 630; (BREIT and ONNES), ii, 631.
liquefier for, and cryostat (LATIMER, BUFFINGTON, and HOENSHEL), ii, 818.
viscosity of (GÜNTHER), ii, 100.
diffusion of, into air (BARUS), ii, 27.
solubility of, in liquid ammonia (LARSON and BLACK), ii, 852.
adsorption of, by cerium and its alloys (SIEVERTS and ROELL), ii, 854.
by electrolytic chromium (HÜTTIG and BRODKORB), ii, 702.
by palladium (LAMBERT and GATES), ii, 785.
by palladium–silver alloys (KRUGER and SACKLOVSKY), ii, 1125.
adsorbed in silica gels, reduction by (LATSHAW and REVERSON), ii, 412.
equilibrium of carbon dioxide and, with carbon monoxide and water vapour (PARTINGTON and SHILLING), ii, 395.
explosion of mixtures of air and (BONE, NEWITT, and TOWNEND), ii, 800.
influence of trichloroethylene on inflammability of mixtures of air and (JORISSEN and ONGKIEHONG), ii, 875.
photochemical combination of bromine and (BODENSTEIN and LÜTKEMEYER), ii, 218.
interaction of carbon dioxide and, in the electric discharge (LUNT), ii, 579.
action of carbon dioxide with, on platinum (PRICHARD and HINSHELWOOD), ii, 564.
action of carbon dioxide with, on the surface of tungsten (HINSHELWOOD and PRICHARD), ii, 983.
photochemical reaction of carbonyl chloride with (BREDIG and v. GOLDBERGER), ii, 142.
photochemical reaction between chlorine and (MARSHALL), ii, 883; (KORNFELD and MÜLLER), ii, 984; (NORRISH), ii, 1080, 1179.
in presence of oxygen (NORRISH and RIDEAL), ii, 572.
effect of water vapour (COEHN and JUNG), ii, 142.
Hydrogen, catalytic combination of ethylene and, in presence of copper (PEASE and STEWART), ii, 691.
reaction of nitrogen with, in presence of mercury vapour (NOYES), ii, 573.
catalysis of the formation of water from oxygen and (HOFMANN and DOLDE), ii, 139.
combination of oxygen and, in presence of silver and gold (CHAPMAN, RAMSBOTTOM, and TROTMAN), ii, 310.
effect of water and of carbon dioxide on the catalytic oxidation of (LAMB and VAIL), ii, 567.
oxidation of, by potassium permanganate (WILKE and KUHN), ii, 51.
reduction of metallic halides by (DE CARLI), ii, 51.
Hydrogen chloride. See Hydrochloric acid under Chlorine.
cyanide. See Hydrocyanic acid under Cyanogen.
halides. See Halogen hydrides.
iodide. See Hydriodic acid under Iodine.
*per*oxide, formation of, by bacteria (MCLEOD and GORDON), i, 1362.
vapour pressure of (MAASS and HIEBERT), ii, 188.
partition of, between water and ethyl ether (DE KOLOSOVSKI), ii, 506.
in the oxy-hydrogen flame (RIESENFELD), ii, 148.
decomposition of (DAVEY), ii, 1181.
by catalase (NORTHROP), i, 469.
by cobaltic hydroxide (TRYHORN and JESSOP), ii, 807.
in presence of nickel hydroxide (VEIL), ii, 412.
catalytic decomposition of (QUARTAROLI; SPITALSKY and PETIN), ii, 53.
by animal charcoal (FIRTH and WATSON), ii, 310.
by "Norit" charcoals (FIRTH and WATSON), ii, 880.
in chlorine–chloride solutions (LIVINGSTON and BRAY), ii, 981.
promotion of copper salts in the decomposition of, by ferric salts (ROBERTSON), ii, 690.
mode of reaction of (WIELAND, HAUSSMANN, and LÖVENSKIOLD), ii, 1173.
oxidising action of (HATCHER and HOLDEN; ERNST and FORSTER), ii, 684.
destruction of organic matter by (MAGNIN), ii, 594.

Hydrogen *per*oxide, action of, on bacteria (BURNET), i, 1117; (PETROVANU), i, 1362.
titration of, with potassium permanganate in presence of ammonium sulphate (TANANAEV), ii, 440.
determination of (RUPP and SIEBLER), ii, 432.
phosphide. See Phosphorus *tri*hydride.
sulphide in minerals (NENADKEVITSCH; VERNADSKI), ii, 997.
formation of, by bacteria (MULSOW and PAINE), i, 1510.
electrolytic preparation of (FISCHER), ii, 807.
generation of (HENWOOD, GAREY, GOLDBERG, and FIELD), ii, 705.
pure liquid, preparation of, and reactions therein (QUAM), ii, 582.
liquid, as a source of supply of the gas (MOORE), ii, 1195.
conductivities in (QUAM and WILKINSON), ii, 542.
condensation of acetylene and, in presence of catalysts (TOMKINSON), i, 58.
action of iodine on (PARSONS), ii, 880.
action of, on mercuric salts (PÉLABON), ii, 986.
toxicity of (HAGGARD), i, 1357.
*per*sulphide (v. DIENES), ii, 228.
Hydrogen determination:—
determination of, in organic compounds (HESLINGA), ii, 65; (LINDNER), ii, 901.
Hydrogen electrodes. See Electrodes.
Hydrogen ions, adsorption of, by charcoal (KROETZ), ii, 191.
mobility of (DAVIES), ii, 871.
in air (ERIKSON), ii, 1107.
velocity of, in gels (ISGARISCHEV and POMERANZEVA), ii, 300.
concentration of, in culture fluids (CHRISTENSEN and FULMER), i, 1216.
in soils (ARRHENIUS), i, 1525; (PIERRE; NIKLAS and HOCK), i, 1526.
in blood (BIGWOOD), i, 1342.
of normal and cancer subjects (CORRAN and LEWIS), i, 188.
in tissues and cells (SCHMIDTMANN), i, 99.
determination of concentration of (MISLOWITZER), i, 1483; (TRÉNEL), ii, 64.
colorimetrically (RICHARD), ii, 596.
electrometrically (GLASSTONE), ii, 822.
Hydrogen ions, determination of concentration of, with the quinhydrone electrode (SCHAEFER and SCHMIDT), i, 611; (KOLTHOFF), ii, 671; (O'SULLIVAN), ii, 822.
from potentials of hydrogen and quinhydrone electrodes (KOLTHOFF), ii, 794.
spectrophotometrically (VLÈS), ii, 595; (HOLMES and SNYDER), ii, 999.
in blood (HOLLO and WEISS), i, 709.
in soils (ATKINS; BARNETTE, HISSINK, and VAN DER SPEK), i, 220; (TRÉNEL), i, 874; (CROWTHER), i, 875; (NIKLAS and HOCK), ii, 325.
in distilled water (DAWSON), ii, 680.
electrodes for (CULLEN and BIILMANN; BODINE and FINK), i, 1201; (PARKER), ii, 899.
continuous reading meter for (GOODE), ii, 1196.
Hydrogenase, action of, in the cell (GRÜSS), i, 738.
Hydrogenation, kinetics of (LUSH), ii, 411.
Hydrolysis, electrometric study of (JOB), ii, 117.
Hydroxides, amphoteric (JANDER and BRANDT), ii, 988.
Hydroxy-acids, $C_{11}H_{10}O_3$, from atromentin (KÖGL and POSTOWSKY), i, 51.
α- and β-Hydroxy-acids, configurational relationship between (LEVENE and HALLER), i, 1375.
Hydroxy-aldehydes (HELFERICH and SCHÄFER), i, 7; (HELFERICH and FRIES), i, 1039.
Hydroxy-compounds, aromatic, action of sulphites on (BUCHERER and STICKEL), i, 1338.
α-Hydroxy-ketones, synthesis of (SCHMIDT and ASCHERL), i, 364.
Hydroxyl groups, valency of (REIHLEN, SAPPER, and KALL), i, 912.
co-ordination valency of (FERNANDES), i, 912.
mobility of, and tautomerism (FARROW and INGOLD), i, 155.
determination of, microchemically (FLASCHENTRÄGER), ii, 999.
Hydroxyl ions, adsorption of, by charcoal (KROETZ), ii, 191.
Hydroxylamine, preparation of (HURD and BROWNSTEIN), ii, 587.
oxidation of (RASCHIG; KURTENACKER and WENGEFELD), ii, 224.
catalytic decomposition of (KURTENACKER and WENGEFELD), ii, 308.

Hydroxylamine, action of sulphurous acid and sulphites on (RASCHIG), ii, 226.
salts of, with organic acid (OESPER and BALLARD), i, 1233.
alkyl derivatives of (NEUFFER and HOFFMAN), i, 891.
benzenesulphinate (WHALEN and JONES), i, 802.
sulphonic acids of (RASCHIG), ii, 225, 226.
β-Hydroxylamines, formation of (DURAND and NAVES), i, 535.
Hydroxylamine*iso*sulphonic acid (SOMMER, SCHULZ, and NASSAU), ii, 989.
3-Hydroxylaminopyridine. See β-3-Pyridylhydroxylamine.
Hydroxylaminotetraphenylmethane, and nitroso- (GOLDSCHMIDT and CHRISTMANN), i, 649.
Hydroxymethyleneacetophenone. See Phenyl β-hydroxyvinyl ketone.
Hydroxynitrilese, purification and properties of (NORDEFELDT), i, 1506.
Hygrine alkaloids (HESS and BAPPERT), i, 424.
***l*-Hygrinic acid** (KARRER and WIDMER), i, 1084.
Hyocholanic acid, 4-chloro- and 4-hydroxy-, derivatives of (WINDAUS and HOSSFELD), i, 1066.
Hyodeoxybilianic acid, derivatives of (WINDAUS and BOHNE), i, 553.
Hyoscyamine *N*-oxide, and its derivatives (POLONOVSKI and POLONOVSKI), i, 829.
Hyperglycæmia, production of, by glycerol (VOEGTLIN, THOMPSON, and DUNN), i, 1211.
Hypericum perforatum, constituents of (ZELLNER), i, 764.
Hypobromites. See under Bromine.
Hypocerebric acid (FRÄNKEL and KARPFEN), i, 720.
Δ$^{\alpha}$-Hypogæic anhydride (GABEL), i, 504.
Hypoglycæmia (FISCHLER and OTTENSOOSER), i, 715.
Hypoiodites. See under Iodine.
Hyponitritoferropentacyanic acid, sodium salt (UNGARELLI), i, 526.
Hyssopin. See Diosmin.
Hystazarindiquinone (TANAKA), i, 1077.

Ice, infra-red absorption spectrum of (PLYLER), ii, 87.
specific heat and latent heat of fusion of (MAASS and WALDBAUER), ii, 492.
Ice, velocity of crystallisation of, through gelatin gels (CALLOW), ii, 777.
Ignition of gases (WHEELER), ii, 408.
by electric sparks (MORGAN), ii, 553.
influence of non-inflammable vapours on (JORISSEN and VAN DER VALK), ii, 874 ; (JORISSEN and ONGKIEHONG), ii, 875.
Imbibition, application of Röntgen ray methods to (KATZ), ii, 771.
Iminazole. See Glyoxaline.
Iminazoles, complex, colour of (CHAKRAVARTI and GUPTA), i, 980.
4-Iminazole-2(1′)-naphthyl-8′-carboxylic acid (CHAKRAVARTI), i, 162.
Imines, halochromism of, and their compounds (PFEIFFER, RHEINBOLDT, and WOLF), i, 411.
2:5-Imino-1:2:3-triazole (CARNELLEY and DUTT), i, 165.
Immunisation by injection of invertase (BACH, ENGELHARDT, and SAMYSSLOV), i, 1506.
Inchi grass. See *Cymbopogon cæsius*.
Indacene, *di*hydroxy-, diacetyl derivative (JONESCU), i, 1154.
Indandione. See Diketohydrindene.
Indandionyldi-indonylmethane (RADULESCU and GEORGESCU), i, 1287.
Indane, α-halides of (COURTOT and DONDELINGER), i, 654.
***cis*-1:2-Indanediol**, potassium borate of (HERMANS), i, 501.
Indanylamines, optical constants of (COURTOT and DONDELINGER), ii, 274.
Indazole *o*-toluenesulphonate (v. AUWERS), i, 1461.
Indazole, 3-bromo-, nitrobenzoyl derivative, 5:7-*di*- and 3:5:7-*tri*-bromo- (v. AUWERS and LOHR), i, 74.
Indazoles (v. AUWERS and LOHR), i, 73 ; (v. AUWERS and FRESE), i, 1101.
Indazolium salts, quaternary, thermal decomposition of (v. AUWERS and PFUHL), i, 1100.
Indene, polymerides of (STOBBE and FÄRBER), i, 19.
polymerisation and oxidation of the vapour of (BROWN), i, 1258.
bisnitrosochloride (STRAUS and EKHARD), i, 1139.
oxide, chloro- (GOLDSCHMIDT and SCHÜSSLER), i, 498.
Indican, detection and determination of, in urine (GORE), i, 186.
Indicators, influence of alcohol, salts, and temperature on (RICHTER), ii, 237.

Indicators, determination of dissociation constants of (HOLMES and SNYDER), ii, 999.
hydrogen-ion concentration and dissociation constants of (HOLMES and SNYDER), ii, 325.
for use with weak acids and bases (CHABOT), ii, 899.
for determination of hydrogen ions in soils (NIKLAS and HOCK), i, 348.
salt errors of (KOLTHOFF), ii, 596.
Indigo colouring matters (FINGER and KRAFT), i, 73; (REINDEL and RAUCH), i, 438; (SANDER), i, 982.
with a hydrogenated six-membered ring (ARNDT and PUSCH), i, 1312.
of the naphthalene series (FRIEDLÄNDER), i, 956.
Indigotin, action of chromic acid on (EYMER), i, 1174.
metallic derivatives of (KUNZ and STÜHLINGER), i, 1318.
Indigotin, 4:4′-*di*chloro-5:7:5′:7′-*tetra*iodo-, and 5:6:7:5′:6′:7′-*hexa*iodo- (KALB and VOGEL), i, 161.
5:7:5′:7′-*tetra*iodo- (KALB and BERRER), i, 160.
7:7′-*iso*Indigotindisulphonic acid, and its salts (WAHL and FAIVRET), i, 588.
"**Indine**," identity of *iso*indigotin and (SANDER), i, 977.
Indium, spark spectrum of (WEINBERG), ii, 249; (RAO), ii, 610; (CARROLL), ii, 1101.
analysis of (HEYROVSKÝ), ii, 717.
Indole, synthesis of (NENITZESCU), i, 973.
hydrogenation of (WILLSTÄTTER, SEITZ, and V. BRAUN), i, 428.
derivatives, substituted (SEKA), i, 67.
detection of (KOSER and GALT), i, 1510.
determination of, in bacterial cultures (FELLERS and CLOUGH), i, 1015.
Indole, 3-cyano- (GAVRILOV), i, 578.
6-cyano- (KERMACK), i, 68.
Indoles, catalytic synthesis of (KORCZYŃSKI and KIERZEK), i, 973, 1097.
mechanism of Fischer's synthesis of (BODFORSS), i, 698.
catalytic hydrogenation of (V. BRAUN and BAYER), i, 428.
substituted, preparation of (VERLEY and BEDUWÉ), i, 578.
Indole-colouring matters (KÖNIG), i, 1184.
Indole series, syntheses in the (KERMACK), i, 67; (MAJIMA and KOTAKE; MAJIMA and HOSHINO), i, 1450.
Indole-3-aldehyde, derivatives of (MAJIMA and KOTAKE), i, 1450.
Indole-2-carboxydimethylacetalylamide, 6-cyano- (KERMACK), i, 68.
Indole-2-carboxylic acid, 6-cyano-, and its ethyl ester (KERMACK), i, 67.
Indole-6-carboxylic acid (KERMACK), i, 68.
Indole-2:6-dicarboxylic acid, and its ethyl ester (KERMACK), i, 67.
*iso*Indole-2-oxide, 1(or 3)-hydroxy- (GRIFFITHS and INGOLD), i, 1191.
"**3-Indole-2-thionaphthenindigo**," 5′:7′-*di*iodo- (KALB and BERRER), i, 160.
Indolyl-3-acetic acid, and its picrate and derivatives (MAJIMA and HOSHINO), i, 1451.
3-β-Indolylpropionic acid, and its picrate (MAJIMA and HOSHINO), i, 1451.
3-β-Indolylpropionitrile, and its picrate (MAJIMA and HOSHINO), i, 1451.
Indone, *per*chloro-, additive compounds of acenaphthene, durene, fluorene, scatole, and α- and β-naphthols (PFEIFFER, GOEBEL, and ANGERN), i, 271.
Indones (DE FAZI), i, 263, 269.
Indophenols, preparation of (CASSELLA & Co.), i, 397.
oxidation-reduction potentials of (COHEN, GIBBS, and CLARK), i, 25.
Indophenol-α-naphthol-2-sulphonic acid, sodium salt, dissociation constant of (HOLMES and SNYDER), ii, 999.
Indorhodin (KÖNIG), i, 1184.
ψ-**Indoxyl***spirocyclo*pentane, alkali derivatives of (SIDGWICK and PLANT), i, 298.
Induline-6B, synthesis of (KEHRMANN and STANOYÉVITCH), i, 1334.
Infusoria, effect of dyes on the multiplication of (ROBERTSON), i, 1012.
effect of oxycholesterol and cholesterol on growth of (ROBERTSON), i, 1119.
Inosic acid, brucine salt (PEISER), i, 1477.
Inositol (NEEDHAM), i, 192.
Insects, metabolism and development of (FINK), i, 726.
blood of. See Blood.
Insecticides, fatty acids as (SIEGLER and POPENOE), i, 489.
Insulators, liquid, breakdown of (GYEMANT), ii, 1028.
Insulin (CHEADLE), i, 106; (COLLAZO, HÄNDEL, and RUBINO), i, 343; (RENSHAW), i, 617; (ABEL and GEILING), i, 1218; (ABEL, GEILING, ALLES, and RAYMOND), i, 1512.
from fish (MCCORMICK and NOBLE; MCCORMICK), i, 754.
preparation of (SCOTT and BEST), i, 617.
testing preparations of (HÁRI), i, 617.

Insulin, mechanism of the action of (BISSINGER, LESSER, and ZIPF), i, 209; (ISAAC and ADLER; KUHN, BAUR, and HECKSCHER), i, 343; (BAUR and KÜHN), i, 482; (MANSFELD and GEIGER), i, 1016.
co-zymase function of (VIRTÁNEN), i, 753.
distribution of, in normal and depancreatised dogs (NOTHMANN), i, 1219.
antagonism of adrenaline and (GOTTSCHALK; ZONDEK and UCKO), i, 1513.
action of pepsin on (EPSTEIN), i, 1513.
effect of phosphates on action of (DESGREZ, BIERRY, and RATHERY), i, 1016.
and secretin (PENAU and SIMONNET), i, 482.
action of trypsin on (SCOTT), i, 870.
physiological action of (SERONO, TROCELLO, and CRUTO), i, 208.
effect of, on the composition of blood (MAZZOCCO and MORERA; SAVINO), i, 482.
on lactic acid in blood (COLLAZO and LEWICKI), i, 870.
on sugar in blood (HÄUSLER and LOEWI), i, 753.
on lactic acid in blood and tissues (CORI), i, 753; (BEST and RIDOUT), i, 754.
on intermediate carbohydrate metabolism (BRUGSCH and HORSTERS), i, 208.
on cholesterol metabolism (NITZESCU and CADARIU), i, 1364.
muscle tissue and, on dextrose (LUNDSGAARD and HOLBØLL), i, 208.
in diabetes (LAWN and WOLF), i, 483.
on liver glycogen (CORI), i, 753.
on glycolysis (NITZESCU and CADARIU), i, 1352.
on hydrogen-ion concentration in (GIGON), i, 1219.
on lactic fermentation (NOYES and ESTILL), i, 107.
on lactic acid metabolism (COLLAZO and SUPNIEWSKI), i, 342.
on oxidation in muscle (AHLGREN; NITZESCU and COSMA), i, 482.
on functions of oxygenated yeast (FÜRTH), i, 107.
reactions of (STIX), i, 1218; (BENEDICT; EADIE, MACLEOD, and NOBLE), i, 1512.
ninhydrin reaction with (ABDERHALDEN), i, 753.
Insulin, detection of enzymes in (GLASER and WITTNER), i, 209.
biochemical determination of (WYSS), i, 1220.
Interferometric studies (BELTZ and KAUFMANN), i, 1200.
Interferometry, light filter for (FERGUSON), ii, 839.
Intestines, reduction in (BERGEIM), i, 99.
action of atropine and of organic acids on (JENDRASSIK and TANGL), i, 1502.
of lamellibranchs and gastropods, hydrogen-ion concentration in (YONGE), i, 1489.
analyses of gases in cysts of (PASCUAL VILA), i, 329.
Intoxication (DAVIDSON), i, 1503.
Inulin, determination of molecular weight of, in liquid ammonia (SCHMID and BECKER), i, 1386.
Invertase (WILLSTÄTTER, KRAUT, and WENZEL; WILLSTÄTTER and SCHNEIDER), i, 739; (WILLSTÄTTER, SCHNEIDER, and BAMANN), i, 1359.
constitution of (v. EULER and JOSEPHSON), i, 1008.
absorption of the specific radiation of (BARENDRECHT), i, 203.
in leaves (BLAGOVESCHENSKI and SOSSIEDOV), i, 1007.
hydrolysis of sucrose by, in presence of α-methylglucoside (NELSON and FREEMAN), i, 739.
action of, on γ-methylfructoside (SCHLUBACH and RAUCHALLES), i, 1243.
increased content of, in yeast (WILLSTÄTTER, LOWRY, and SCHNEIDER), i, 1214.
immunisation by injection of (BACH, ENGELHARDT, and SAMYSSLOV), i, 1506.
Invert-sugar, mutarotation of (NELSON and BODANSKY), i, 1008.
specific rotation of (ZERBAN), ii, 479.
sweetness of (WILLAMAN, WAHLIN, and BIESTER), i, 1499.
determination of (DE WOLFF), ii, 245.
determination of, in liquids containing sucrose (VAN DEN HOUT, NEETESON, and VAN SCHERPENBERG), ii, 74, 445; (SCHOORL), ii, 445, 828.
determination of boric acid with (GILMOUR), ii, 68.
Iodates. See under Iodine.
Iodine, in atmospheric air (v. FELLENBERG), ii, 316.
occurrence of, in nature (v. FELLENBERG), i, 329, 347; (v. FELLENBERG and GEILINGER), i, 339.

Iodine in rocks and earths (v. FELLENBERG; v. FELLENBERG, GEILINGER, and SCHWEIZER), ii, 321.
in sea foods (TRESSLER and WELLS), i, 183.
evolution of, from sea water (v. FELLENBERG), ii, 306.
intensity of the spectrum of (STEUBING), ii, 330.
absorption spectrum of (FÜCHTBAUER, WAIBEL, and HOLM), ii, 338.
effect of density on the absorption spectrum of (PEROT and COLLINET), ii, 737.
band and line spectra of (CARIO and OLDENBERG), ii, 470.
line spectrum of (FÜCHTBAUER and HOLM), ii, 626.
resonance spectrum of (TURNER and COMPTON), ii, 725; (KRATZER and SUDHOLT), ii, 839.
ultra-violet fluorescence of (OLDENBERG), ii, 88.
vapour, ionisation of, by ultra-violet light (WEST and LUDLAM), ii, 476.
hydrolysis of, measured by the iodine electrode (MURRAY), ii, 555.
liquid, viscosity of (STEACIE and JOHNSON), ii, 376.
adsorption of, by charcoal (WEISSENBERGER and WALDMANN), ii, 655.
by "norit" charcoals (FIRTH and WATSON), ii, 880.
by starch (ANGELESCU and MIRCESCU), ii, 1149.
compound of starch with (MURRAY), i, 889.
blue adsorption compounds with (BARGER and EATON), i, 44.
diffusion of, in pure and mixed solvents (GRÓH and KELP), ii, 1049.
vapour, diffusion of, through nitrogen (MULLALY and JACQUES), ii, 27.
chemical constants of (WOHL), ii, 98.
formation of emulsions by (HOLMES and WILLIAMS), ii, 531.
addition of, to ethylenic compounds (ANDRÉ and FRANÇOIS), i, 356.
catalytic action of, in elimination of hydrogen halides (DESAI), i, 387.
action of, on benzene (COSTEANU), i, 238.
photochemical action of, on *p*-chlorotoluene (SILBERRAD), i, 16.
action of light on the reaction of ferrous salts with (RIDEAL and WILLIAMS), ii, 416.
action of hydrogen sulphide on (PARSONS), ii, 880.
catalysis of the reaction between [illegible] and (ROBERT), ii, 52.
action on metals (PARSONS), ii, 880.

Iodine, action of red phosphorus on carbon disulphide solutions of (TRAXLER and GERMANN), ii, 1087.
effect of light on the reaction of potassium oxalate with (BERTHOUD and BELLENOT), ii, 141.
action of, on pyrrole (G. E. K. and H. E. H. BRANCH), i, 66.
oxidation of uric acid with (FÜRTH), i, 1462.
antilipolytic action of (VOLLMER, SCHMIDT, and SEREBRIJSKI), i, 335.
keeping properties of tincture of (COLLARD), ii, 1168.
absorption, distribution, and determination of, in the thyroid gland (RABINOVITSCH and FRITH), i, 1488; (ABELLES and POPPER; PICKWORTH), i, 1489.
Hydriodic acid, and its sodium salt, conductivities of, in methyl and ethyl alcohols (GOLDSCHMIDT and DAHLL), ii, 128.
oxidation of (WINTHER), ii, 56.
catalytic decomposition of, on the surface of gold (HINSHELWOOD and PRICHARD), ii, 981.
reduction of halogenated malonyl derivatives by (WEST), i, 524.
Iodides, electrolytic preparation of (FISCHER), ii, 808.
reactions between chlorine water and (MÜLLER and JUNCK), ii, 584.
oxidation of, by ferric salts and ferricyanides (WAGNER), ii, 49.
reactions between iodates and (MÜLLER and JUNCK), ii, 585.
reduction of permanganates by (MÜLLER and MÖLLERING), ii, 305.
reaction between persulphates and, in gelatin (RAWLING and GLASSETT), ii, 561.
detection of traces of (WADE), ii, 598.
determination of (SCHULEK) ii, 712.
determination of, microchemically, with bromine and chlorine (STREBINGER and POLLAK), ii, 823.
determination of, volumetrically (SASAKI), ii, 433.
determination of, volumetrically, with iodates (KOLTHOFF), ii, 1000.
determination of, in urine (v. BODÓ), i, 1490.
Iodic acid, use of, in volumetric determination of thiosulphate (RUSZKOWSKI), ii, 156.

Iodine:—
Iodates, presence of in surface waters (HICKETHIER and JACOBUCCI), ii, 1197.
catalysis of the reaction between iodine and (EGGERT), ii, 52.
reactions between iodides and (MÜLLER and JUNCK), ii, 585.
determination of, in the presence of hypoiodites, and bromates (SCHULEK), ii, 1197.
Hypoiodites, determination of, in the presence of iodates (SCHULEK), ii, 1197.
Iodine determination:—
determination of small quantities of (LANGE and WARD), ii, 598.
determination of, in natural products (v. FELLENBERG), i, 329.
determination of, in biological material (KELLY and HUSBAND), i, 183.
Iodoform, compounds of, with quaternary salts (STEINKOPF and BESSARITSCH), i, 495.
Iodomercurates, organic, preparation of, from iodoantimonates (CAILLE and VIEL), i, 68.
Iodometry, standardisation of solutions in (POPOV and WHITMAN), ii, 1093.
benzene as indicator in (KANÔ), ii, 1010.
Ions, refraction and electron constraint in (SMYTH), ii, 843, 1019.
magnetic properties of (FOEX), ii, 345.
emission of, from heated metals (ROY), ii, 731.
liberation of, in gaseous reactions (BREWER), ii, 919.
electric field of, and neutral salt action (DEBYE and MCAULAY), ii, 171.
determination of the charge on (HULL and WILLIAMS), ii, 253.
dimensions of, in aqueous solutions (JABŁCZYŃSKI), ii, 33.
theory of diffusion of, in discharge tubes (SCHOTTKY), ii, 79.
adsorption of (AUDUBERT and QUINTIN), ii, 384; (MUKHERJEE and RAY), ii, 385.
ammoniation of, in aqueous solutions (LOŠAN), ii, 654.
antagonism of (MINAKAMI), ii, 860.
hydration of (FRICKE), ii, 36; (BABOROVSKY), ii, 1151.
mobility of (MESTREZAT and GARREAU), ii, 543.
in air (GRINDLEY and TYNDALL), ii, 80.
in ethyl ether (LOEB), ii, 832.
in gases (LOEB and ASHLEY), ii, 7; (LOEB), ii, 461; (WAHLIN), ii, 615.
in liquids (LINDEMANN), ii, 127.
Ions, diffusible (NORTHROP), i, 864.
electrolytic. See Electrolytic ions.
isotropic, in relation to molecular and crystal structure (HUND), ii, 1132.
negative, mobility of, in flames (WATT), ii, 170.
triatomic, stability and heats of formation of (HEISENBERG), ii, 16.
Ionisation, Bohr's theory of (ANSLOW), ii, 343.
formula for (MILNE), ii, 920.
influence of radiation on (SAHA and SWE), ii, 254; (WOLTJER), ii, 343.
and vapour pressure of gases (BECKER), ii, 342.
energy absorbed by (GREBE), ii, 615.
in air (LEHMANN and OSGOOD), ii, 832.
of electrolytes (SCARPA), ii, 128.
of binary electrolytes (SEMENTSCHENKO), ii, 117.
of weak electrolytes in aqueous-alcoholic solutions (MIZUTANI), ii, 867.
of gases (LANGMUIR and JONES), ii, 169.
by α-particles (GURNEY), ii, 256.
by slow-moving electrons (JESSE), ii, 919.
by collision of electrons (FOWLER), ii, 7; (COMPTON and VAN VOORHIS; TUVE; TATE; WALDIE), ii, 1106.
of salt vapours (KONDRATÉEV), ii, 615.
lecture experiments to illustrate (KOLTHOFF), ii, 819.
thermal, of metallic salts (ROLLA and PICCARDI), ii, 1018.
Ionisation potential, method of estimating (HARTREE), ii, 5.
of rare gases (HERTZ and KLOPPERS), ii, 342.
Ionium (KAMMER and SILVERMAN), ii, 1186.
Ionogens (BLUM), ii, 402.
Ipecacuanha alkaloids (KELLER and BERNHARD), i, 1086.
azo colouring matters of (PALKIN and WALES), i, 1087.
Iridium chloride, compound of carbon monoxide and (MANCHOT and GALL), ii, 232.
halides (KRAUSS and GERLACH), ii, 1089.
*tetr*oxide (KRAUSS and GERLACH), ii, 424.
Irisin, and its derivatives (v. EULER and ERDTMAN), i, 1369.
Iron, pure, structure and thermo-electric power of (GOETZ), ii, 485.
spectrum of (LAPORTE), ii, 4; (CATALÁN), ii, 167; (GOUDSMIT), ii, 611.

Iron, spark spectrum of (L. and E. Bloch), ii, 78, 727.
soft *X*-rays from (Thomas), ii, 336.
magnetic properties of crystals of (Webster), ii, 369.
films, magnetic properties of (Sorensen), ii, 82.
magnetic permeability of (Nikitin), ii, 173.
magnetostrictive effects in (McCorkle), ii, 487.
magnetisation of cobalt, nickel, magnetite, and (Ashworth), ii, 944.
magnetisation of nickel and (de Waard; Peschard), ii, 751.
magnetic, constitution of (Gross), ii, 1134.
magneton numbers of, in complex salts (Welo), ii, 943; (Jackson), ii, 944.
electrolytic behaviour of (Liebreich and Wiederholt), ii, 44.
critical potential in electron emission from (Petry), ii, 1017.
quantitative deposition of, from oxalate electrolytes (Frölich), ii, 604.
thermoelectric behaviour of, at its transition points (Goetz), ii, 187.
atomic heat of (Rodebush and Michalek), ii, 949.
lattice constant of (Blake), ii, 844.
orientation of crystals of, on heating under strain (Elam), ii, 946.
tensile strength of crystals of (Edwards and Pfeil), ii, 946.
corrosion of (Evans), ii, 687; (Whitney; Shipley, McHaffie, and Clare), ii, 688.
tests on (Beeny), ii, 1068.
effect of metals on (Utida and Saitô), ii, 1069.
by salt solutions (Evans), ii, 140.
composition of the rust of (Stumper), ii, 702.
passivity of (Russell), ii, 406.
pyrophoric phenomena in (Smits and Wallach), ii, 276.
as an oxidative catalyst (Warburg), i, 471.
effect of alkaloids on the solution of, in hydrochloric acid (Rane and Prasad), ii, 410.
and its alloys, action of dilute acids on (Girard), ii, 879.
displacement of alkali metals by (Hackspill and Grandadam), ii, 286.
and its oxides, dissociation equilibrium with water vapour and of carbon dioxide over (Hofmann), ii, 537.
Iron, action of, on copper (Siebe; Hanson and Ford), ii, 317.
oxygen in (Tritton and Hanson), ii, 316.
action of sodium chloride on (Girard), ii, 1192.
commercial, constitution of (Wever), ii, 503.
ferrous, equilibrium of, with silver ions (Tananaev), ii, 121.
physiological effects of zinc and (Bertrand and Nakamura), i, 1114.
as oxygen carrier in respiration (Ellinger), i, 1342; (Warburg), i, 1481.
in blood in scurvy (Mourignand, Leulier, and Michel), i, 330.
from hæmoglobin, and its action with digestive ferments (Lintzel; Barkan), i, 1482.
Iron alloys, electrolytic corrosion of (Thornton and Harle), ii, 303.
with carbon, temper-colours of (Tammann and Siebel), ii, 1169.
equilibria of (Daeves), ii, 401.
ternary (v. Vegesack), ii, 535.
with carbon and nickel (Kase), ii, 973.
with carbon and silicon (Becker), ii, 973.
with carbon and titanium (Tamaru), ii, 787.
with cobalt and nickel, expansion coefficients of (Honda and Okubo), ii, 104.
with cobalt and with nickel (Grenet), ii, 973.
with copper and manganese (Ostermann), ii, 1050.
with nickel (Deloraine), ii, 639.
magnetic properties of (Yensen), ii, 372.
thermomagnetic properties of (Peschard), ii, 651.
effect of tension on magnetic properties of (Buckley and McKeehan), ii, 945.
Iron bases (*iron ammines*):—
Aquopentamminoferrous sulphate (Weitz and Müller), ii, 318.
Iron compounds, importance of, in nutrition (Hart, Steenbock, Elvehjem, and Waddell), i, 1354.
pharmacology of (Sabbatani), i, 196.
Iron salts, catalysis of hydrogen peroxide by (Spitalsky and Petin), ii, 53.
action of, on fermentation (Hodel and Neuenschwander), i, 615.

Iron carbonyls (FREUNDLICH and MALCHOW), ii, 231.
oxide, catalytic properties of (BAUDISCH and WELO), ii, 881.
oxides (SIMON and SCHMIDT), ii, 534.
reduction of (HOFMANN), ii, 991.
Ferric salts, oxidation of iodides by (WAGNER), ii, 49.
reduction of, by thiosulphates (HOLLUTA and MARTINI), ii, 305, 702.
precipitation of, by ammonium sulphide (KŘEPELKA and PODROUZEK), ii, 703.
promotion by copper salts in the decomposition of hydrogen peroxide by (ROBERTSON), ii, 690.
detection of, with alloxantin (DENIGÈS), ii, 441.
determination of, in silicates (HACKL), ii, 1004.
chloride, effect of a magnetic field on the reduction of (PARKER and ARMES), ii, 683.
effect of neutral salts on the reaction of stannous chloride with (TIMOFEEV, MUCHIN, and GUREVITSCH), ii, 586.
reaction of potassium thiocyanate with (BAILEY; BAILEY and KIDD), ii, 422.
catalysis of the reaction of sodium thiosulphate with (HOLLUTA and MARTINI), ii, 215.
hydroxide, colloidal, preparation of solutions of (GAVRILOV), ii, 860; (STADNIKOV and GAVRILOV), ii, 861.
sols, coagulation of (GHOSH and DHAR), ii, 778.
and their mixtures with aluminium hydroxide (KÜHNL and PAULI), ii, 776.
action of, on aqueous solutions of gelatin (WINTGEN and MEYER), ii, 524.
precipitation of, electrometrically (BRITTON), ii, 1204.
oxide, effect of temperature on hygroscopicity of (AARNIO), ii, 1157.
equilibrium of magnesia and (FORESTIER and CHAUDRON), ii, 1159.
catalytic activity of (WELO and BAUDISCH), ii, 1071.
hydrosols, electric transport in (PUIGGARI), ii, 129, 792.
sol-gel transformation of (FREUNDLICH and ROSENTHAL), ii, 967.

Iron:—
Ferric oxide, solid solutions of aluminium and chromic oxides in (FORESTIER and CHAUDRON), ii, 534.
reduction of, by hydrogen (BENTON and EMMETT), ii, 216; (KAMURA), ii, 981.
magnetic (ABRAHAM and PLANIOL), ii, 587; (CHEVALLIER), ii, 639; (SOSMAN and POSNJAK), ii, 944.
sulphate, action of alkalis on (KRAUSE), ii, 1192.
Ferrous salts, action of ammonia on aqueous solutions of (WEITZ and MÜLLER), ii, 317.
reaction of cuprous salts with (WELLS), ii, 148.
action of light on the reaction of iodine with (RIDEAL and WILLIAMS), ii, 416.
dissociation equilibria of nitric oxide compounds of (MANCHOT and HAUNSCHILD), ii, 298; (MANCHOT and LINCKH), ii, 317.
reduction of permanganates by (MÜLLER and MÖLLERING), ii, 305.
carbonate and hydroxide, ageing of (BAUDISCH and WELO), ii, 992.
chloride, ammoniate of (BILTZ and RAHLFS), ii, 1191.
hydroxide, solubility of, and its influence on corrosion (WHITMAN, RUSSELL, and DAVIES), ii, 505.
precipitation of, electrometrically (BRITTON), ii, 1203.
nitride (BERGSTROM), ii, 231.
oxide, magnetic form of (FERGUSON), ii, 846.
apparatus for determination of (MEYER), ii, 898.
selenide (MOSER and ATYNSKI), ii, 583.
sulphate, miscibility of ammonium sulphate and (ZWEIGLÓWNA), ii, 189.
reduction of chloric acid and its salts by (HARVEY), ii, 1197.
ammonium sulphate, magnetic properties of (FOEX), ii, 346.
sulphide, colloidal, toxicity of (SABBATANI), i, 196.
telluride (BRUKL), ii, 895.
Ferric acid, and its salts (LOSANA), ii, 1088.

Iron organic compounds:—
Ferrous tetramminethiocyanate (BERGSTROM), ii, 231.
Chloroferrates of ammonium bases (REMY and ROTHE), ii, 1088.
Iron:—
Cast iron, definition of (HONDA), ii, 378.
Steel, definition of (HONDA), ii, 378.
martensitic structure of (SAUERWALD and JACKWIRTH), ii, 22.
secondary crystallisation of (SCHEIL), ii, 122.
recrystallisation of, after hot deformation (HANEMANN), ii, 1134.
specific volume of (ANDREW and HONEYMAN), ii, 278.
temper-brittleness of (GREAVES and JONES), ii, 487.
temper colours of (GALE), ii, 109.
corrosion of (EVANS), ii, 637; (ENOS), ii, 1068.
tests on (BEENY), ii, 1068.
effect of metals on (UTIDA and SAITÔ), ii, 1069.
by salt solutions (EVANS), ii, 140.
effect of carbon and carbides in, on its properties (CAMPBELL and WHITNEY), ii, 274.
action of sodium chloride on (GIRARD), ii, 1192.
carbon, formation of martensite in (HONDA), ii, 972.
quenched carbon, structure of (ENLUND), ii, 486.
determination of chromium and vanadium in (KOLTHOFF and TOMIČEK), ii, 72.
Iron detection, determination, and separation:—
detection of (NICHOLS and COOPER), ii, 715.
detection of, without nitric acid (LONGINESCU and PETRESCU), ii, 1206.
determination of, colorimetrically (WALKER), ii, 717.
determination of, gravimetrically (TANANAEV), ii, 603.
determination of, volumetrically (RUPP), ii, 71; (ASMUS), ii, 1206.
determination of, in presence of chromium and vanadium (KOLTHOFF and TOMIČEK), ii, 72.
determination of, in biological material (MURRAY), i, 183.
determination of, in tissues and in tumours (YABUSOE), i, 724.
determination of, in water (HOPKINS), ii, 1096.
Iron detection, determination, and separation:—
ferric and ferrous, determination of, in magnetites (ADAM), ii, 717.
determination of oxygen in (ROONEY), ii, 327.
separation of, from copper and nickel (ARDAGH and BROUGHALL), ii, 603.
separation of, from manganese and magnesium and from phosphoric acid (MOSER, BRUKL, and VÉN), ii, 329.
separation of, from mercury (SPACU), ii, 1206.
separation of nickel and, in presence of chromium (ROUSSEAU), ii, 441.
separation of zirconium from (WENGER and MÜLLER), ii, 1207.
Iron ores, reduction of, by hydrogen (KAMURA), ii, 981.
analysis of (MCMILLAN and FERGUSON), ii, 441.
Iron wire, magnetic spectrum of (ARKADIEV), ii, 82.
effect of absorption of gas on resistance of (KLEINE), ii, 947.
Irradiation, biochemistry of (KROETZ), i, 178.
Isaria virescens, formation of pigments by (DANILOV), i, 1013.
Isatin, action of, and its α-chloride on hydantoins (HILL and HENZE), i, 305.
condensation of, with rhodanic acids (HANN), i, 987.
mercuric derivative, and 5-bromo-, silver and benzoyl derivatives (HANTZSCH), i, 701.
Isatin, 4-chloro-5:7-*di*iodo- and 5:6:7-*tri*iodo- (KALB and VOGEL), i, 161.
5:7-*di*iodo-, and its derivatives (KALB and BERRER), i, 160.
Isatin series, isomerism of (HELLER and FUCHS), i, 1166.
Isatin-*N*-chloroanilide (RUPE and GUGGENBÜHL), i, 1100.
Isatinrhodamine (SEN and SIRCAR), i, 555.
Isatoic acid, 5:6:7-*tri*iodo-, sodium derivative (KALB and VOGEL), i, 161.
Isatoid, and its silver derivative (HANTZSCH), i, 700.
Isatole, so-called (HANTZSCH), i, 700.
Isoagglutinins in dogs' blood (MCENERY, IVY, and PECHOUS), i, 1344.
Isoelectric point, theory of (KUHN), ii, 117.
Isomeric transformations (NAMETKIN and JARCEVA), i, 1081.
Isomerides, molecular diameters and volumes of (WÖHLISCH), ii, 269.
solubility of (JOHNSTON; ANDREWS, KOHMAN, and JOHNSTON), ii, 852.

Isomerism, influence of the solvent on (DIMROTH), ii, 36; (VIXSEBOXSE), ii, 396.
and polymorphism (PFEIFFER, KALCKBRENNER, and BEHR), i, 547.
dynamic (BURGESS and LOWRY), i, 46; (FAULKNER and LOWRY), ii, 632; (LOWRY; LOWRY and RICHARDS), i, 886.
electron (SWINNE), ii, 922.
geometric (SUGDEN and WHITTAKER), ii, 937.
Isomorphism (WINCHELL), ii, 1122.
Isotopes, band spectra of (MULLIKEN), ii, 833.
and mass spectra of elements (ASTON), ii, 618.
mass ratio of (JAEGER and DIJKSTRA), ii, 83.
in relation to periodic classification of elements (SCHTSCHUKAREV), ii, 462.
separation of (KENDALL and WHITE), ii, 83.
Itaconic acid, esters, action of ammonia on (STOSIUS and PHILIPPI), i, 892.

J.

Jaborandi leaf oil, constituents of (SCHIMMEL & Co.), i, 417.
Jasmine, Spanish. See *Jasminium grandiflorum*.
Jasminium grandiflorum, indole in flowers of (CERIGHELLI), i, 621.
Jatrorrhizine, constitution of (SPÄTH and DUSCHINSKY), i, 1313.
Jaundice, determination of phenolsulphonephthalein in urine in (ABRAMSON), i, 329.
Jellies (v. WEIMARN), ii, 390.
Juglans regia (walnut), phosphorus compounds in (BIELECKI and SZTENCEL), i, 215.
Juline chloroaurate (REINWEIN), i, 189.
Juniper oil, constituents of (PALAZZO and ALINARI), i, 565.
Juniperus communis, constituents of oil from (SIMONSEN), i, 565.
Jute, cellulose of (LEHNE and SCHEPMANN), i, 518.

K.

Kachi-grass oil (RAO and SUDBOROUGH), i, 1164.
Kaempferide trimethyl ether (TASAKI), i, 1444.
Kaki-fruit, ripening of (KOMATSU and ISHIMASA), i, 759.
Kakishibu (KOMATSU, MATSUNAMI, and ISHIMASA), i, 759; (KOMATSU and MATSUNAMI), i, 950.
Kamala, Indian, constitution of (DUTT), i, 1296.
Kaolinite (*kaolin*), structure of (DOMINIKIEWICZ), ii, 1036.
action of heat on (MELLOR and SCOTT), ii, 698.
colloidal (POPE and HAINES), ii, 1152.
sedimentation of suspensions of (KERMACK and WILLIAMSON), ii, 523.
dehydration of (SAMOILOV), ii, 698.
Kerasin in the spleen in Gaucher's disease (LIEB), i, 189.
Keratin, action of alkalis on (BERGMANN and STATHER), i, 847.
bromination of (STARY), i, 847.
Kerosene, from kubiki oil, naphthenic acids from (TANAKA and NAGAI), i, 252.
Kerr effect in gases (SZIVESSY), ii, 15.
Keten, preparation of (HURD and TALLYN), i, 785, 885.
polymeride of (STAUDINGER and STIRNEMANN), i, 787.
action of, on hydroxybenzoic acids (VAN ALPHEN), i, 1149.
Ketens (STAUDINGER), i, 786.
ultra-violet absorption spectra of, and their dimerides (LARDY), ii, 87, 181.
autoxidation of (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 933.
action of, on hydrazine derivatives (VAN ALPHEN), i, 80.
Ketipinic acid. See Diketoadipic acid.
1-Keto-6-acetamido-4-anilino-2-oxythionaphthenylidene-1:2-dihydronaphthalene (SANDER), i, 982.
Keto-alcohol, $C_{10}H_{16}O_2$, and its derivatives, from chenopodium oil (HENRY and PAGET), i, 1163.
1-Keto-4-anilino-2-indoxenyl-1:2-dihydronaphthalene (SANDER), i, 982.
4-Keto-2-anisyl-1:4-dihydropyrimidine, 5-cyano- (MITTER and PALIT), i, 1320.
2-Keto-2-anisyl-1:4-dihydropyrimidine-5-carboxylic acid, ethyl ester (MITTER and PALIT), i, 1320.
β-Keto-bases, preparation of (MANNICH), i, 374.
1-Keto-2-benzylideneoctahydroanthracene (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
trans-**2-Ketodecahydronaphthalene-3-carboxylic acid**, ethyl ester (HÜCKEL and GOTH), i, 402.
Keto-7-demethylo-ψ-corydaline (HAWORTH and PERKIN), i, 971.

3-Keto-4:5:4′:5′-dibenz-2:3′-dicoumaran (FRIES and PUSCH), i, 569.
2-Keto-2:3-dihydropyriminazole, and 5:7-*di*bromo-, and 3-oximino-, and their salts (TSCHITSCHIBABIN), i, 158.
α-Keto-ββ-dimethylglutaric acid, ethyl ester (ROTHSTEIN, STEVENSON, and THORPE), i, 884.
α-Keto-ββ-dimethylpentane-αγ-dicarboxylic acid, and its diethyl ester (ROTHSTEIN, STEVENSON, and THORPE), i, 884.
2-Keto-3:6-di-*o*-nitrophenyl-1:2-dihydro-1:4-diazine (HELLER and SPIELMEYER), i, 838.
2-Keto-3:4-diphenyl-2:3-dihydro-1:3-thiazoleacetylhydrazone, and its hydrobromide (BOSE), i, 1465.
2-Keto-3:4-diphenyl-3:3-dihydro-1:3-thiazoleanisylidenehydrazone (BOSE), i, 1465.
2-Keto-3:4-diphenyl-2:3-dihydro-1:3-thiazolebenzylidenehydrazone (BOSE), i, 1465.
2-Keto-3:4-diphenyl-2:3-dihydro-1:3-thiazolehydrazone, and its derivatives (BOSE), i, 1465.
2-Keto-3:4-diphenyl-2:3-dihydro-1:3-thiazole*iso*propylidenehydrazone (BOSE), i, 1465.
2-Keto-1:5-diphenyl-4-methylpyrrolidine, 5-cyano-, and its 3-carboxylic acid, ethyl ester (HIGGINBOTHAM, LAPWORTH, and SIMPSON), i, 35.
2-Keto-1:5-diphenyl-4-methylpyrrolidine-5-carboxylamide (HIGGINBOTHAM, LAPWORTH, and SIMPSON), i, 35.
2-Keto-4:6-diphenyl-3-*p*-nitrophenyltetrahydropyridine (ALLEN), i, 964.
3-Keto-2:2-diphenyltetrahydroquinoxaline-4-carboxylic acid, ethyl ester, and its acetyl derivative (INGOLD and WEAVER), i, 580.
β-Keto-esters, structure of enolic forms of (SIDGWICK), i, 630.
1-Keto-2-ethylhydrindene, and its semicarbazone (SPEIGHT, STEVENSON, and THORPE), i, 32.
δ-Ketoheptdiethylamide, and its semicarbazone (BLAISE and MONTAGNE), i, 633.
δ- and γ-Ketoheptoic acids, semicarbazones of (CLUTTERBUCK and RAPER), i, 882.
1-Ketohydrindene-3-acetic acid, and its semicarbazone (SPEIGHT, STEVENSON, and THORPE), i, 32.
1-Ketohydrindene-3-carboxylic acid, and its derivatives (SPEIGHT, STEVENSON, and THORPE), i, 32.
Ketohydroxybutyric acid (GOEBEL), i, 1038.
Ketohydroxymethylsuccinic acid (GOEBEL), i, 1038.
1:4-*endo*-Keto-2-keto-3:3-diphenyltetrahydroquinoxaline, and its chloro-derivatives (INGOLD and WEAVER), i, 580.
3-Keto-Δ¹-*p*-menthene oxide (KÖTZ and HOFFMANN), i, 911.
2-Keto-7-methyldihydropyriminazole, salts of (TSCHITSCHIBABIN), i, 159.
4-Keto-2-β-naphthyl-1:4-dihydropyrimidine, 5-cyano- (MITTER and PALIT), i, 1320.
4-Keto-2-naphthyl-1:4-dihydropyrimidine-5-carboxylic acid, ethyl ester (MITTER and PALIT), i, 1320.
Ketone, $C_9H_{14}O$, and its semicarbazone (HENRY and PAGET), i, 1163.
Ketones, absorption spectra of (LECOMTE; PURVIS), ii, 627; (PLOTNIKOV), ii, 837; (LANGEDIJK), ii, 1116.
and their alcoholic solutions (BÖESEKEN, COHEN, and LANGEDIJK), i, 408.
ultra-red absorption spectra of (BONINO), ii, 838.
decomposition of (HURD and TALLYN), i, 885.
reduction of (MEERWEIN and SCHMIDT), i, 1239.
interchange of groups between alcohols and (VERLEY), i, 1034.
preparation of acetylenic hydrocarbons from (BOURGUEL), i, 364.
action of, with aluminium organic compounds (LEONE and BRAICOVIC), i, 677.
and their semicarbazones from naphthenic acids (ZELINSKI and RJACHINA), i, 39.
excretion of, after extirpation of the pancreas (BIERRY and RATHERY), i, 856.
cyclic, preparation of (RIEDEL), i, 407.
condensations of (HILL and HENZE) i, 305.
fatty-aromatic, condensation of 2-aminopyridine with (SCHMID and BANGLER), i, 1459.
saturated aliphatic, *X*-ray investigation of (SAVILLE and SHEARER), ii, 366.
reaction of halogens with (RICE and FRYLING), ii, 556.
unsaturated, absorption spectra and halochromism of (SCHEIBE, RÖSSLER, and BACKENKÖHLER), ii, 352.
α-unsaturated phenolic (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 267.
determination of, by action of sulphites on (ROMEO and D'AMICO), i, 1380.

Ketonic acids, unsaturated (BOGERT and RITTER), i, 255, 816.
γ- and δ-Ketonic acids, and their esters, thermal decomposition of (WINDAUS and BOHNE), i, 552.
δ-Keto-nitriles, reactions of (ALLEN), i, 963.
β-Keto-α-*o*-nitrophenylpropane, α-oximino-, and its derivatives (NEBER, HARTUNG, and RUOPP), i, 1073.
4-Keto-*s*-octahydroanthracene, derivatives of (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
1-Keto-*s*-octahydrophenanthrene, and its derivatives (RIEDEL), i, 407.
Keto-octahydrophenanthrenes, and their derivatives (SCHROETER, VAN HULLE, and MÜLLER), i, 130.
δ- and γ-Keto-octoic acids, semicarbazones of (CLUTTERBUCK and RAPER), i, 882.
4-Keto-oxythionaphthenylidenedihydronaphthalenes, amino- and hydroxy- (FRIEDLÄNDER), i, 957.
γ-Ketopalmitic acid, oxime of (G. M. and R. ROBINSON), i, 355.
γ-Ketopentadienes, photodimerides of derivatives of (STOBBE, FÄRBER, and RAU), i, 1282.
γ-Ketopentadienedicarboxylic acid, methyl ester, dimeride of (STOBBE, FÄRBER, and RAU), i, 1283.
4-Keto-6-phenyldihydropyrimidine (SEIDE), i, 437.
4-Keto-2-phenyl-1:4-dihydropyrimidine, 5-cyano-, and its derivatives (MITTER and PALIT), i, 1319.
2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole, hydrazones of (BOSE), i, 167.
1-Keto-2-phenyl-3:5-dimethyl-1:2-dihydro-2:4:3-naphtha*iso*triazine (GULLAND and ROBINSON), i, 1187.
4-Keto-6-phenyl-1:2-divinylenedihydropyrimidine, and its salts (SEIDE), i, 437.
2-Keto-3-phenyl-5-methylcoumaranyl-3-acetic acid, and its ethyl ester (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
2-Keto-4-phenyl-3-methyl-2:3-dihydro-1:3-thiazoleanisylidenehydrazone, and its hydrobromide (BOSE), i, 1466.
2-Keto-4-phenyl-3-methyl-2:3-dihydro-1:3-thiazole*iso*propylidenehydrazone, and its hydrobromide (BOSE), i, 1466.
2-Keto-4-phenyl-3-α-naphthyl-2:3-dihydro-1:3-thiazolehydrazone, and its hydrobromide (BOSE), i, 1466.
2-Keto-4-phenyl-3-*o*-tolyl-2:3-dihydro-1:3-thiazolehydrazone, and its hydrobromide (BOSE), i, 1466.
α-Ketopimelic acid, and its derivatives (ADICKES), i, 230.
Ketopiperazines, action of alkalis on (LEVENE and PFALTZ), i, 1474.
3-Keto-4:5-pyrido-2:3-dihydrothiophen, and its phenylhydrazone, and 2:2-*di*-bromo-, and its salts (KOENIGS and GEISSLER), i, 167.
2-Ketopyrrolidine-4-carbamide (STOSIUS and PHILIPPI), i, 892.
δ-Ketosebacic acid, semicarbazone of (HÜCKEL and BRINKMANN), i, 259.
Ketosis (WIGGLESWORTH), i, 191.
α-Ketosuberic acid, and its derivatives (ADICKES), i, 230.
3-Keto-1:2:3:4-tetrahydro-1:2:4-benztriazine (GUHA and RAY), i, 1462.
1-Keto-1:2:3:4-tetrahydronaphthalene, transformations of (SCHROETER, ZADEK, and HOFFMANN), i, 677.
1-Ketotetrahydronaphthalene, β-bromo- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
2-hydroxy-, and its acetyl derivative (STRAUS, BERNOULLY, and MAUTNER), i, 1155.
2-nitro-, and 2-oximino-, and their potassium salts (STRAUS and EKHARD), i, 1139.
Ketotetrahydronaphthalenes, nitro-, and their semicarbazones (RIEDEL), i, 407.
4-Keto-*s*-tetrahydrophenanthrene, derivatives of (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
5-Keto-1:2:3:4-tetrahydro*iso*tetrazole, 5-thio- (GUHA and DE), i, 600.
3-Keto-4:6:4′:6′-tetramethyl-2:3-dihydro-2:3′-dicoumaran (FRIES and BARTENS), i, 568.
β-Keto-αα′γγ′-tetramethylglutaric anhydride (STAUDINGER, FELIX, and HARDER), i, 786.
β-Keto-γ-thiol-α-benzoyl-αγγ-triphenyl-*di*thiobutanoic acid, γ-thiolactone of (MEYER), i, 424.
4-Keto-2-tolyl-1:4-dihydropyrimidine, 5-cyano- (MITTER and PALIT), i, 1320.
4-Keto-2:3:3-triphenyldimethylene-1:2-di-imine-1-carboxylic acid, ethyl ester (INGOLD and WEAVER), i, 580.
Ketoximes, acid nature of (PFEIFFER ARMBRUSTER, BACKES, and OBERLIN), i, 270; (PFEIFFER), i, 677.
Kidneys, ratio of alkali salts in blood in disease of (RABINOVITCH), i, 462.
isolated, effect of inorganic salts on the secretion of (EICHHOLTZ and STARLING), i, 860.
Kinetics of chemical reactions (TOLMAN), ii, 799.

Kinetic salt effect, secondary (BRÖNSTED and KING), ii, 1171.
Konyaku sols, action of alkalis on (DOKAN), ii, 967.
Kubiki oil, naphthenic acids from (TANAKA and NAGAI), i, 252.
Kynurenic acid, formation of, in the animal body (MATSUOKA, TAKEMURA, and YOSHIMATSU), i, 731.

L.

Laboratory apparatus (WIGGERS), ii, 319; (STEINKOPF, OHSE, and BUCHHEIM), ii, 590.
Laccase (FLEURY), i, 471, 614.
action of hydrocyanic acid on (FLEURY), i, 1360.
Lactacidogen, formation of, in muscle (EMMRICH and LANGE; EMBDEN, KAHLERT, and LANGE; ABRAHAM and KAHN), i, 728; (DEUTICKE; EMBDEN and ZIMMERMANN), i, 729.
Lactarinic acid, synthesis of (G. M. and R. ROBINSON), i, 354.
Lactation, effect of ultra-violet light on mineral metabolism in (ORR, MAGEE, and HENDERSON), i, 1210.
Lactic acid (*i-ethylidenelactic acid; α-hydroxypropionic acid*), formation of, in muscular exercise (FURUSAWA, HILL, LONG, and LUPTON), i, 92; (HENTSCHEL), i, 728; (FURUSAWA), i, 849; (LYTHGOE and PEREIRA; PEREIRA), i, 1341.
and its anhydrides, equilibrium of, in aqueous solution (DIETZEL and KRUG), i, 1036.
and its calcium salt, bromination of, in presence of light (GHOSH and BASU), i, 1234.
oxidation of, in muscle (v. SZENT-GYÖRGYI), i, 708.
metabolism of. See Metabolism.
destruction of, by yeast (MYRBÄCK and EVERITT), i, 105.
in arthritis and rheumatism (CAJORI, CROUTER, and PEMBERTON), i, 328.
in blood at high altitudes (LAQUER), i, 324.
effect of aliphatic compounds on (KNOOP and JOST), i, 180.
effect of insulin on (COLLAZO and LEWICKI), i, 870.
and tissues, effect of insulin and adrenaline on (CORI), i, 753; (BEST and RIDOUT), i, 754.
in urine after muscular exercise (LILJESTRAND and WILSON), i, 1115.
detection of, colorimetrically (EKKERT), ii, 1007; (KUTTER), ii, 1210.
Lactic acid (*i-ethylidenelactic acid; α-hydroxypropionic acid*), detection of, in fruit juices (BORNTRÄGER), ii, 1007.
determination of, in animal organs (HIRSCH-KAUFFMANN), i, 96; (EMBDEN; MEYERHOF), i, 719.
d-**Lactic acid**, transformation of, into *l*-alanine (FREUDENBERG and HUBER), i, 229.
Lactoisocitric acid (NELSON), i, 619.
Lactone, $C_9H_{14}O_3$, and its derivatives, from *Alstonia* bark (GOODSON and HENRY), i, 1166.
Lactones, catalysis by acids of the formation of (TAYLOR and CLOSE), ii, 1070.
Lactose (*milk-sugar*) (WHITTIER), i, 792.
origin of, in cows (CAMPUS), i, 327.
bromo-, chloro-, and iodo-acetyl derivatives of (HUDSON and KUNZ), i, 1043.
determination of (BIERMAN and DOAN), ii, 245.
Lævulic acid, α-alkyl derivatives of (GAULT and SALOMON), i, 115.
esters, hydrolysis of (SKRABAL, PFAFF, and AIROLDI), ii, 139.
Lævulic acid, chloro-oximino-, and its ethyl ester (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
Lævulosans in plants (COLIN), i, 618.
Lævulose (*d-fructose*; *fruit-sugar*), solution volume and refraction constants of (RIIBER, ESP, and BERNER), i, 635.
effect of phosphates on rotation of (v. EULER and NILSSON), i, 1042.
Lake water. See under Water.
Lamellibranchs, intestines of. See Intestines.
Laminaria flexicaulis, combustion analysis of (LELIÈVRE and MÉNAGER), i, 619.
Lamps, mercury, energy distribution in (FRANKLIN, MADDISON, and REEVE), ii, 809.
gold in (RETSCHINSKY), ii, 465.
constricted mercury arc, for photochemistry (FORBES and HARRISON), ii, 1194.
quartz mercury (REEVE), ii, 234.
Landolt reaction (EGGERT), ii, 52; (EGGERT and PFEFFERMANN), ii, 407.
Lantana camara, constituents of oil from leaves of (MOUDGILL), i, 565.
Lanthanum, spectrum of (GOUDSMIT), ii, 454.
arc spectrum of (PINA DE RUBIES), ii, 612.
Lanthanum alloys with cerium, adsorption of hydrogen by (SIEVERTS and ROELL), ii, 854.

Lanthanum, potassium chromates (CAROBBI), ii, 315.
copper nitrate (CAROBBI), ii, 145.
potassium sulphates (ZAMBONINI and CAROBBI), ii, 222.
thallous sulphates (ZAMBONINI and CAROBBI), ii, 579.
Larkspur. See *Delphinium consolida*.
Lathyrism (ANDERSON, HOWARD, and SIMONSEN), i, 1000.
Laudanidine (SPÄTH and BERNHAUER), i, 294.
l-**Laudanosine** (SPÄTH and BERNHAUER), i, 294.
Laue effect, quantum theory of (ORNSTEIN), ii, 733.
Lauric acid, calcium salt (KLIMONE, v. MOLTINI, and BENEDIK), i, 506.
thallous salt (HOLDE and TAKEHARA), i, 1233.
3-hydroxybenzaldehyde-2-mercuric and 4-hydroxy-*tert*.-butylbenzene-dimercuric esters (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1154.
Lead, absorption spectrum of the vapour of (NARAYAN and RAO), ii, 927.
arc spectrum of (SPONER), ii, 454; (MCLENNAN, YOUNG, and MCLAY), ii, 455; (GIESELER and GROTRIAN), ii, 1103.
ultra-violet absorption spectrum of (ZUMSTEIN), ii, 914.
X-ray absorption coefficient of (WARBURTON and RICHTMYER), ii, 1103.
isotopes of (BRENNEN), ii, 174, 1109; (PERRETTE), ii, 646.
in Norwegian clevite, atomic weight of (GLEDITSCH, DORENFELDT, and BERG), ii, 732.
band spectra of (BIELER), ii, 732.
vapour pressure and entropy of (RODEBUSH and DIXON), ii, 492.
adsorption of, by platinum (MAXTED), ii, 884.
containing radium-Ω for the preparation of formaldehyde (STOLFI), ii, 1111.
effect of colloids in the displacement of, by zinc (GRAY), ii, 578.
possible transformation of, into thallium (RUSSELL), ii, 924.
Lead alloys with antimony and zinc (TAMMANN and DAHL), ii, 535.
with bismuth and cadmium or tin, hardness of (DI CAPUA), ii, 1051.
with cadmium and with sodium, electrolysis of (KREMANN, KIENZL, and MARKL), ii, 132.
with cadmium and thallium (DI CAPUA), ii, 787.
Lead alloys with mercury, electrolysis of (KREMANN, KAPAUN, and BUDAN), ii, 313.
with silver, electrolysis of (KREMANN and BENDA), ii, 679.
Lead compounds, condition of, in the organism (SCREMIN), i, 465.
Lead bromate (GÜNZEL and MARCUS), ii, 1086.
carbonate, heat of formation of (MARSHALL and BRUŽS), ii, 1040.
dissociation of (CENTNERSZWER, FALK, and AWERBUCH), ii, 400.
chloride, solubility of, in acetic acid (HERZ and MARTIN), ii, 283.
solubility of, in chloride solutions (KENDALL and SLOAN), ii, 1052.
chromate, adsorption of ions by (MUKHERJEE and RAY), ii, 385.
hydroxide, equilibrium of sodium hydroxide, plumbite, and (MÜLLER, REISSMANN, and BALLIN), ii, 125.
precipitation of, electrometrically (BRITTON), ii, 1204.
iodide, action of, with zinc sulphate (STOFFELLA), ii, 1064.
nitrate, activity coefficient of aqueous solutions of (RANDALL and VANSELOW), ii, 33.
ageing of dilute solutions of (BERNHARDT), ii, 1003.
nitrite (THIEL and STOLL), ii, 419.
*sub*oxide (VAN ARKEL), ii, 815.
*mon*oxide, structure of (DICKINSON and FRIAUF), ii, 18.
additive compounds of, with lead salts of nitro compounds (AKTIEN-GESELLSCHAFT LIGNOSE), i, 1145.
*di*oxide, crystal structure of (FERRARI), ii, 1125.
colloidal, preparation of, from lead tetra-acetate (GUTBIER and MEYER), ii, 290.
solubility of, in water (REMY and KUHLMANN), ii, 119.
selenide (MOSER and ATYNSKI), ii, 583.
sulphide, equilibria in roasting of (SCHENCK and BORKENSTEIN), ii, 419; (SCHENCK), ii, 1160.
equilibrium of thallous sulphide and (CANNERI and FERNANDES), ii, 887.
*di*sulphide, attempted preparation of (STĚRBA-BÖHM and AUERSPERGROVA), ii, 699.
sulphobismuthite, volcanic (ZAMBONINI, DE FIORE, and CAROBBI), ii, 709.

Lead organic compounds (CALINGAERT), i, 798.
diacetato-diplumbo-bromate (GÜNZEL and MARCUS), ii, 1086.
di-*m*-nitrophenyl *di*nitrate (VORLÄNDER), i, 1255.
di- and tri-phenyl methyls, *cyclo*hexyls, and xylyls (KRAUSE and SCHLÖTTIG), i, 449.
resinates (COFFIGNIER), i, 1294; (UZAC), i, 1295.
tetraethyl, preparation of (MEYER), i, 893.
Lead detection, determination, and separation :—
detection of (KOLTHOFF), ii, 1095.
determination of (RICHARDS; SCOTT), ii, 903.
determination of, electrolytically, in presence of copper (BILTZ), ii, 715.
determination of, in animal tissues (BERNHARDT), ii, 1003; (NAKASEKO and NAKANO), ii, 1205.
separation of antimony, bismuth, and copper from (LASSIEUR), ii, 159.
separation of antimony, copper, tin, and (LASSIEUR), ii, 328.
separation of, from bismuth (FEIGL and ORDELT), ii, 442.
Lead accumulator. See Accumulator.
Lead cathodes. See Cathodes.
Leaves, carbohydrates in, in relation to water content (HORN), i, 1121.
effect of light on the growth and formation of chlorophyll in (PALLADIN), i, 1518.
invertase in (BLAGOVESCHENSKI and SOSSIEDOV), i, 1007.
peptase in (BLAGOVESCHENSKI and BIELOZEVSKI), i, 1009.
autumn, effect of light on decomposition of chlorophyll in (COMBES), i, 1120.
chlorotic and green, mineral matter in (COLIN and GRANDSIRE), i, 1123.
etiolated, effect of light on growth of (PALLADIN), i, 1517.
Lecitiburin (PONCE), i, 97.
Lecithin, synthesis of, in the organism (ECKSTEIN), i, 458.
natural crystalline (ESCHER), i, 1232.
spontaneous decomposition of (KATO and SHINODA), i, 773.
in fatty oils (BOEDTKER), i, 1114.
compounds of, with bile acids and their salts (BOEHRINGER SOHN), i, 824.
and cholesterol in relation to cell membranes (CORRAN and LEWIS), i, 198.
serological differentiation of cholesterol and (SACHS and KLOPSTOCK), i, 1486.
Lecithin, determination of, in blood (GRIGAUT), i, 453.
Lecithins, synthetic (LEVENE and ROLF), i, 92.
Lecithins, bromo- (LEVENE and ROLF), i, 1520.
Lecture experiments to illustrate catalysis and ionisation (KOLTHOFF), ii, 819.
Lemons, insulin-like substances in (FISHER and MCKINLEY), i, 1016.
See also *Cortex limonis*.
Lemon juice, effects of orange juice and of, on calcification (KORENCHEVSKY and CARR), i, 211.
antiscorbutic factor of (ZILVA), i, 1220; (LIOTTA), i, 1365.
Lemon oil, new constituent of (ROMEO), i, 1293.
Lepidine, 2-hydroxy-, condensation of, with aromatic aldehydes (TRÖGER and DUNKER), i, 432.
Leprosy (WRENSHALL and DEAN; DEAN, WRENSHALL, and FUJIMOTO), i, 1414.
Leucine, esters, hydrolysis of, by pancreatic enzymes (RONA and SPEIDEL), i, 103.
ethyl esters of its campholyl and chloroacetyl derivatives, and its amide, acetyl derivative (GRÄNACHER), i, 594.
l-**Leucine,** naturally-occurring, configuration of (KARRER, JÄGGI, and TAKAHASHI), i, 1046.
Leverrierite, schists formed of (CORBETT), ii, 997.
Lichenase, saccharification of cellulose by (KARRER), i, 118.
Lichenin, constitution of (PRINGSHEIM, KNOLL, and KASTON), i, 1385.
Röntgen spectra of cellulose and (HERZOG and GONELL), i, 371.
*iso***Lichenin** (KARRER and JOOS), i, 1028; (PRINGSHEIM), i, 1029; (KARRER), i, 1370.
Lichosan, and its triacetate (PRINGSHEIM, KNOLL, and KASTON), i, 1385.
Lichotriose (KARRER and LIER), i, 793.
Liesegang's rings, theory of (OSTWALD), ii, 530; (DHAR and CHATTERJI), ii, 865.
formation of (DHAR and CHATTERJI; v. WEIMARN), ii, 959.
phenomena of (STEOPOE), ii, 1158.
in gelatin gels (SCOTT-BLAIR), ii, 519.
Light, absorption of, by fluorescent substances (PIENKOVSKI and JABLONSKI), ii, 1031.
absorption of, by electrolytes (v. HALBAN), ii, 1083.

Light, diffusion of, by active and inactive molecules (DE MALLEMANN), ii, 1030.
in liquids (ROCARD), ii, 265.
by methane and its homologues (CABANNES and GAUZIT), ii, 1030.
scattering of, in mixtures of air and carbon dioxide (BANERJI), ii, 1118.
by liquids (RAMAN and RAMDAS), ii, 952, 1046; (KRISHNAN), ii, 1030.
by salt solutions (SWEITZER), ii, 512.
chemical action of (JOHN), i, 1258.
biological action of (HARRIS), i, 1021.
oxidation in (ECKERT), i, 413.
action of, on dibasic acids (VOLMAR), ii, 575.
influence of, on enzymes (PINCUSSEN), i, 468; (PINCUSSEN and KLISSIUNIS), i, 469.
fluorescent, absorption of, by the emitting substance (DUSEBERG), ii, 262.
polarised, photochemical action of (BALY and SEMMENS), i, 12.
in organic vapours (GANESAN), ii, 643.
ultra-violet, measurement of (WEBSTER, HILL, and EIDINOV), i, 750.
irradiation by (HESS, WEINSTOCK, and HELMAN; HESS and WEINSTOCK), i, 750.
growth-promoting properties of air irradiated by (NELSON and STEENBOCK), i, 484.
absorption of, in dilute solutions (GRIEVESON), ii, 472.
absorption of, by organic compounds (KEPIANKA and MARCHLEWSKI; DE LÁSZLÓ), ii, 179.
quantity required to develop a grain of silver bromide (HELMICK), ii, 143.
action of, on dyes and textiles (HEERMANN), ii, 144.
action of, on oils and green vegetables (HESS and WEINSTOCK), i, 212.
action of, on vitamins (ŠPINKA), i, 212.
action of, on alcoholic fermentation (ROMOLO and REMO DE FAZI), i, 475.
germicidal action of (COBLENTZ and FULTON), i, 616.
effect of, on growth and calcification of rats (HUME and SMITH), i, 211.
Lignin (KÜRSCHNER), i, 1387.
chemistry of (POWELL and WHITTAKER), i, 372.
Lignin, sublimation of (KÜRSCHNER), i, 890.
degradation of, by fungi (WEHMER), i, 521.
pine (KLASON), i, 371, 1246.
determination of (SCHWALBE), i, 643.
α-Lignin, homogeneity of (HÄGGLUND), i, 1026.
aldehyde structure of (HÄGGLUND), i, 643.
Lignite, constituents of (CIUSA and GALIZZI), i, 1045.
Lignoceric acid from arachis oil (HEIDUSCHKA and PYRIKI), i, 229.
Ligulin, and its salts (PFAU), i, 572.
Lilium, phytosterol from bulb scales (MIRANDE), i, 872.
Lilium candidum, optical properties of plastids and phytosterol from (MIRANDE), i, 618.
Limestone, hydrogen sulphide in (NENADKEVITSCH; VERNADSKI), ii, 997.
Limit dextrin I. See Dextrin.
Limonene, electrical birefringence of (DE MALLEMAN), ii, 642.
catalytic transformation of (ZELINSKI), i, 146.
action of hydrogen peroxide on (SWORD), i, 1163.
Linamarase (ROSENTHALER), i, 1008.
Linoleic acid, and its anhydride (HOLDE and GENTNER), i, 882.
Linolenic acid, calcium salt (KLIMONT, v. MOLTINI, and BENEDIK), i, 506.
Linoxyn (EIBNER and RIED), i, 1377.
Linseed oil, colloid chemistry of (VOLLMANN), ii, 517.
catalytic oxidation of (SLANSKY), i, 114, 115.
Lipase (CAPPELLI), i, 725.
from papain (SANDBERG and BRAND), i, 1009.
action of, from rats of various ages (FALK, NOYES, and SUGIURA), i, 1360.
activity of, in tissues of different animals (NOYES and FALK; FALK, NOYES, and SUGIURA), i, 471.
gastric (WILLSTÄTTER, HAUROWITZ, and MEMMEN), i, 201.
favourable hydrogen-ion concentration for (WILLSTÄTTER, HAUROWITZ, and PETROU), i, 742.
pancreatic, conditions for action of (PLATT and DAWSON), i, 1506.
from the thyroid (HERZFELD and ENGEL), i, 201.
determination of, stalagmometrically (DEMUTH), i, 103.
determination of, in body fluids and tissues (RONA and LASNITZKI), i, 471.

Lipases, specificity of (WILLSTÄTTER), i, 1008.
Lipins, action of paraldehyde on (COOPER), i, 91.
in liver (SACCHETTO), i, 1357.
Lipoids (FRÄNKEL and KARPFEN), i, 720.
effect of, on osmosis in gels (YUMIKURA; TRAUBE and YUMIKURA), i, 735.
extraction and determination of, in cereals (RASK and PHELPS), ii, 448.
adsorption by mixtures of (SCHÄFER), ii, 1149.
protection of colloids by (BECK), ii, 527.
colloidal, interaction of colloidal fats and (EICHHOLTZ), i, 199.
determination of, in blood-serum (MINOVICI and ILIESCO), i, 452.
determination of the phosphorus of, in cereals (RASK and PHELPS), ii, 328.
Liquids, diffusion of light in (ROCARD), ii, 265.
molecular scattering of light in (KRISHNAN), ii, 1030.
Kerr effect in, in relation to the depolarisation of scattered light (MARTIN), ii, 90.
scattering of light by, and their surface tension (RAMAN and RAMDAS), ii, 952, 1046.
electrical dispersion of (COFMAN), ii, 1060.
potential differences at the junction of (VOSNESSENSKI), ii, 673.
potential differences between air and (FRUMKIN), ii, 544.
fall of potential in, produced by small bubbles of air (KLEEMAN and PITTS), ii, 659.
potential at interfaces of gases with (FRUMKIN), ii, 873.
action of charged particles in (BURTON and CURRIE), ii, 531.
dielectric constants of (SAYCE and BRISCOE), ii, 263; (BELL and POYNTON), ii, 477; (HARRIS), ii, 631.
heat of vaporisation and surface tension of (PLĂCINTEANU), ii, 39.
superheating of (KENRICK, GILBERT, and WISMER), ii, 99.
specific heat of (GHOSH), ii, 275; (SCHULZE), ii, 491; (FOA), ii, 1138.
mutual solubilities of (KABLUKOV and MALISCHEVA), ii, 768.
relation between critical temperature and expansion of (DE KOLOSOVSKI), ii, 646.
coefficient of expansion of (SASLAWSKI), ii, 26.
Liquids, viscosity of, at the boiling point (MACLEOD), ii, 1049.
under pressure (BRIDGMAN), ii, 1143.
containing dissolved gases (LEWIS), ii, 377.
molecular weight and viscosity of (MACLEOD), ii, 498.
absorption of gases by (LEWIS and WHITMAN), ii, 106.
density of (VAN LAAR), ii, 278.
velocity of sound in, and their heat of vaporisation (IONESCU), ii, 644.
kinetic theory of evaporation of (MACLEOD), ii, 784.
vaporisation and changes at contact surface of (SANO), ii, 681.
apparatus for volatilisation of (YANT and FREY), ii, 897.
separated by a membrane, equilibria of (SCHREINEMAKERS), ii, 399.
orientation of molecules on the surfaces of (HARKINS), ii, 1148.
surface tension at the interface of (DU NOÜY), ii, 647.
interfacial properties of, in contact with gases (GILBERT and SHAW), ii, 795.
kinetic theory of surface films of (SCHOFIELD and RIDEAL), ii, 960.
velocity of reaction of two (JABŁCZYŃSKI, WIECKOWSKI, and KLEIN), ii, 410.
saturation pressure of (HERZ), ii, 850.
influence of indifferent gases on the saturated vapour concentration of (POLLITZER and STREBEL), ii, 104.
supersaturation of gases in (KENRICK, WISMER, and WYATT), ii, 105; (WYATT), ii, 504.
molecular interaction in (ANTONOV), ii, 865.
anisotropic, Born's theory of (SZIVESSY), ii, 1123.
binary mixed (FAUST), ii, 29.
composition of (FRANK), ii, 188.
physical properties of, near the critical point (PERRAKIS), ii, 764.
refractive index of (LICHTENECKER), ii, 632.
specific heats of (WILLIAMS and DANIELS), ii, 765.
opalescence of (RAO), ii, 739.
compressibility of (KAR), ii, 970.
effect of a non-volatile solute on the boiling point and partial pressure of (CARROLL, ROLLEFSON, and MATHEWS), ii, 858, 859.

Liquids, binary mixed, vapour pressure and miscibility of (HERZFELD), ii, 1143.
pressure curves of (FRANK), ii, 648.
viscosity of (MACLEOD), ii, 280.
corrosive, distillation flask for (BROWN), ii, 897.
dust-free, preparation of (GARRARD), ii, 704.
fluorescent, modifications of (ASTERBLUM), ii, 1026.
inorganic, surface potential of (WESSEL), ii, 795.
mixed, dielectric constants of (GRÜTZMACHER), ii, 263.
evaporation of (KING and SMEDLEY), ii, 101.
volume of (LORENZ and HERZ), ii, 101.
influence of proximity to critical solution temperature on volume of (FERRAKIS), ii, 29.
organic, refractive index of (EISELE), ii, 264.
double refraction of (VORLÄNDER and WALTER), ii, 183.
electrical double refraction of (BECKER), ii, 755.
electrical resistance of films of (BHATNAGAR, PRASAD, MITRA, and SHRIVASTAVA), ii, 948.
velocity of sound and ratio of ...c heats of (BUSSE), ii, 373.
compressibility of (SCHMIDT), ii, 497; (HEBEISEN), ii, 763.
dielectric constants of (GRENACHER; FRANCKE), ii, 741.
dielectric constant and molecular association of (LANGE), ii, 840.
molecular volume, viscosity, and ionic mobility of (WÖHLISCH), ii, 277.
temperatures of equal viscosity of (HERZ), ii, 1049.
mixed, vapour pressure of (LESLIE and CARR), ii, 1050.
polymerised, diffraction of Röntgen rays by (DE SMEDT), i, 6.
supercooled, entropy of (PAULING and TOLMAN), ii, 952.
ternary mixed, critical solution temperature of (BOUTARIC and CORBET), ii, 103.
determination of solid matter in (v. BÖRNEGG), ii, 324.
Listera ovata, loroglossin in (CHARAUX and DELAUNEY), i, 874.
Lithium (HÜTTIG and SCHLIESSMANN), ii, 1181.
arc spectrum of (AUSTIN), ii, 995.
Lithium, red line in spectrum of (AINSLIE), ii, 450; (GREEN), ii, 1013.
spark spectrum of (SCHÜLER), ii, 339; (WERNER), ii, 1013.
isotope of (COSTA), ii, 619.
radiation and ionisation potentials of (ROLLEFSON), ii, 722.
vapour pressure of, in liquid ammonia (KRAUS and JOHNSON), ii, 389.
equilibrium between barium and, and their fused chlorides (JELLINEK and CZERWINSKI), ii, 124.
Lithium salts, density and refractivity of solutions of (HÜTTIG and KELLER), ii, 963.
Lithium chloride, activity coefficient of (SCATCHARD), ii, 397.
vapour pressure of hydrochloric acid solutions of (YANNAKIS), ii, 401.
fluoride, crystal structure of, and isomorphism of, with magnesium fluoride (FERRARI), ii, 845.
equilibrium of magnesium fluoride and (TACCHINI), ii, 122; (BRUNI and LEVI), ii, 281.
hydride (HÜTTIG and KRAJEWSKI), ii, 296.
potassium sulphate, crystal structure of (BRADLEY), ii, 638.
*mono*sulphide, crystal structure of (CLAASSEN), ii, 845.
mono- and *di*-sulphides (THOMAS and JONES), ii, 58.
tungstate, equilibria of, with alkali tungstates and tungsten trioxide (VAN LIEMPT), ii, 421.
Lithium organic compounds:—
Lithium benzyl (HEIN, PETZCHNER, WAGLER, and SEGITZ), ii, 217.
Lithium determination and separation:—
determination and separation of (SMITH and ROSS), ii, 601.
Lithium minerals, analysis of (GUNTZ and BENOIT), ii, 1202.
Liver, physiology of (BOLLMANN, MANN, and MAGATH), i, 1496.
autolysis of the pulp of (STEPPUHN and UTKIN-LJUBOVZOV), i, 864.
production of urea in autolysis of (MCCANCE), i, 472.
intermediate carbohydrate metabolism in (BRUGSCH and HORSTERS), i, 483.
carbohydrate metabolism and gaseous exchange of (BRUGSCH, HORSTERS, and SHINODA), i, 192.
proteolytic enzymes of (ZACHRISSON), i, 335; (UTKIN-LJUBOVZOV), ii, 864.

Liver, glycogen content of (FRANK and FÖRSTER), i, 1503.
effect of insulin on (CORI), i, 753.
lipins and fats in, during fasting and phosphorus poisoning (SACCHETTO), i, 1357.
metabolism in diseases of (v. FEJÉR and HETÉNYI), i, 725.
influence of, on protein metabolism (ROSENBAUM), i, 464.
effect of alcohols on sugar in (LESSER), i, 613.
detoxicating function of (HÄNDEL), i, 610.
Lobelane, and *di*chloro-, and their salts (WIELAND and HERMSEN), i, 1089.
n- and *iso*-**Lobelanidines**, and their salts and derivatives (WIELAND, SCHÖPF, and HERMSEN), i, 1087, 1089.
Lobelanine (WIELAND, SCHÖPF, and HERMSEN), i, 1087.
n- and *iso*-**Lobelanines**, and their salts (WIELAND, SCHÖPF, and HERMSEN), i, 1088.
Lobelia, alkaloids from (WIELAND, SCHÖPF, and HERMSEN), i, 1087.
Lobelia inflata, alkaloids of (STENZL), i, 347.
Lobelide, chloro-, and its hydrochloride (WIELAND and HERMSEN), i, 1089.
Lobeline, and its benzoate hydrochloride (WIELAND and HERMSEN), i, 1089.
α-**Lobeline**, preparation of (BOEHRINGER SOHN), i, 425.
Locust tree. See *Robinia pseudocacia*.
Loroglossin, occurrence of, in plants (CHARAUX and DELAUNEY), i, 874.
from orchids (DELAUNEY), i, 487.
Lucerne (*alfalfa*), nitrogenous constituents of the juice of (VICKERY; VICKERY and VINSON), i, 1370; (VICKERY and LEAVENWORTH), i, 873.
non-volatile organic acids of (TURNER and HARTMAN), i, 1124.
proteins from leaves of (CHIBNALL and NOLAN), i, 215.
Luminescence, decay and regeneration of (VIOL, KAMMER, and MILLER), ii, 474.
from α-rays, decay of (WITMER), ii, 89.
Lungs, extractives of the (KAPLANSKY), i, 97.
Lupanine, constitution and derivatives of (THOMS and BERGERHOFF), i, 575.
d-**Lupanine**, isolation of, from *Lupinus kingii* (CROUCH), i, 1447.
Lupeose, constitution of (CASTORO), i, 1244.
Lupinane, and its picrate (KALLE & Co.), i, 294.
Lupines, studies on (CROUCH), i, 1447.
Lupinus kingii, isolation of *d*-lupanine from (CROUCH), i, 1447.
Lupinus luteus, enzymic decomposition of arginine in (WALTER), i, 1358.
Lupinus spathulatus, alkaloid from (COUCH), i, 61.
Lupulon, and its derivatives (WÖLLMER), i, 690.
Luteolin acetate (OESTERLE and WANDER), i, 1439.
2:6-Lutidine, 3-amino-, and its hydrochloride (GULLAND and ROBINSON), i, 1186.
Lutidinic acid, phenyl ester (MEYER), i, 836.
4-Lutidone-3-carboxylic acid, ethyl ester (RASSWEILER and ADAMS), i, 299.
4-Lutidone-3:5-dicarboxylic acid, ethyl ester (RASSWEILER and ADAMS), i, 299.
Lycopin, determination of, colorimetrically (CONNELL), i, 214.
Lymph, changes in, in anaphylactic shock (PETERSEN and HUGHES), i, 724.
Lysine, synthesis of, in the organism (MCGINTY, LEWIS, and MARVEL), i, 100.
synthesis of precursors of (MARVEL, MACCORQUODALE, KENDALL, and LAZIER), i, 234.
behaviour of, in the liver (FELIX and ROTHLER), i, 859.
Lysolecithin, acyl derivatives of (LEVENE and ROLF), i, 92.

M.

Magnesium, structure of (COLLINS), ii, 1023.
electrolytic preparation of (RUFF and BUSCH), ii, 569; (HARVEY), ii, 570.
spectrum of (GREEN and PETERSEN), ii, 451.
K-absorption spectrum of (ROBINSON), ii, 614.
vapour, absorption spectrum of (NARAYAN, GUNNAIYA, and RAO), ii, 337; (NARAYAN and RAO), ii, 927.
arc spectrum of (RUARK), ii, 1016.
spark spectrum of (BROWN and BEAMS), ii, 913.
spectra of mixed vapours of the alkali metals and (BARRATT), ii, 927.
optical constants of crystals of (GRABER), ii, 1041.
conductivities of (SCHOFIELD), ii, 273.
potential of (SMITS), ii, 544.

Magnesium, polarisation of, in alkaline solution (JIRSA and LORIS), ii, 45.
isotopes of (PILLEY), ii, 464.
sizes of electron-kernels of aluminium, silicon, sodium, and (TURNER), ii, 349.
influence of, on pressure in the eye (KANEKO), i, 333.
Magnesium alloys with aluminium (DANIELS), ii, 103; (WARIS), ii, 786.
with aluminium and cadmium (VALENTIN and CHAUDRON), ii, 205.
with cerium, adsorption of hydrogen by (SIEVERTS and ROELL), ii, 854.
Magnesium compounds, isomorphism of beryllium compounds and (ZAMBONINI and CAROBBI), ii, 144.
Magnesium boride, action of water and acids on (RAY), ii, 417.
carbonate, dissociation of (CENTNERSZWER and BRUŽS), ii, 206, 685.
equilibrium of, in ammoniacal solutions (LAFONTAINE), ii, 785.
chloride, hydrolysis of aqueous solutions of, in presence of textile fibres (SCHWALBE and SCHEPP), i, 1045.
fluoride, crystal structure of (BUCKLEY and VERNON), ii, 484.
crystal structure and isomorphism of, with lithium fluoride (FERRARI), ii, 845.
equilibrium of lithium fluoride and (TACCHINI), ii, 122; (BRUNI and LEVI), ii, 281.
hydroxide, solubility of (GJALDBAEK), i, 652, 653.
precipitation of, electrometrically (BRITTON), ii, 1203.
rhythmic precipitation of (POPP), ii, 667.
precipitation of aluminium hydroxide with (PARISELLE and LANDE), ii, 903.
oxide (*magnesia*), solubility of, in water (REMY and KUHLMANN), ii, 30.
equilibrium of ferric oxide and (FORESTIER and CHAUDRON), ii, 1159.
condensation of formaldehyde with (SCHMALFUSS and KALLE), i, 116.
action of, on silicates at high temperatures (TAMMANN and GREVEMEYER), ii, 580.
ammonium phosphate, precipitation of, in presence of aluminium (HAHN and SCHEIDERER), ii, 69.
silicate, artificial (DAMIENS), ii, 812.
silicide, atomic structure of (OWEN and PRESTON), ii, 93.
Magnesium sulphate, miscibility of ammonium sulphate and (ZWEIGLÓWNA), ii, 189.
equilibrium of sodium chloride with (KURNAKOV and SHEMTSCHUSHNI), ii, 299.
reduction of (ALTHAMMER), ii, 145.
Magnesium organic compounds, luminescence spectra of (DUFFORD, NIGHTINGALE, and CALVERT), ii, 89.
electrolytic properties of (KONDYREV; KONDYREV and MANOJEV), i, 529.
Grignard's, constitution of (MEISENHEIMER), i, 527.
reducing action of (STAS), i, 1052.
reduction of azobenzene by (GILMAN and PICKENS), i, 1336.
reaction of cupric chloride with (GILMAN and PARKER), i, 237.
action of ethyl hypochlorite on (DURAND and NAVES), i, 1054.
action of methyl cyanoformate on (FINGER and GAUL), i, 1431.
action of, on naphthaquinones (FRANSSEN), i, 1146.
action of, on nitriles (BRECKPOT), i, 14; (BRUYLANTS), i, 15; (CHRISTIAEN), i, 23; (ECTORS), i, 138; (JASPERS), i, 936.
reactions of, with alkyl sulphonates (GILMAN and BEABER), i, 802.
with acyl halides (TISTOHENKO), i, 775.
with di-iodobenzenes (THOMAS), i, 1055.
alkoxides (TERENTIEV), i, 110.
p-anisyl and *p*-tolyl bromides, action of, on camphor (LEDUC), i, 821.
arsines (JOB, REICH, and VERGNAUD), i, 173.
arylamines, action of hydrogen peroxide on (DURAND and NAVES), i, 535.
ethyl bromide, electrical conductivity of (KONDYREV and MANOJEV), i, 529.
compound of diphenylcarbazide and (FEIGL and LEDERER), i, 171.
halides, etherates of (MEISENHEIMER, PIPER, and LANGE), i, 1252.
alkyl halides, reaction of aryl sulphonates with (GILMAN, BEABER, and MYERS), i, 1057.
alkyl and aryl halides, reducing action of (RHEINBOLDT and ROLEFF), i, 542.
aryl halides, luminescence of (DUFFORD, NIGHTINGALE, and CULVERT), ii, 474.
mercapto-halides, reactions of (GILMAN and KING), i, 810.

Magnesium organic compounds:—
α-naphthyl bromide, reactions between inorganic antimony compounds and (MATSUMIYA), i, 1472.
action of methyl cyanoformate on (FINGER and GAUL), i, 1431.
phenyl bromide, action of, on organic acids (PETERS, GRIFFITH, BRIGGS, and FRENCH), i, 543.
action of, on *β*-bromoethylphthalimide and *γ*-bromopropylphthalimide (KOHN and LAKNER), i, 1276.
Magnesium detection, determination, and separation:—
detection of (FEIGL), ii, 435; (MURMANN), ii, 437.
detection of, in small quantities (HAHN), ii, 1095.
determination of (CONGDON and VANDERHOOK), ii, 601; (STEWART and ARCHIBALD), ii, 824.
determination of, nephelometrically (KRISS), i, 852.
determination of, in presence of aluminium (HAHN), ii, 601; JANDER, WENDEHORST, and WEBER), ii, 715.
determination of, in copper alloys with zinc (SCHÜRMANN and SCHOB), ii, 902.
separation of calcium and (RODT and KINDSCHER), ii, 158; (LUFF), ii, 438.
Magnesylpyrrole, syntheses with (ODDO), i, 295, 978; (ODDO and MINGOIA), i, 978.
netic permeability, effect of an alternating field on (SPOONER), ii, 487.
susceptibility and radii of atoms (CABRERA), ii, 624.
and constitution of organic compounds (PASCAL), ii, 624.
Magnetism, researches on (WOLTJER; WOLTJER and ONNES), ii, 1038.
of polymerides (PASCAL), ii, 371.
and valency of complex salts (WELO and BAUDISCH), ii, 1031.
See also Ferromagnetism and Paramagnetism.
Magnetite, transformation of, into hæmatite (WELO and BAUDISCH), ii, 845.
magnetisation of iron cobalt, nickel, and (ASHWÖRTH), ii, 944.
Magnetochemistry (SCHUKAREV), ii, 47, 264.
of cyclic compounds (PASCAL), ii, 1123.
Magneton numbers, spectroscopic (STONER), ii, 618.
Ma Huang, ephedrine from (CHEN and SCHMIDT), i, 194.
Mahua flowers, production of acetone from (GOKHALE), i, 1216.
Mahua oil, bio-genesis of (FOWLER and DINANATH), i, 346.
Maize, influence of soil temperature and moisture on (ECKERSON and DICKSON), i, 217.
electrosilage of (BRAHM), i, 623.
proteins of (ARBUCKLE and THIES), i, 1518.
vitamin-*E* in extracts of (SURE), i, 212.
effect of a diet of, on creatine and creatinine excretion (PALLADIN and KRATINOVA), i, 1514.
effect of nitrogen nutrition on growth of (RIPPEL and LUDWIG), i, 485.
Maize kernels, constituents of (JODIDI), i, 1027.
Malachite, formation of, from basic copper carbonate (HEPBURN), ii, 696.
Malacon, zirconium and hafnium from (MARQUIS, P. and G. URBAIN), ii, 699.
Maleic acid, crystal structure of (YARDLEY), ii, 1126.
conversion of, into fumaric acid (TERRY and EICHELBERGER), i, 780.
halogenation of (TERRY and EICHELBERGER), i, 631.
oxidation of, to tartaric acid (MILAS and TERRY), i, 780.
sodium salt, surface tension of solutions of (RIBAS), ii, 647.
esters, transformation of, into fumaric esters (MEERWEIN and WEBER), i, 1038.
Maleic acid, *di*hydroxy-, decomposition of (GOEBEL), i, 1038.
Maleinimide, *di*iodo- (TERENTIEV and TSCHELINCEV), i, 295.
Malic acid, and its salts, action of boric acid on the rotation of (DARMOIS), ii, 357.
decomposition of, by sulphuric acid (WHITFORD), ii, 559.
and its salts, pharmacology of (UNDERHILL and PACK), i, 1211.
copper salts, optical activity of (DARMOIS), ii, 15.
lead salt, solubilities of (AUERBACH and WEBER), i, 1130.
detection of, in tissues (KLEIN and WEINER), i, 871.
Malic acid, bromo- and chloro- (KUHN and EBEL), i, 781.
d- and *l*-chloro-, and their salts (SONN and ROSINSKY), i, 1237.
Malol (RIVIÈRE and PICHARD), i, 345.
Maloloic acid, and its salts (RIVIÈRE and PICHARD), i, 345.

Malonamides, action of hydrazine on halogen derivatives of (HIRST, MACBETH, and TRAILL), i, 1251.
Malonbenzyl-*p*-tolylamide, and bromo- (WEST), i, 524.
Malon-*p*-bromophenylethylamide, bromo- (WEST), i, 524.
Malon-*p*-bromophenylmethylamide, bromo- (WEST), i, 524.
Malon*iso*butylamide, and bromo- (WEST), i, 524.
Malondi*iso*propylamide, and bromo- (WEST), i, 524.
Malondi-*p*-tolylamide, bromo- (WEST), i, 524.
Malonethylamide, and bromo- (WEST), i, 524.
Malonethyl*iso*propylamide, and bromo- (WEST), i, 524.
Malonhydrazide (HIRST, MACBETH, and TRAILL), i, 1251.
Malonic acid, dissociation constants of (BRITTON), ii, 977.
alkaline earth salts, solubilities of (WALKER), ii, 769.
aniline trihydrogen salt (RAMBECH), i, 385.
esters, velocity of hydrolysis of (SKRABAL and MATIEVIC), ii, 36.
di-β-chloroethyl esters (BENNETT), i, 884.
ethyl ester, addition of, to anils (WAYNE and COHEN), i, 550.
potassium ethyl ester, electrolysis of (ROBERTSON), ii, 1178.
Malonic acid, halogen derivatives, quantitative reduction of, by hydriodic acid (WEST), i, 524.
chloronitro-, ethyl ester (MACBETH and TRAILL), i, 782.
Malonoguanidic acid (MITTER and PALIT), i, 1320.
Malononitrile, halogenation of (OTT and FINKEN), i, 1251.
Malononitrile, amino-, action of nitrous acid on (GRISCHKEVITSCH-TROCHIMOVSKI), i, 1104.
benzoyl derivative and compounds with aldehydes (GRISCHKEVITSCH-TROCHIMOVSKI and SEMENCOV), i, 1069.
Malonphenylmethylamide (WEST), i, 524.
Malon*iso*propylamide, and bromo- (WEST), i, 524.
Malon-*p*-tolylamide, bromo- (WEST), i, 524.
Malon-*p*-tolyl*iso*butylamide, and bromo- (WEST), i, 524.
Malon-*p*-tolylethylamide, and bromo- (WEST), i, 524.
Malon-*p*-tolylmethylamide, and bromo- (WEST), i, 524.
Malon-*p*-tolyl*iso*propylamide, and bromo- (WEST), i, 524.
Maltodextrins, nature of (LING and NANJI), i, 516.
Maltose, octa-acetyl derivative and chloro-, hepta-acetyl derivative (FREUDENBERG, v. HOCHSTETTER, and ENGELS), i, 635.
Mandelic acid, configuration of, and its acetyl, benzoyl, and cinnamoyl derivatives, esters of (FREUDENBERG and MARKERT), i, 1275.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
Mandelonitrile, transformation of, to the *iso*-form (WOOD and LILLEY), i, 400.
Manganese, occurrence of, in soils, plants, and animals (MCHARGUE), i, 1023.
atomic volume of (CAMPBELL), ii, 762.
crystal structure of (WESTGREN and PHRAGMÉN), ii, 1035.
K doublets in spectrum of (SELJAKOV and KRASNIKOV), ii, 914.
spark spectrum of (L. and E. BLOCH), ii, 829.
electro-deposition of (ALLMAND and CAMPBELL), ii, 305; (BŘEZINA), ii, 676.
ionised, ionisation potential of (HARTREE), ii, 918.
allotropy of (BRADLEY), ii, 1124.
Manganese alloys with copper, crystal structure of (PATTERSON), ii, 1130.
with copper and iron (OSTERMANN), ii, 1050.
Manganese compounds in arable soils (BERTRAND), i, 223.
Manganese arsenates (DEISS), ii, 893.
halides, ammoniates of (BILTZ and RAHLFS), ii, 1191.
oxide, colloidal (ANARGYROS), ii, 1152.
*di*oxide, colloidal, formation of, in reduction of permanganates (GELOSO), ii, 661.
oxidation of carbon monoxide and of hydrogen by (FRAZER and GREIDER), ii, 1064.
hydrated, adsorption of silver by (PAVLOV), ii, 507.
phosphates, equilibria of formation of (GRUBE and STAESCHE), ii, 893.
selenide (MOSER and ATYNSKI), ii, 583.
sulphate, equilibrium of aluminium sulphate, water, and (CAVEN and MITCHELL), ii, 396.
Manganic fluoride, orthoarsenate and phosphates (TRAVERS), ii, 586.

Manganese:—
Manganous salts, oxidation of, to permanganic acid (TRAVERS), ii, 585.
hydroxide, precipitation of, electrometrically (BRITTON), ii, 1203.
Permanganates, thermal decomposition of (MOLES and CRESPI), ii, 877.
mechanism of reduction of (HOLLUTA), ii, 49, 407.
effect of a magnetic field on the reduction of (PARKER and ARMES), ii, 683.
reduction of, by arsenious acid (TRAVERS), ii, 585; (GELOSO), ii, 661.
reduction of, by ferrous salts and by iodides (MÜLLER and MÖLLERING), ii, 305.
spectrophotometric determination of the oxidising power of (GOMBOS), ii, 237.
oxidation of unsaturated compounds with (NAMETKIN), i, 1145.
catalysis of the reaction of oxalic acid with (RIDLEY), ii, 689.
Manganese detection, determination, and separation:—
detection of, without nitric acid (LONGINESCU and PETRESCU), ii, 1206.
determination of (JÄRVINEN), ii, 602.
determination of, volumetrically (ANGELESCU), ii, 330; (HECZKO; HACKL), ii, 440.
determination of, in hydrofluoric acid solution (HOLLUTA and OBRIST), ii, 160.
separation of cobalt, nickel, zinc, and (LEMARCHANDS), ii, 242.
Manganese steel, hardness of (BENEDICKS), ii, 188.
Manganolangbeinite from Vesuvius (ZAMBONINI and CAROBBI), ii, 898.
Mannito-aluminates (HERASYMENKO), i, 774.
Mannitol, formation of, by bacterial fermentation of sugars (STILES, PETERSON, and FRED), i, 1216.
solubility of mixtures of boric acid and (HERMANS), i, 501.
fermentation of, by yeast (LVOV), i, 1509.
d-**Mannitol** from *Gardenia turgida* (FORSTER and RAO), i, 1295.
Mannobiose, and its phenylhydrazone (PRINGSHEIM and GENIN), i, 214.
Mannose di*iso*propylidene ether, constitution of (FREUNDENBERG and WOLF), i, 367.
Manometer, glass, for gases attacking mercury (KLEMENC), ii, 995.
lever (FRANK), ii, 995.
mercury (SWAN), ii, 707.
filling of (WEATHERILL), ii, 896.
Manures, iodine in (V. FELLENBERG), i, 347.
artificial, physiological reactions of salts used as (KAPPEN and LUKACS), i, 1523.
determination of urea oxalates in (SABALITSCHKA and KUBISCH), i, 347.
stable, nitrogen in (SANI and GRILLI), i, 218.
Margosa oil, physiological action of (NORD and SCHWEITZER), i, 734.
Marking nut. See *Semecarpus anacardium*.
Marmite, effects of yeast and of, on calcification (KORENCHEVSKY and CARR), i, 211.
Martensite (WHEATLEY), ii, 488.
formation of, in carbon steel (HONDA), ii, 972.
heat of transformation of (SCHNEIDER), ii, 95.
Mass action, constant of (KLEEMAN), ii, 1170.
Mass action law for gases (GILLESPIE), ii, 532.
Masurium (NODDACK, TACKE, and BERG), ii, 939.
Matter, theory of state of (SCHUSTER), ii, 951, 1142.
properties of (WEISSENBERG), ii, 1129.
optical constants of (DARWIN), ii, 2.
and radiation (STERN; WESTPHAL), ii, 926.
living, chemical processes in (CROZIER), i, 101.
representation of analyses of (VERNADSKI), i, 606.
Matteuchia orientalis, constituents of (MUNESADA), i, 620.
Matteucinol (MUNESADA), i, 620.
Mauveine, preparation of (COBENZL), i, 436.
Meat, effect of cooking on (RICHET and MONCEAUX), i, 859.
Meconic acid, manganous salts (VERKADE), i, 421.
m-**Meconine**, nitration of (RÂY and ROBINSON), i, 1153.
Meconines, synthesis of (EDWARDS, PERKIN, and STOYLE), i, 404.
Melaleuca erubescens and *hypericifolia*, oils from (PENFOLD), i, 688.
Melamine, *tricyano-*, and its salts (BURDICK), i, 1048.

Melampyrum arvense and *pratense*, changes in, during growth (BRAECKE), i, 619.
Melanin in urine, and its detection (AUFRECHT), i, 1350.
Melanins (HEINLEIN), i, 449.
absorption spectrum of (GALLERANI), ii, 266.
Melibiose octamethyl ether (SCHLUBACH and RAUCHENBERGER), i, 889.
Melilite, composition of (WINCHELL), ii, 152; (GOSSNER), ii, 821.
Melonic acid, silver and sodium salts (BURDICK), i, 1048.
Melting point and critical temperature (VAN LAAR and LORENZ), ii, 374.
relation between boiling point, critical temperature, and (PRUD'HOMME), ii, 99.
of benzene derivatives (PASTAK), ii, 759.
of halides of the fourth group (HANTZSCH and CARLSOHN), ii, 1044.
of inorganic compounds and of elements (FRIEDERICH and SITTIG), ii, 848.
Membranes, equilibria with (HÜCKEL), ii, 528, 668.
permeability of (BANCROFT and GURCHOT), ii, 110.
permeability and electrical properties of (MICHAELIS), ii, 1150; (FUJITA), ii, 1151.
collodion, diffusion of water through (ADOLPH), ii, 859.
protein films on (HITCHCOCK), ii, 1054.
for physico-chemical analysis (FOUARD), ii, 324.
mammalian serous, electro-endosmosis through (MUDD), i, 468, 1355.
semi-permeable, equilibria with (KAMEYAMA), ii, 1062; (SCHREINEMAKERS), ii, 1062, 1063.
Men, calcium and phosphorus metabolism in (HEINELT), i, 1497.
Mentha pulegium, Δ^1-menthen-3-one in oil from (MORANI), i, 146.
Δ^3-**Menthene** nitrosochloride (MEREJKOVSKI), i, 1291.
Menthol, surface tension of aqueous solutions of (EDWARDS), ii, 387.
l-**Menthol**, catalytic oxidation of (KOMATSU and KURATA), i, 687.
Menthols, and their derivatives, from 2-chloro-5-methyl*cyclo*hexanols (BEDOS), i, 1078.
Menthone, and its derivatives (BEDOS), i, 1078.
condensation of, with *p*-tolualdehyde (SAMDAHL), i, 414.
l-**Menthone**, catalysis of inversion of (KOMATSU and KURATA), i, 1290.
Menthones, catalytic formation of, from *l*-menthol (KOMATSU and KURATA), i, 943.
Menthyl compounds, crystallography of (GREENWOOD), ii, 1037.
l-**Menthyl** sodium *di*thiocarbonate (HOLMBERG and ROSEN), i, 1291.
l-O-**Menthyl-*N*-dimethylthiourethane** (HOLMBERG and ROSEN), i, 1291.
l-O-**Menthyl-*N*-methylthiourethane** (HOLMBERG and ROSEN), i, 1291.
δ-**Menthylsemicarbazide**, and its derivatives (WILSON and CRAWFORD), i, 318.
l-O-**Menthylthiourethane**, and its derivatives (HOLMBERG and ROSEN), i, 1291.
Menyanthes trifoliata, constituents of (ZELLNER), i, 763.
Mercaptans, alkylation of (GILMAN and BEABER), i, 811.
Mercapturic acid, synthesis of, in dogs (COOMBS and HELE), i, 1496.
Mercellulose (DEHNERT and KÖNIG), i, 370.
Mercuration of aromatic compounds (COFFEY), i, 844.
Mercurialis (HAAS and HILL), i, 759.
seeds of (GILLOT), i, 1224.
Mercurialis perennis, extraction of maltose from tubers of (GILLOT), i, 487.
Mercuric salts. See under Mercury.
Mercury, spectrum of (WOOD), ii, 339, 1015; (TURNER and COMPTON; FUKUDA), ii, 613.
shifting of lines in the spectrum of (FUKUDA), ii, 1101.
spectrum of illuminated vapour of (GROSS and TERENIN), ii, 915.
arc spectrum of (TAKAMINE and FUKUDA), ii, 166, 725; (RAYLEIGH), ii, 738; (NICHOLS and TEAR), ii, 917.
and its excitation (ELDRIDGE; HAYNER; MCCURDY, TURNER, and COMPTON), ii, 1102.
atomic and band spectra of (HULTHÈN), ii, 1113.
band spectrum of (HULTHÈN), ii, 11, 470.
resonance spectrum of, in a magnetic field (FERMI and RASETTI), ii, 839.
vapour, resonance fluorescence spectrum of (RUMP), ii, 473.
spark spectrum of (BAYEN), ii, 168; (CARROLL), ii, 1101.
ultra-red spark spectrum of (LAFFAY), ii, 334.

Mercury vapour, fluorescence of (WOOD), ii, 3; (GHOSH), ii, 1026.
resonance fluorescence of (STUART; HANLE), ii, 629.
radiation excited in (HAYNER), ii, 1017.
resonance radiation of (NOYES), ii, 573.
polarisation of the resonance radiation of (FERMI and RASETTI), ii, 473; (RAMANATHAN), ii, 729.
glow discharge in (COMPTON, TURNER, and MCCURDY), ii, 86.
ionisation of (TUVE; TATE), ii, 1106.
by ultra-violet light (ROUSE and GIDDINGS), ii, 919.
photo-electric effect of small drops of (WASSER), ii, 80.
electrolytic behaviour of (LIEBREICH and WIEDERHOLT), ii, 44.
electrolytic purification of (BRUMMER and V. NÁRAY-SZABÓ), ii, 303.
capillary and photo-electric properties of (POPESCO), ii, 952.
influence of colloidal solutions on the electrocapillarity of (ŠANDERA), ii, 659.
electrical resistance of, in magnetic fields (JONES), ii, 754.
polarisation of, in alkaline solution (JIRSA and LORIS), ii, 45.
isotopes of (METCALFE and VENKATESACHAR), ii, 82; (STUMPF), ii, 619; (ASTON), ii, 833.
saturation pressure of (BERNHARDT), ii, 492.
molecular weight of, at varying temperatures (JOUNIAUX), ii, 23.
atoms, metastable forms of (MARSHALL), ii, 339; (RASETTI), ii, 340.
life of excited atoms of (GERLACH and SCHÜTZ), ii, 171.
heat of dissociation of, calculated from the band spectrum (KOERNICKE), ii, 848.
vapour, diffusion of, through nitrogen (MULLALY and JACQUES), ii, 27.
velocity of diffusion of metals in (COHEN and BRUINS), ii, 648.
adsorption of vapours at the surface of (IREDALE), ii, 508.
adsorption coefficient of electrons in vapour of (BRODE), ii, 1020.
adsorption of, by platinum (MAXTED), ii, 384.
vapour, trapping of, with potassium (HUGHES and POINDEXTER), ii, 895.
colloidal, colour of (FEICK), ii, 1153.
action of chlorine on (GETMAN), ii, 59.

Mercury, conversion of, into gold (KAUL), ii, 177; (NAGAOKA), ii, 835, 1111; (STAMMREICH), ii, 1208.
combination of helium and (MANLEY), ii, 57, 314, 696; (LIND and BARDWELL), ii, 1181.
photochemical reactions of, with oxygen and nitrogen dioxide (NOYES), ii, 1081.
purification of (RUSSELL and EVANS), ii, 1205.
distillation apparatus for (ŠVÉDA), ii, 428; (WETZEL), ii, 589.
Mercury alloys (*amalgams*), dilute, electrical conductivity of (WILLIAMS), ii, 946.
velocity of reaction of, with aqueous solutions (KLEIN), ii, 802.
use of, in volumetric analysis (SOMEYA), ii, 904, 1201.
with aluminium, reduction of sugars by (NANJI and PATON), i, 117.
with bismuth, lead, and tin, electrolysis of (KREMANN, KAPAUN, and BUDAN), ii, 313.
with cadmium, with calcium, and with potassium, electrolysis of (KREMANN, MÜLLER, and ORTNER), ii, 132.
with copper and silver (TAMMANN and STASSFURTH), ii, 377.
with potassium and sodium, effect of light on the action of water with (BHATNAGAR, PRASAD, and MUKERJI), ii, 811.
with silver and tin (TAMMANN and DAHL), ii, 502.
with sodium, preparation of (READ and LUCARINI), ii, 587.
electrolysis of (KREMANN, MÜLLER, and KIENZL), ii, 132.
Mercury compounds, antiseptic action of (JOACHIMOGLU and KLISSIUNIS), i, 466.
with ammonia salts (RAY and BANDOPADHYAY), ii, 813.
complex, spectrographic study of (JOB), ii, 887.
Mercury halides, solubilities of, in aqueous glycerol (MOLES and MARQUINA), ii, 283.
ammoniates of (BILTZ and MAU), ii, 1184.
helide (MANLEY), ii, 314, 696.
hydride, band spectrum of (LUDLOFF), ii, 1113.
sulphides, crystal structure of (BUCKLEY and VERNON), ii, 1037.
Mercuric salts, action of hydrogen sulphide on (PÉLABON), ii, 986.
complex halides of (NAIK and AVASARE), ii, 221.

Mercury:—
Mercuric salts, determination of, volumetrically (ELLMAN), ii, 1205.
Mercuric bromide, reduction of, by sodium formate (BOURION and PICARD), ii, 685.
oxybromides, formation of (PÉLABON), ii, 697.
chloride, equilibrium of ammonium and potassium chlorides, water, and (OSAKA and ANDO), ii, 123.
antiseptic action of, in various solvents (HELLENBRAND and JOACHIMOGLU), i, 466.
additive compound of 3:5-dibromo-*o*-toluidine and (HANN and SPENCER), i, 653.
oxychlorides (PÉLABON), ii, 222.
halides, double salts of, with corresponding halides of potassium and sodium (TOURNEUX and PERNOT), ii, 380.
hydroxide, precipitation of, electrometrically (BRITTON), ii, 1204.
iodide, allotropy of (BOKHORST and VAN DER ZEE; DAMIENS), ii, 490.
selenide (MOSER and ATYNSKI), ii, 583.
sulphide, crystal structure of (KOLKMEIJER, BIJVOET, and KARSSEN), ii, 93, 145, 484.
sols, formation of (MOROSOV), ii, 197.
telluride (BRUKL), ii, 895.
Mercurous salts, potentiometric determinations with (MÜLLER and AARFLOT), ii, 65.
action of ammonia on (FEIGL and SUCHARIPA), ii, 1184.
Mercurous chloride, preparation of, in saturated potassium chloride for use in the calomel electrode (EWING), ii, 571.
halides, crystal structure of (HAVIGHURST), ii, 748.
Mercury organic compounds (ALBERT), i, 844.
colloidal (ROSSI and BOCCHI), i, 601.
bactericidal action of (HENRY, SHARP, and BROWN), i, 1006.
unsymmetrical, preparation and decomposition of (KHARASCH and GRAFFLIN), i, 1107.
with 1-phenylpyrrole (PLANCHER and ROSSI), i, 601.
Mercury diaryls, compounds of, with diphenylcarbazide (FEIGL and LEDERER), i, 170.
mercaptide, compounds of mercury sulphide and (SACHS and BALASSA), i, 1034.
Mercury α-naphthyl compounds, reactions of arsenic trichloride with (MATSUMIYA), i, 1339.
di-bromo-, -chloro-, and -nitro-phenyls (HEIN, WAGLER, and RETTER), i, 1341.
di-*m*-chloro-*p*-aminophenyl (VECCHIOTTI and MICHETTI), i, 1058.
Mercuric methyl carbylamine and cyanide (ENKLAAR), i, 1394.
Mercuri-*p*-benzyloxybenzoic anhydride, hydroxy- (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 1473.
Mercuribis(hydroxymercuri-β-naphtholazobenzenesulphonic acid) (PROSKOURIAKOFF and RAIZISS), i, 1108.
Mercuribis(nitrobenzeneazosàlicylic acid) (PROSKOURIAKOFF and RAIZISS), i, 1108.
Mercuribis-*o*-thiolbenzoic acid, and its salts and derivatives (SACHS and BLESSL), i, 1274.
Mercuri-2-chloroanilines (VECCHIOTTI and MICHETTI), i, 1058.
Mercuridihydroxyazobenzenesulphonic acid, *di*hydroxy-, and its potassium salt (PROSKOURIAKOFF and RAIZISS), i, 1107.
Mercurisethoxychaulmoögric anhydride, hydroxy- (DEAN, WRENSHALL, and FUJIMOTO), i, 545.
Mercurihydroxyazobenzenesulphonic acid, *di*hydroxy-, and its sodium salt (PROSKOURIAKOFF and RAIZISS), i, 1108.
Mercuri-β-naphtholazobenzenesulphonic acid, *di*hydroxy- (PROSKOURIAKOFF and RAIZISS), i, 1108.
Mercuri-*o*-phenoxybenzoic anhydride, hydroxy- (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 1473.
Mercurisalicylic acids, 3- and 5-cyano-, and their salts (BOEDECKER and WUNSTORF), i, 1107.
Mercurisulphophenoxide, sodium salt (SACCHARIN-FABRIK AKTIEN-GESELLSCHAFT VORM. FAHLBERG, LIST & Co.), i, 1197.
Mercurisulphotolyloxide, sodium salts (SACCHARIN-FABRIK AKTIEN-GESELLSCHAFT VORM. FAHLBERG, LIST & Co.), i, 1197.
Mercury determination and separation:—
determination of, volumetrically, with potassium cyanide (RUPP, WEGNER, and MAIHS), ii, 716.
separation of copper and (SPACU), ii, 1004.
separation of iron from (SPACU), ii, 1206.

Mercury cathode. See Cathodes.
Mercury lamp. See Lamp.
Meriandra benghalensis, constituents of oil of (PALAZZO and ALINARI), i, 418.
Merrillite in meteorites (SHANNON and LARSEN), ii, 321.
Mesaconic acid, esters, action of ammonia on (STOSIUS and PHILIPPI), i, 892.
Mesitylene, *ωω'-di*bromo-, preparation of (v. BRAUN and ENGEL), i, 382.
Mesityl oxide, *p*-nitrophenylhydrazone of (v. AUWERS and KREUDER), i, 1454.
Mesobilirubin and its copper salt, and bromo- (FISCHER and NIEMANN), i, 1198.
Mesobilirubinogen, absorption coefficient of (NIEMANN), i, 1206.
Mesoporphyrin, conversion of, into ætioporphyrin (FISCHER and MÜLLER), i, 845.
Mesothorium, β-ray spectrum of (BLACK; THIBAUD), ii, 10.
Mesothorium-2, magnetic spectrum of β-rays from (YOVANOVITCH and D'ESPINE), ii, 85.
γ-ray spectrum from (THIBAUD), ii, 85.
period of (WIDDOWSON and RUSSELL), ii, 468.
Metabolism in avitaminosis (SHINODA), i, 610.
influence of sexual glands on (KORENCHEVSKY and CARR), i, 1513.
of aromatic acids (CERECEDO and SHERWIN), i, 100.
human, of ammonium salt and urea (ADOLPH), i, 1353.
calcium, in laying hens (BUCKNER, MARTIN, and PETER), i, 190.
in man (JANSEN), i, 190.
calcium and creatine, effect of parathyroid feeding on (WOODMAN), i, 1210.
calcium and phosphorus, effect of irradiation and diet on (HENDERSON), i, 485.
in men (HEINELT), i, 1497.
carbohydrate (LUNDSGAARD and HOLBØLL), i, 1494.
in relation to blood phosphates (BOLLIGER and HARTMAN), i, 1000.
hormone regulation of (GOTTSCHALK), i, 481.
in the liver (BRUGSCH and HORSTERS), i, 483.
in liver diseases (v. FEJÉR and HETÉNYI), i, 725.
of tumours (C. F. and G. T. CORI), i, 999.
Metabolism, intermediate carbohydrate, effect of insulin on (BRUGSCH and HORSTERS), i, 208.
cholesterol, effect of insulin on (NITZESCU and CADARIU), i, 1364.
creatine and purine, relation of histidine and arginine (ROSE and COOK), i, 1003.
cystine, in children (LIGNAC), i, 610.
of frogs (HSÜ), i, 1208.
of galactose (ROWE and CHANDLER), i, 1354.
of glycerol in diabetes (CHAMBERS and DEUEL), i, 1352.
of glyoxalines (LEITER), i, 1003.
lactic acid, in the animal organism (MEVERHOF and MEIER), i, 612.
effect of insulin and other substances on (COLLAZO and SUPNIEWSKI), i, 342.
in diabetes (COLLAZO and LEWICKI), i, 1364.
mineral, in the animal organism (SASAKI), i, 331.
in lactation, effect of ultra-violet light on (ORR, MAGEE, and HENDERSON), i, 1210.
of cows (MONROE and PERKINS; MILLER, YATES, JONES, and BRANDT), i, 1498.
nitrogen, action of acetoacetic acid on (LABBÉ and LAVAGNA), i, 191.
of ruminants, effect of asparagine and ammonium nitrate on (STARZEWSKA), i, 1115.
and sulphur, relation between (WILSON), i, 729; (SEUFFERT, ITO, and YOKOYAMA), i, 730.
human, effect of iodides on (GRABFIELD and PRENTISS), i, 1002.
of isolated organs, effect of amino-acids on (MÉLON), i, 190.
phosphate (DEMUTH), i, 1497.
phosphoric acid, in the submaxillary gland (CAMIS), i, 191.
phosphorus, of moulds (SCHNÜCKE), i, 204.
of pigments (KORTSCHAGIN), i, 200.
protein, effect of ultra-violet light on (YOSHINE), i, 1356.
influence of liver on (ROSENBAUM), i, 464.
purine, in diabetes (LE BRETON and KAYSER), i, 610.
in man (HARPUDER), i, 613.
of sulphur (LEWIS), i, 1354.
tryptophan (ROBSON), i, 297.
Metacyanilic acid, and its salts and derivatives (WIELAND), i, 1048.
Metaindene (STOBBE and FÄRBER), i, 20.

Metals, structure of (CZOCHRALSKI), ii, 186.
theory of (FRENKEL), ii, 479.
mixed vapours of, absorption spectra of (BARRATT), ii, 927.
and their salts, cathode spectra of (KIMURA and NAKAMURA), ii, 166, 167.
reflective power of (EBELING), ii, 643.
electron theory of (ORNSTEIN), ii, 733.
kinetic theory of conduction of (DAVIES and LIVENS), ii, 630.
theory of conductivity of (CASSEL; WOLF), ii, 942.
electrical conductivity of (SIMON), ii, 94.
and their place in the periodic system (EPSTEIN), ii, 623.
electrical conductivity of films on (TAMMANN and BREDEMEIER), ii, 541.
effect of a magnetic field on the electrical resistance of (WILLIAMS), ii, 753.
photo-electric resistance of, at low temperatures (BARTLETT), ii, 943.
photo-electric effect on films of (GROSS), ii, 344.
used as electrodes, polarisation of (DRESBACH and HOSMER), ii, 1068.
electrodeposition of, from non-aqueous solutions (MÜLLER, PINTER, and PRETT), ii, 882.
deposition of, by molecular radiation (ESTERMANN), ii, 1053.
from pyridine (MÜLLER, HOLZL, KNAUS, PLANISZIG, and PRETT), ii, 133; (MÜLLER, HÖNIG, and KONETSCHNISS), ii, 134.
emission of electrons by (BECKER), ii, 616; (KOLLER), ii, 617.
electrode potential of (HEYROVSKÝ), ii, 404.
potentials of, against pure water (SMITS, GERDING, and KROON), ii, 795.
potential difference between electrolytes and (GUYOT), ii, 402.
potential changes in (DOWLING), i, 796.
fall of potential in the gas emitted from glowing (v. LAUE and SEN), ii, 7.
lattice constants of (DAVEY), ii, 747.
passivity of (BECKER and HILBERG), ii, 405; (RUSSELL), ii, 406.
influence of anions on (ROTHMUND, EISENKOLB, and STEINHERZ), ii, 131.
anodic behaviour and passivity of (SBORGI), ii, 550.
Metals, influence of colloids on cathodic overvoltage of (MARIE and LEJEUNE), ii, 115.
Hall and other effects in (HALL), ii, 846.
ionisation of (PISARSHEVSKI), ii, 210.
escape of positive ions from (GÜNTHER-SCHULZE), ii, 342.
free electrons with (HALL), ii, 252.
emission of electrons from films of, exposed to Röntgen rays (SIMONS), ii, 81.
bombardment of, by electrons (FARNSWORTH), ii, 169.
specific heat of (BEHRENS and DRUCKER), ii, 24.
heats of oxidation of (MOOSE and PARR), ii, 208.
relation between density and temperature of condensation of vapours of (ESTERMANN), ii, 962.
elastic modulus of (WIDDER), ii, 1043.
corrosion of (MAASS and LIEBREICH), ii, 140; (EVANS), ii, 688; (WHITMAN and RUSSELL), ii, 689.
by acids in capillaries (MCCULLOCH), ii, 879.
by carbon tetrachloride (RHODES and CARTY), ii, 1084.
by naphtha solutions of sulphur and its compounds (WOOD, SHEELY, and TRUSTY), ii, 980.
self-diffusion in (HEVESY and OBRUTSHEVA), ii, 500.
velocity of diffusion of, in mercury (COHEN and BRUINS), ii, 648.
hardening of (SCHIEBOLD), ii, 186; (PÓLÁNYI; SACHS), ii, 370.
effect of temperature on hardness of (SAUERWALD and KNEHANS), ii, 279.
adhesion between surfaces of (SAUERWALD and JAENICHEN), ii, 387.
fusion of (JOUNIAUX), ii, 645.
effect of alloying and cold-drawing on crystals of (ROSBAND and SCHMIDT), ii, 488.
cold working of (GEISS and VAN LIEMPT), ii, 372.
tensile strength of, in relation to temperature and cold work (INGALL), ii, 190.
temper colours of (MASON), ii, 108; (BANGHAM and STAFFORD), ii, 138; (EVANS), ii, 288.
transparent films on (MÜLLER), ii, 1039.
deformation and recrystallisation of (GLOCKER), ii, 272.
volume of channels to the surface of (TAMMANN and BREDEMEIER), ii, 388.

Metals, change in volume of, during solidification (ENDO), ii, 281.
periodic dissolution of (HEDGES and MYERS), ii, 309.
equilibrium in systems of, in relation to the ideal solubility curve (ANDREWS and JOHNSTON), ii, 206.
equilibria of fused salts with (LORENZ), ii, 536, 537.
action of ammonium chloride vapour on (HOFMANN, HARTMANN, and NAGEL), ii, 685.
action of iodine on (PARSONS), ii, 880.
action of nitric acid on (DHAR), ii, 315.
affinity of, for sulphur (JELLINEK and ZAKOVSKI), ii, 401.
replacement of, from solutions of their salts (BERGSTROM), ii, 885.
precipitation of, from their salts, by metals in liquid ammonia (KRAUS and KURTZ), ii, 577.
of the cerium group, double nitrates of copper and cadmium with (CAROBBI), ii, 222.
colloidal. See Colloidal metals.
crystalline (GRÜNEISEN and GOENS), ii, 22, 488.
finely-divided, catalysis by (FORESTI), ii, 692.
of Group III, separation of, and phosphoric acid (JÄRVINEN), ii, 602.
heated, emission of ions from (ROY), ii, 731.
of the iron group and their alloys as catalysts (REMY and GÖNNINGEN), ii, 1176.
noble, catalytic action of (ZELINSKI and TUROVA-POLLAK), i, 1052.
of the platinum group, arc spectra of (MEGGERS), ii, 454.
colloidal, catalytic action of (PAAL and BOETERS), ii, 1072; (REMY and GÖNNINGEN), ii, 1176; (DUPARC, WENGER, and URFER), ii, 1177.
and their alloys, synthesis of water with (REMY and SCHAEFFER), ii, 563.
rare, fusion of ores of (SEARS and QUILL), ii, 580.
determination and separation of (MOSER and LESSING), ii, 718.
strained, Röntgen ray analysis of (ONO), ii, 746.
determination of, in amalgams (RUSSELL and EVANS), ii, 1205.
Metal ammines, composition of ions of (DE WIJS), ii, 889.
Metal ammoniums (KRAUS and JOHNSON), ii, 389.
Metal wires, influence of occluded gas on the electrical resistance of (SEXL), ii, 642.
exploded, spectra of (SMITH), ii, 1017.
heated, emission of electrons by (ROLLA and PICCARDI), ii, 1018.
Metallic bromides, decomposition potentials of, in molten aluminium bromide (ISBEKOV), ii, 796.
chlorides, vapour pressure of (MAIER), ii, 850.
use of, in decomposition of aliphatic acids (MAILHE), i, 503.
fused, electrical conductivity of (BILTZ and KLEMM), ii, 127.
couples, decomposition of water by (HEDGES and MYERS), ii, 306.
halides, ultra-violet absorption spectra of (GETMAN), ii, 837.
reduction of, by hydrogen (DE CARLI), ii, 51.
dithiolated, heats of chelation of (MORGAN, CARTER, and HARRISON), ii, 1042.
hydroxides, electrometric precipitation of (BRITTON), ii, 1203, 1204.
ageing of (FRICKE), ii, 578.
amphoteric (JANDER and SCHULZ), ii, 701.
iodides, action of $\alpha\beta$-dibromo-compounds on (VAN DUIN), i, 802; (CONANT, KIRNER, and HUSSEY), i, 803.
and selenides, preparation of (FISCHER), ii, 808.
lustre (BANCROFT and ALLEN), ii, 658.
oxides, adsorption of vapours by (PEARCE and ALVARADO), ii, 381.
dissociation of (BORN), ii, 785.
reduction of, by alkali cyanides (HACKSPILL and GRANDADAM), ii, 419.
lower, preparation of (FRIEDRICH and SITTIG), ii, 889.
solid, reactions between (BALAREFF), ii, 893.
salts, scattering of light by solutions of (SWEITZER), ii, 512.
electrical conductivity as an indicator in titration of, with alkali hydroxides (DEMJANOVSKI), i, 1113.
temperature of vapours above boiling solutions of (BAHLKE and WILSON), ii, 514.
thermal ionisation of (ROLLA and PICCARDI), ii, 1018.
vapour pressure of (LORENZ and HERZ), ii, 493.
molecular volumes of, at the melting point (LORENZ and HERZ), ii, 840.

Metallic salts, solubilities of, in organic solvents (MÜLLER), ii, 380.
solvolysis of, in sulphuric acid (DAVIDSON), ii, 505.
compounds of, formed in the electric arc (PECZALSKI and MOKRZYCKI), ii, 814.
oxidation of, by oxygen (REINDERS and VLES), ii, 308.
polyatomic, dissociation of (SASAKI), ii, 512.
solid, electrical conductivity of, in relation to their spectra (VAILLANT), ii, 165.
separation of, by fractional precipitation (RUFF and HIRSCH), ii, 992.
See also Salts.
sulphates, thermal decomposition of (MARCHAL), ii, 870, 1162.
sulphides, electrolytic preparation of (FISCHER), ii, 807.
of the heavy metals, analysis of (FEIGL, PAVELKA, and SCHACHERL), ii, 70.
tellurides, preparation of (BRUKL), ii, 895.
Metallography, modified reflexion in (CZOCHRALSKI), ii, 487.
Metastability, in relation to physical constants (COHEN), ii, 1138.
and allotropy (COHEN and HELDERMAN), ii, 23; (COHEN and MOESVELD), ii, 374, 950.
Meta-stationary states (SMEKAL), ii, 1022.
Meteorites, merrillite and chlorapatite in (SHANNON and LARSEN), ii, 321.
iron–nickel, structure of (VOGEL), ii, 709.
Methæmoglobin (CONANT and FIESER), i, 455.
formation of (NEILL and HASTINGS; KLEIN), i, 709; (MEIER), i, 1476.
re-formation of (SAKURAI), i, 1199.
oxidation-reduction of (NEILL), i, 868, 993.
oxygen content of (QUAGLIARIELLO), i, 89; (NICLOUX and ROCHE), i, 993.
determination of (CONANT and FIESER), i, 456.
Methane, catalytic formation of (CHAKRAVARTY and GHOSH), ii, 1175.
equilibria in formation of (NEUMANN and JACOB), ii, 532.
and its homologues, diffusion of light by (CABANNES and GAUZIT), ii, 1030.
critical potential of, and its ultra-violet absorption (GLOCKER), ii, 262.
influence of vapours of organic liquids on the inflammability of mixtures of air and (JORISSEN and MEUWISSEN), ii, 53.
Methane, halogen derivatives, reactivities of, with various reagents (PETRENKO-KRITSCHENKO, TALMUD, BUTMI DE KATZMAN, and GANDELMAN), ii, 802.
bromonitro-, reaction of aromatic compounds with, in presence of aluminium chloride (SHERRILL), i, 237.
bromo*di*nitro-, potassium salt (TRÉNEL and WILKENDORF), i, 112.
bromo*tri*nitro- (SCHMIDT, BARTHOLOMÉ, and ASMAS), i, 136.
Methanedisulphonic acid, barium salt (KOLKER and LAPWORTH), i, 353.
Methanesulphonic acid, chlorobromo-, optical activity of (READ and MCMANUS), i, 1126.
Methanesulphonyl groups, directing influence of (TWIST and SMILES), i, 894.
Methazonic acid, cyano-. See Propionitrile, β-nitro-α-oximino-.
Methenyl-5′-(5′-methyl)hydantoin-5-hydantoic acid, bromo- (DAVIDSON and JOHNSON), i, 584.
Methiodo-*o*-methyl-ψ-geneserolimethine (POLONOVSKI and POLONOVSKI), i, 293.
Methoxyacethydroxamic acid, and its potassium salt and derivatives (JONES and POWERS), i, 14.
2-Methoxyacetophenone, 4:6-*di*hydroxy- (SONN and BÜLOW), i, 1268.
***p*-Methoxyacetophenone**, phenylhydrazones of (KORCZYŃSKI and KIERZEK), i, 973.
Methoxyacetophenoneoximes (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
4(5′-Methoxy-4′-acetoxybenzylidene)-2-phenyl-5-oxazolone, 3′-nitro- (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
Methoxyacetylanthranils (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
γ-Methoxyallene (BOURGUEL), i, 770.
Methoxyallyloxybenzaldehydes (SONN and PATSCHKE), i, 1280.
6-Methoxyanthraquinone, 8-amino-1:8-*di*hydroxy-, 1:8-*di*hydroxy-, and 1:3:8-*tri*hydroxy- (EDER and HAUSER), i, 563.
3-Methoxyatophan. See 3-Methoxy-2-phenylquinoline-4-carboxylic acid.
3-Methoxybenzaldehyde, bromo and nitro derivatives, and their derivatives (HODGSON and BEARD), i, 675.
4-Methoxybenzaldehyde, 5-nitro-2-hydroxy-, and its derivatives (RAO, SRIKANTIA, and IYENGAR), i, 675.

Methoxybenzaldehydes, bromohydroxy- and nitrohydroxy-, and their *p*-nitrophenylhydrazones (RUBENSTEIN), i, 1279.

4-Methoxybenzamide, 3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.

***p*-Methoxybenzil**, oximes of, and their derivatives (MEISENHEIMER, LANGE, and LAMPARTER), i, 1073.

Methoxybenzils, *di*hydroxy-, and their diacetyl derivatives (MARSH and STEPHEN), i, 1158.

3-Methoxybenzoic acid, 4-bromo- (HODGSON and BEARD), i, 675.

4-Methoxybenzoic acid, 5-bromo-2-amino-, and its copper salt (GRIFFITH and HOPE), i, 827.

***o*- and *m*-Methoxybenzoic anhydrides** (RULE and PATERSON), i, 29.

Methoxybenzopyrones, 3-hydroxy- (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.

2-Methoxy-*p*-benzoquinoneimine (KEHRMANN and HOEHN), i, 561.

1-Methoxy-2:3-benzoxazine (GRIFFITHS and INGOLD), i, 1190.

***o*-Methoxybenzoyl cyanide** (MARSH and STEPHEN), i, 1158.

4-Methoxybenzoyl chloride, 3:5-*di*nitro- (LINDEMANN and WESSEL), i, 1099.

4-Methoxybenzoylformic acid, 2-bromo-2-hydroxy- and 2-hydroxy- (FRIES and SAFTIEN), i, 570.

Methoxybenzoyloxybenzamides (ANSCHÜTZ, ASCHENBERG, KUCKERTZ, KRONE, RIEPENKRÖGER, and ZERBE), i, 666.

6-Methoxybenzthiopyrone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.

2-*o*-Methoxybenzylidenecoumaranone, 4:6-*di*hydroxy-, diacetyl derivative, and its derivatives (KALFF and ROBINSON), i, 1303.

2-Methoxybenzylidenediacetophenone (DILTHEY and FLORET), i, 56.

***p*-Methoxybenzylidenemalonic acid**, ethyl ester (CHRZASZCZEWSKA), i, 956.

Methoxybenzylmandelic acids (MALKIN and ROBINSON), i, 559.

3-*p*-Methoxybenzyloxindole (WINDAUS and EICKEL), i, 33.

Methoxybenzyloxybenzaldehydes (SONN and PATSCHKE), i, 1280.

Methoxy-γ-bromo-β-methoxypropylbenzenes (SCHMIDT, BARTHOLOMÉ, and ASMAS), i, 136.

Methoxychelidonine, and its salts and derivatives (GADAMER and WINTERFELD), i, 238.

4-Methoxy-ω-chloroacetophenone, 5-bromo-2-hydroxy- (FRIES and SAFTIEN), i, 570.

***p*-Methoxy-γ-chlorallylbenzene** (BERT), i, 804.

3-Methoxy-6-ββ-*di*chloroethyl-*p*-toluic acid (MELDRUM and ALIMCHANDANI), i, 1272.

3-Methoxy-6-βββ-*tri*chloro-α-hydroxyethyl-*p*-toluic acid, and its calcium salt and acetyl derivative (MELDRUM and ALIMCHANDANI), i, 1272.

Methoxychromanones, and their derivatives (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.

3-Methoxycinnamic acid, α-amino-β-5-nitro-4-hydroxy-, α-benzoyl derivative (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.

***p*-Methoxycinnamic acids**, bromo- (HARIHARAN and SUDBOROUGH), i, 1149.

4-Methoxycinnamic anhydride (ROBINSON and SHINODA), i, 1301.

***p*-Methoxycinnamylidene-*m*-nitroacetophenone** (GIUA), i, 1283.

6-Methoxycoumaran-2:3-dione (FRIES and SAFTIEN), i, 570.

6-Methoxycoumaran-3-one semicarbazone (SONN and PATSCHKE), i, 282.

6-Methoxycoumaran-3-one, bromo and chloro derivatives, and their derivatives (FRIES and SAFTIEN), i, 570.
2-oximino- (FRIES and SAFTIEN), i, 570.

6-Methoxycoumaran-3-one-2-*p*-aminoanil (FRIES and SAFTIEN), i, 571.

6-Methoxycoumaran-3-one-2-anil, and 5-bromo- (FRIES and SAFTIEN), i, 570.

6-Methoxycoumaran-3-one-2-*p*-dimethylaminoanil (FRIES and SAFTIEN), i, 570.

6-Methoxy-*m*-cresol, 5-bromo-2:4-*di*nitro- (KOHN and MARBERGER), i, 1265.

α-Methoxy-αβ-dibenzoylethylene (CONANT and LUTZ), i, 682.

α-Methoxy-αβ-di-(4-chlorobenzoyl)-ethylene (CONANT and LUTZ), i, 682.

α-Methoxy-αβ-di-(6-chloro-*m*-toluoyl)-ethylene (CONANT and LUTZ), i, 682.

7-Methoxy-4:3′-dicoumaryl (DEY and ROW), i, 150.

α-Methoxy-αβ-di-(2:4-dimethylbenzoyl)-ethylene (CONANT and LUTZ), i, 682.

5-Methoxy-1:2-dihydrocoumarone
3:6-*di*hydroxy-, and its diacetyl derivative (DEAN and NIERENSTEIN), i, 281.

3-Methoxy-9:10-dihydrophenanthrene-9-carboxylic acid, and its derivatives (WINDAUS and EICKEL), i, 33.

5-Methoxy-1:2-dihydro-3:6-quinocoumarone (DEAN and NIERENSTEIN), i, 281.

Methoxydihydrothebenol (SPEYER and ROSENFELD), i, 962.

2-Methoxy-3:5-dimethylacetophenone, and its oxime (V. AUWERS, LECHNER, and BUNDESMANN), i, 266.

4′-Methoxy-4″-dimethylamino-2:4-distyrylbenzopyrylium chloride, 7-hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.

7-Methoxy-4′-dimethylamino-2-styryl-1-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.

Methoxydimethyldehydroindoles, and their picrates (SPÄTH and BRUNNER), i, 574.

Methoxydimethyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.

Methoxydiphenylacetic acid (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 934.
and its acid chloride (KAHIL and NIERENSTEIN), i, 52.

4-Methoxy-2:5-diphenylfuran (CONANT and LUTZ), i, 682.

2-Methoxydiphenylmethyl chloride (KAHIL and NIERENSTEIN), i, 52.

2-Methoxydiphenylmethyl chloromethyl ketone (KAHIL and NIERENSTEIN), i, 52.

***o*-Methoxydiphenyl-α-naphthylcarbinol**, and its chloride (GOMBERG and MCGILL), i, 1270.

***o*-Methoxydiphenyl-α-naphthylmethyl**, and its *per*oxide (GOMBERG and MCGILL), i, 1270.

β-Methoxy-αγ-diphenylpropane, α-hydroxy- (MALKIN and ROBINSON), i, 559.

***p*-Methoxydiphenylsuccinic acid**, and its nitrile (BRAND and LOEHR), i, 684.

Methoxy-2:4-distyrylbenzopyrylium chlorides, *di-* and *tri*-hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.

***p′*-Methoxydistyryl ketone**, *p*-nitro- (PFEIFFER), i, 409.

Methoxyditoluimides, hydroxy- (ANSCHÜTZ and ASCHENBERG), i, 667.

α-Methoxy-αβ-ditoluoylethylene (CONANT and LUTZ), i, 682.

α-Methoxy-αβ-di-(2:4:6-trimethylbenzoyl)-ethylene (CONANT and LUTZ), i, 682.

3-Methoxy-2-ethoxybenzaldehyde, nitration of (RUBENSTEIN), i, 1428.

4-Methoxy-2-ethoxybenzaldehyde, and 5-nitro-, and their derivatives (RAO, SRIKANTIA, and IYENGAR), i, 676.

4-Methoxy-3-ethoxybenzaldehyde, and its oxime (SPÄTH and BERNHAUER), i, 294.

4-Methoxy-3-ethoxybenzamide (SPÄTH and BERNHAUER), i, 294.

6-Methoxy-7-ethoxy-3:4-dihydro*iso*quinoline, and its picrate (SPÄTH and DOBROWSKY), i, 1085.

7-Methoxy-6-ethoxy-3:4-dihydro*iso*quinoline, and its picrate (SPÄTH and DOBROWSKY), i, 1085.

Methoxyethoxy-1-keto-1:2:3:4-tetrahydro*iso*quinolines (SPÄTH and DOBROWSKY), i, 1086.

3-Methoxy-8-ethoxy-2-*p*-methoxyphenylbenzopyrylium salts (RIDGWAY and ROBINSON), i, 55.

4′-Methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride, 3-chloro- (RIDGWAY and ROBINSON), i, 693.

α-3-Methoxy-4-ethoxyphenylethane, β-amino-, and its derivatives (SPÄTH and DOBROWSKY), i, 1085.

α-4-Methoxy-3-ethoxyphenylethane, β-amino-, and its derivatives (SPÄTH and DOBROWSKY), i, 1085.

3-Methoxy-4-ethoxystyrene, ω-nitro- (SPÄTH and DOBROWSKY), i, 1085.

4-Methoxy-3-ethoxystyrene, ω-nitro- (SPÄTH and DOBROWSKY), i, 1085.

β-Methoxyethylcarbimide (JONES and POWERS), i, 14.

5-Methoxy-3-ethyl-4:5-dihydrouric acid, 4-hydroxy- (BILTZ and PEUKERT), i, 1463.

4′-Methoxyflavanone (HATTORI), i, 1444.

3-Methoxyflavone, 7-hydroxy- (ALLAN and ROBINSON), i, 149.

4′-Methoxyflavone (HATTORI), i, 1444.

7-Methoxy*iso*flavone (BAKER and ROBINSON), i, 1299.

2-Methoxy-Δ^1-*cyclo*hexene, 1-cyano- (V. AUWERS, BAHR, and FRESE), i, 312.

7-Methoxy-3-homoveratryl-2-methylchromone (BAKER and ROBINSON), i, 926.

8-Methoxy-2-α-hydroxylcinnamylmethylquinoline hydrochloride (TRÖGER and DANEHL), i, 975.

3-Methoxy-2-β-hydroxy-β-*o*-hydroxyphenylethylquinoline, and its diacetyl derivative (TRÖGER and DUNKER), i, 434.

3-Methoxy-2-β-hydroxy-β-*p*-methoxyphenylethylquinoline, and its salts (TRÖGER and DUNKER), i, 434, 975.

3-Methoxy-2-β-*p*-hydroxy-*m*-methoxystyrylquinoline, and its salts (TRÖGER and DUNKER), i, 434.

4-Methoxy-2-β-*p*-hydroxy-3′-methoxystyrylquinoline, and its hydrochloride (TRÖGER and DUNKER), i, 434.

8-Methoxy-2-β-hydroxy-β-*o*- and -*m*-nitrophenylethylquinolines, and their salts (TRÖGER and DANEHL), i, 974

3-Methoxy-2-β-hydroxy-β-phenylethylquinoline, and its salts (TRÖGER and DUNKER), i, 434.
4-Methoxy-2β-*o*-hydroxystyrylquinoline (TRÖGER and DUNKER), i, 434.
3-Methoxy-2-β-*mp*-*di*hydroxystyrylquinoline, and its *per*chlorate (TRÖGER and DUNKER), i, 434.
1(or 3)-Methoxy*iso*indole-2-oxide (GRIFFITHS and INGOLD), i, 1191.
6-Methoxy-3-keto-2-coumaran-6′-dimethylaminobenzthiazole-2′-spiran, and its derivatives (FRIES and SAFTIEN), i, 571.
***ar*-7-Methoxyketotetrahydronaphthalenes**, and their derivatives (RIEDEL), i, 407.
Methoxyl groups, determination of microchemically (SMITH), ii, 905.
1-Methoxy-3-*o*-methoxyphenyl-5-*p*-dimethylaminostyryl-$\Delta^{1,5}$-*cyclo*hexadiene-2-carboxylic acid, ethyl ester (HEILBRON, FORSTER, and WHITWORTH), i, 1285.
7-Methoxy-4-*p*-methoxystyrylcoumarin (DEY and ROW), i, 953.
4-Methoxy-2-β-*p*-methoxystyrylquinoline, and its salts (TRÖGER and DUNKER), i, 434.
4-Methoxy-2-β-*o*-methoxystyrylquinoline, and its dibenzyl ether (TRÖGER and DUNKER), i, 434.
Methoxymethylacetophenones, and their oximes (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
Methoxymethylanthranilic acids, and their amides (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
3-Methoxy-2-methylbenzopyrone, 7-hydroxy-, and its acetyl derivative (ALLAN and ROBINSON), i, 148.
Methoxymethylcarbimide (JONES and POWERS), i, 14.
3-Methoxy-2-methylchromone, 5:7-*di*hydroxy- (KALFF and ROBINSON), i, 1303.
Methoxymethylene-*p*-bromoaniline. See Methyl *iso*formo-*p*-bromoanilide.
3-Methoxy-6:7-methylenedioxy-2-*mp*-dimethoxyphenylquinoline (PRATT and ROBINSON), i, 422.
3″-Methoxy-3′:4′-methylenedioxy-2:4-distyrylbenzopyrylium chloride, 4″:7-*di*hydroxy- (HEILBRON, WALKER, and BUCK), i, 695.
3-Methoxy-6:7-methylenedioxy-2-*p*-methoxyphenylquinoline (PRATT and ROBINSON), i, 422.
Methoxy-3′:4′-methylenedioxy-2-styrylmethyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
3-Methoxy-6:7-methylenedioxy-2-*mm′p*-trimethoxyphenylquinoline, and its salts (PRATT and ROBINSON), i, 423.
9-Methoxymethylenefluorene (WIELAND and KRAUSE), i, 902.
Methoxy-2-methylindoles (SPÄTH and BRUNNER), i, 574.
Methoxymethylisatoic anhydrides (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
3-Methoxy-3-methyl*cyclo*propane-1:2-dicarboxylic acid, constitution of, and its anhydride (GOSS, INGOLD, and THORPE), i, 550.
Methoxy-2-methyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
3-Methoxy-2-methylquinoline, and its salts (TRÖGER and DUNKER), i, 433.
8-Methoxy-2-methylquinoline, condensation of *o*- and *m*-nitrobenzaldehydes with (TRÖGER and DANEHL), i, 974.
10-Methoxy-β-naphthacridine, and its 12-carboxylic acid (SAFTIEN), i, 1318.
1-Methoxynaphthalene, 5-bromo- (FUSON), i, 254.
2-Methoxy-3-naphthamide (LESSER, KRANEPUHL, and SAD), i, 1425.
5-Methoxy-α-naphthoic acid (FUSON), i, 254.
2-Methoxy-3-naphthonitrile (LESSER, KRANEPUHL, and SAD), i, 1425.
3-Methoxy-β-naphthyldi-α-naphthafluorene (GOMBERG and MCGILL), i, 1270.
8-Methoxy-2-*m*-nitrostyrylquinoline, and its salts and derivatives (TRÖGER and DANEHL), i, 974.
ε-Methoxy-Δ^{α}-pentinene-γδ-diol (LESPIEAU), i, 1376.
4-Methoxyphenol, *di*bromo- and *di*chloro-*di*nitro-, and their salts (KOHN and MARBERGER), i, 1265.
β-*o*-Methoxyphenoxypropionic acid (PFEIFFER, OBERLIN, and KONERMANN), i, 1304.
***p*-Methoxyphenyl *m*-acetamidostyryl ketone** (PFEIFFER), i, 410.
***p*-Methoxyphenylamino-*p*-methoxyphenyl-acetonitrile** and **-carbamide** (COGHILL), i, 583.
***p*-Methoxyphenyl*m*-aminostyryl ketone**, and its benzoyl derivative (PFEIFFER, PRAHL, FITZ, and STOLL), i, 681.
3-Methoxy-3-phenylbenzopyran, and 2-chloro- and 2-hydroxy- (KAHIL and NIERENSTEIN) i, 53.
2-*p*-Methoxyphenylbenztriazole (ELBS), i, 163.
***p*-Methoxyphenyl benzyl diketone** (MALKIN and ROBINSON), i, 559.

2-*p*-Methoxyphenyl-3-benzylquinoxaline (MALKIN and ROBINSON), i, 559.

***α*-3-Methoxyphenyl-*n*-butane, *α*-4-hydroxy-, and its benzoyl derivative** (NOMURA and HOTTA), i, 1156.

***p*-Methoxyphenylcarbamide** (COGHILL and JOHNSON), i, 582.

***p*-Methoxyphenyl *β*-2:3-dimethoxyphenylethyl ketone**, and its oxime (PFEIFFER, ARMBRUSTER, BACKES, and OBERLIN), i, 270.

***p*-Methoxyphenyl *β*-*p*-dimethoxystyryl ketone** (MALKIN and ROBINSON), i, 559.

***p*-Methoxyphenyl 2:3-dimethoxystyryl ketone** (PFEIFFER, ARMBRUSTER, BACKES, and OBERLIN), i, 270.

3-4′- and -5′-Methoxyphenyl-5-*p*-dimethylaminostyryl-Δ⁵-*cyclo*hexen-1-ones, 3-2′-hydroxy- (HEILBRON, FORSTER, and WHITWORTH), i, 1284.

3-*o*-Methoxyphenyl-5-*p*-dimethylaminostyryl-Δ⁵-*cyclo*hexen-1-one-2-carboxylic acid, ethyl ester (HEILBRON, FORSTER, and WHITWORTH), i, 1284.

***p*-Methoxyphenyl *p*-dimethylaminostyryl ketone**, additive compound of, with *α*-naphthol (PFEIFFER, GOEBEL, and ANGERN), i, 262.

***o*-Methoxyphenyldi-*α*-naphthafluorene** (GOMBERG and MCGILL), i, 1270.

3-Methoxyphenylethyl *n*-amyl ketone, *β*-4-hydroxy-, and its benzoyl derivative (MURAI), i, 1157.

3-Methoxyphenylethyl butyl ketones, *β*-4-hydroxy-, and their benzoyl derivatives (NOMURA and HOTTA), i, 1157.

3-Methoxy-2-*β*-phenylethylchromone, 7-hydroxy- (ROBINSON and SHINODA), i, 1301.

3-Methoxyphenylethyl ethyl ketone, *β*-4-hydroxy (ICHIKAWA), i, 1156. and its benzoyl derivative (NOMURA and HOTTA), i, 1157.

***β*-3-Methoxyphenylethylmethylcarbinol, *β*-4-hydroxy-, and its diacetyl derivative** (NOMURA and HOTTA), i, 1156.

4-Methoxyphenylethyl methyl ketone, *β*-3-hydroxy-, and its benzoyl derivative (MURAI), i, 1158.

3-Methoxyphenylethyl *n*-propyl ketone, *β*-4-hydroxy-, and its benzoyl derivative (NOMURA and HOTTA), i, 1157.

***β*-*p*-Methoxyphenylethylquinoline, 4:2-*β*-*di*hydroxy-, and its salts** (TRÖGER and DUNKER), i, 434.

7-Methoxy-4-phenylflavylium salts (ARMIT and ROBINSON), i, 1178.

***p*-Methoxyphenylfluorene** (GOMBERG and SNOW), i, 668.

4-Methoxyphenylglyoxal, 5-bromo-2-hydroxy-, osazone (FRIES and SAFTIEN), i, 570.

***p*-Methoxyphenyl *p*-hydroxystyryl ketone**, and its salts (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 267.

1-*o*-Methoxyphenylimino-*β*-naphthaquinone (SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES), i, 413.

2-*p*-Methoxyphenylindole (KORCZYŃSKI and KIERZEK), i, 973, 1098.

5-Methoxy-2-phenylindole (KORCZYŃSKI and KIERZEK), i, 973.

***p*-Methoxyphenyl *p*-methoxybenzyl diketone** (MALKIN and ROBINSON), i, 559.

2-*p*-Methoxyphenyl-3-*p*-methoxybenzylquinoxaline (MALKIN and ROBINSON), i, 559.

2-*p*-Methoxyphenyl-5-methoxyindole (KORCZYŃSKI and KIERZEK), i, 973, 1098.

2-Methoxyphenyl 4-methoxystyryl ketone, *di*hydroxy- (SONN and BÜLOW), i, 1268.

4-Methoxyphenyl *β*-methoxystyryl ketone (MALKIN and ROBINSON), i, 559.

***p*-Methoxyphenyl-3-methoxyxanthydrol** (GOMBERG and SNOW), i, 661.

***p*-Methoxyphenylmethylhydrazine** (SPÄTH and BRUNNER), i, 575.

***p*-Methoxyphenyl nitrostyryl ketones** (PFEIFFER, PRAHL, FITZ, and STOLL), i, 680.

***p*-Methoxyphenylpropionic acid, *ααβ-tri*bromo-** (HARIHARAN and SUDBOROUGH), i, 1149.

5-Methoxy-3-phenylpyrazole (v. AUWERS and MAUSS), i, 1179.

3-Methoxy-2-phenylquinoline-4-carboxylic acid (DILTHEY and THELEN), i, 1317.

***3-p*-Methoxyphenylquinoxaline, 2:3-*o*-*di*hydroxy-** (FRIES and SAFTIEN), i, 570.

3-4′-Methoxyphenylquinoxaline, 5′-bromo-2-hydroxy-, 5′-bromo-2:2′-*di*hydroxy-, and 3′:5′-*di*chloro-2′-hydroxy- (FRIES and SAFTIEN), i, 570.

4′-Methoxy-2-phenyl-4-styrylbenzopyrylium chloride, 5:7-*di*hydroxy- (WALKER and HEILBRON), i, 693.

***3-p*-Methoxyphenyl-2-thiohydantoin** (COGHILL and JOHNSON), i, 582.

5-*p*-Methoxyphenyl-2-thiohydantoin, and its 1-acetyl derivative (COGHILL and JOHNSON), i, 582.

***β*-*p*-Methoxyphenylthiolpropionic acid** (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.

4-Methoxyphenyl 3:4:5-trimethoxystyryl ketone, 2-hydroxy-, and its acetyl derivative (DEAN and NIERENSTEIN), i, 952.
1-Methoxyphthalazine, 4-hydroxy- (RADULESCU and GEORGESCU), i, 1185.
3-Methoxy-*o*-phthalic acid, 4-hydroxy-, and its anhydride (SPÄTH and DUSCHINSKY), i, 1313.
***N*-Methoxyphthalimidine** (GRIFFITHS and INGOLD), i, 1191.
4-Methoxypropenylbenzene, 3-hydroxy-, and its ethyl ether (KAFUKU), i, 1413.
β-Methoxypropionhydroxamic acid, and its potassium salt and derivatives (JONES and POWERS), i, 14.
Methoxypropoxybenzaldehydes (SONN and PATSCHKE), i, 1280.
β-Methoxypropylbenzene, γ-bromo- (SCHMIDT, BARTHOLOMÉ, and ASMAS), i, 136.
4-Methoxypyridanthrone (SEKA and SCHRECKENTAL), i, 1316.
2-Methoxypyridine, 5-amino-, 5-iodo-, and 5-nitro-, and their derivatives (MAGIDSON and MENSCHIKOFF), i, 302.
6-Methoxy-4-quinolyl ε-aminoamyl ketone, and its dipicronolate (RUZICKA, SEIDEL, and LIEBL), i, 289.
6-Methoxy-4-quinolyl ε-benzoylmethylamino-α-carbethoxyamyl ketone (RUZICKA, SEIDEL, and LIEBL), i, 289.
6-Methoxy-4-quinolyl ε-methylaminoamyl ketone, and its dipicrate (RUZICKA, SEIDEL, and LIEBL), i, 289.
6-Methoxy-4-quinolyl *N*-methyl-2-pyrrolidyl ketone, and its salts (RUZICKA, SEIDEL, and LIEBL), i, 290.
3′-Methoxystilbene, 2:4-*di*nitro-4′-hydroxy- (GULLAND and ROBINSON), i, 1188.
Methoxystilbenes, bromo-, hydroxy-, and *di*nitrohydroxy-, and their α-carboxylic acids (DEY and ROW), i, 954.
Methoxystilbenecarboxylic acids, nitro-, and their salts and derivatives (PFEIFFER, KALCKBRENNER, and BEHR), i, 547.
***p*-Methoxystyrene**, αβ-*di*bromo- (HARIHARAN and SUDBOROUGH), i, 1150.
3-Methoxystyryl *n*-amyl ketone, 4-hydroxy- (MURAI), i, 1157.
***p*-Methoxystyryl amyl ketone** (RYAN and SHANNON), i, 558.
3-Methoxystyryl butyl ketones, 4-hydroxy- (NOMURA and HOTTA), i, 1157.
3-Methoxy-2-styrylchromone, 7-*mono*-, and 5:7-*di*hydroxy- (ROBINSON and SHINODA), i, 1301.
3-Methoxystyryl ethyl ketone, 4-hydroxy- (ICHIKAWA), i, 1156.
***p*-Methoxystyryl ethyl ketone**, and its *di*bromide (RYAN and CAHILL), i, 558.
7-Methoxy-2-styryl*iso*flavone (BAKER and ROBINSON), i, 1299.
Methoxystyrylmethylbenzopyrylium chlorides, hydroxy derivatives (HEILBRON, WALKER, and BUCK), i, 694.
***p*-Methoxystyryl methyl ketone**, chlorooximino- and oximino- (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
4-*p*-Methoxystyryl-α-naphthapyrone (DEY and ROW), i, 954.
***p*-Methoxystyryl nitrocinnamylidenemethyl ketones** (PFEIFFER), i, 409.
3-Methoxystyryl *n*-propyl ketone, 4-hydroxy- (NOMURA and HOTTA), i, 1157.
4′-Methoxy-2-styryl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
2-*p*-Methoxystyrylquinoline, derivatives of (PFEIFFER, RHEINBOLDT, and WOLF), i, 412.
2-β-*p*-Methoxystyrylquinoline, 4-hydroxy- (TRÖGER and DUNKER), i, 434.
4-β-*m*-Methoxystyrylquinoline, 2:4-*p*-*di*hydroxy- (TRÖGER and DUNKER), i, 431.
3- and 4-Methoxy-2-β-styrylquinolines (TRÖGER and DUNKER), i, 434.
***o*-Methoxytetraphenylmethane** (GOMBERG and FORRESTER), i, 1267.
6-Methoxythiochromanone, and its derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
4-Methoxy-2-thiolbenzoic acid, 5-bromo- (GRIFFITH and HOPE), i, 828.
Methoxytoluamides, benzoyl derivatives (ANSCHÜTZ and ASCHENBERG), i, 667.
2-Methoxytoluene, 5-bromo- (GOMBERG and ANDERSON), i, 1064.
Methoxytoluic acids, methyl esters (ANSCHÜTZ and ASCHENBERG), i, 667.
Methoxytoluoyl chlorides (ANSCHUTZ and ASCHENBERG), i, 667.
α-Methoxyvinyl groups, directing effect of, in aromatic substitution (C. K. and E. H. INGOLD), i, 657.
Methyl alcohol, pure, preparation of (HARTLEY and RAIKES), i, 498.
synthesis of (PATART), i, 110.
dissociation constant of (BJERRUM, UNMACK, and ZECHMEISTER), ii, 1062.
latent heat of fusion of (MAASS and WALDBAUER), ii, 492.
thermal properties of (PARKS), ii, 491.
surface tension of (ALI), ii, 763.

Methyl alcohol, surface tension of, and its mixtures with *cyclo*hexanol (WEISSENBERGER and SCHUSTER), ii, 648.
vapour pressure and specific heat of mixtures of carbon disulphide and (DRUCKER and WEISSBACH), ii, 953.
dehydrogenation of, with catalytic copper (GHOSH and CHAKRAVARTY), ii, 1161.
catalytic dehydration of β-naphthol and (PLÜSS), i, 1410.
equilibrium of carbamide with (WALTON and WILSON), ii, 505.
effect of nitrogen and carbon dioxide dilutions on the explosion of, and its mixtures with acetone (CROUCH and CARVER), ii, 682.
determination of (WIMMER), ii, 1006.
Methyl alkyl ethers, chloro- (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
chloride, density and compressibility of the vapour of (BATUECAS), ii, 753.
ether, compressibility and molecular weight of (BATUECAS), ii, 16, 497.
inhalation of (DAVIDSON), i, 1503.
*s-di*chloro-, condensation of, with phenylethylamine (SHORT), i, 387.
Methylacetophenoneoximes, and hydroxy- (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
γ-Methylacetylacetone. See γ-Methyl-Δβ-penten-δ-one, β-hydroxy-.
Methylacetylanthranilic hydrazide, and its nitrosoamine (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1323.
***N*-Methylacridone**, 1-nitro- (BURTON and GIBSON), i, 154.
β-Methyladipic anhydride (WEDEKIND, MILLER, and WEINAND), i, 511.
β-Methyladipyl chloride, action of triethylamine on (WEDEKIND, MILLER, and WEINAND), i, 510.
αα-Methylallybutyrophenone (HALLER, BAUER, and RAMART), i, 261.
Methylallylindazoles, and their picrates (v. AUWERS and LOHR), i, 74.
Methylallylindazolium iodides (v. AUWERS and PFUHL), i, 1101.
Methylallylmalonic acid (BHIDE and SUDBOROUGH), i, 1128.
Methylallylmalonic acid, amino- (MANNICH and SUTTER), i, 1037.
3-Methyl-1-allylpyrazole, and its picrate (v. AUWERS and DANIEL), i, 1180.
Methylamine, detection of, in presence of ammonia (VALTON), ii, 446.
***o*-Methylaminobenzhydrazide**, acetyl and benzoyl derivatives (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1322.
***p*-Methylaminobenzoic acid**, phenyl ester (RIVIER and RICHARD), i, 1417.
2-Methylamino-5-ethoxy-4-methyl-4:5-dihydrothiazole, and its salts (BURTLES, PYMAN, and ROYLANCE), i, 697.
6-Methyl-1-amino*cyclo*hexanol, 2-cyano- (v. AUWERS, BAHR, and FRESE), i, 312.
Methylaminomethylallylmalonic acid, and its benzoyl derivative (MANNICH and SUTTER), i, 1037.
5-Methyl-5-aminomethylpyrrole, salts of (SHMOOK), i, 577.
α-Methylaminomethylvalerolactone, and δ-bromo- and δ-iodo-, and their derivatives (MANNICH and SUTTER), i, 1037.
2-Methylamino-oxazolidine, 2-amino-, hydrochloride, and its derivatives (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 595.
β-Methylamino-β-phenylethyl alcohol. See Phenylethanolmethylamine.
2-Methylamino-5-phenyl-1:3:4-thiodiazine (BOSE), i, 1466.
α-Methylaminopropionacetal (BURTLES, PYMAN, and ROYLANCE), i, 697.
4-Methylaminopyridine, and its salts (TSCHITSCHIBABIN and OSSETROVA), i, 1328.
α-Methylamino-β-3:4:5-trimethoxyphenylacrylic acid, α-benzoyl derivative (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
α-Methylamino-β-3:4:5-trimethoxyphenylpropionic acid, α-benzoyl derivative (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
Methylammonium chloroferrates (REMY and ROTHE), ii, 1089.
*tri*iodide (STEINKOPF and BESSARITSCH), i, 497.
3-Methyl-5-amylpyrazole (v. AUWERS and DANIEL), i, 1180.
Methylanhydrobromochelidonine, and its methiodide (GADAMER and WINTERFELD), i, 285.
Methylaniline, vapour pressure of (NELSON and WALES), ii, 494.
d-camphorsulphonate (WEDEKIND), i, 678.
hydroferri- and hydroferro-cyanides (CUMMING), i, 122.
m-nitrobenzenesulphonamide (MARVEL, KINGSBURY, and SMITH), i, 245.
4-Methylanilinoquinaldinium salts (FISCHER, MÜLLER, and VILSMEIER), i, 440.
6-Methylanilinoquinoline (COBENZL), i, 436.

1-Methyl-4-anisylidenehydantoin-3-acetic acid, and its sodium salt and derivatives (HAHN and RENFREW), i, 581.

Methylanthranilic hydrazide (HELLER, GÖHRING, KLOSS, and KÖHLER), i, 1323.

β-Methylanthraquinone, derivatives of (EDER and HAUSER), i, 562, 563.

2-Methylanthraquinone, 1-amino-, benzoyl derivative (BEISLER and BRAY), i, 1288.

and 4-chloro-1-amino-, action of nitrosyl chloride on (BADISCHE ANILIN- & SODA-FABRIK) i, 414.

5:6:7:8-*tetra*chloro-2-*di*bromo-, 5:6:7:8-*tetra*chloro-1-nitro-2-*di*bromo- and 1-nitro-2-*di*bromo- (RUGGLI and BRUNNER), i, 561.

4-fluoro- (QUAYLE and REID), i, 1289.

7-Methylanthraquinone, 1:2:8-*tri*hydroxy- (JACOBSON and ADAMS), i, 278.

Methylanthraquinones, hydroxy- (JACOBSON and ADAMS), i, 272, 278.

*tri*hydroxy-, and their triacetyl derivatives (JACOBSON and ADAMS), i, 1077.

2-Methyl-5:6-anthraquinone-1-oxa-3:4-diazine (TANAKA), i, 1106.

γ-Methylarabinoside (BAKER and HAWORTH), i, 365.

Methyl-*l*-arabinosides, rotation of (HUDSON), i, 232.

Methylation, wandering of acetyl groups in (KUBOTA and PERKIN), i, 1159.

Methylbenzamidosuccinimide, *N*-chloro- and *N*-hydroxy- (CHERBULIEZ and CHAMBERS), i, 1047.

4-Methylbenziminazole-2-benzoic acid (CHAKRAVARTI), i, 162.

Methylbenziminazoletrimethylcyclopentanecarboxylic acids (CHAKRAVARTI and GUPTA), i, 981.

Methylbenzoic acid, *p*-chloro-, *p*-carboxybenzyl ester (BARKENBUS and HOLTZCLAW), i, 1148.

p-hydroxy-, esters of, and their derivatives (CASE), i, 815.

Methylbenzonitrile, *m*-bromo- (v. BRAUN and REICH), i, 1406.

4-Methylbenzophenone, 3′-chloro-2-hydroxy- (SKRAUP and POLLER), i, 143.

2-Methylbenzopyrone, 3:7-*di*hydroxy- (ALLAN and ROBINSON), i, 148.

Methylbenzoquinoneoximes, 2-nitro-4- and -6-nitroso-5-hydroxy- (SCHULTZ and GANGULY), i, 647.

1-Methylbenzoxazole, derivatives of (KÖNIG and MEIER), i, 705.

α-Methyl-β-benzoylacrylic acid (BOGERT and RITTER), i, 816.

4-Methylbenzoyl-*o*-benzoic acid, 2-fluoro- (QUAYLE and REID), i, 1289.

3-Methyl-1-benzoylpyrazole, and its perchlorate (v. AUWERS and DANIEL), i, 1181.

1-Methylbenzthiazole, derivatives of (KÖNIG and MEIER), i, 705.

6-Methylbenzthiopyran, and its sulphone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

6-Methylbenzthiopyrone, and 3-bromo-, and their derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMEYER), i, 1305; (ARNDT), i, 1309.

2-Methylbenzyl alcohol, 6-bromo-4-hydroxy- (KOHN and WEISSBERG), i, 655.

Methylbenzyl chloride, *o*-chloro- (v. BRAUN and REICH), i, 1407.

Methylbenzylamines, chloro-, salts of (v. BRAUN and REICH), i, 1406.

Methylbenzyldihydro*iso*indole, *o*-amino-, and its derivatives, and *o*-hydroxy- (v. BRAUN and ZOBEL), i, 1456.

2-α-Methylbenzylideneaminopyridine, and its derivatives (SCHMID and BANGLER), i, 1459.

***p*-Methylbenzylmenthol** (SAMDAHL), i, 415.

Methylbenzylpiperidine, *o*-amino-, and its picrate and derivatives (v. BRAUN and ZOBEL), i, 1456.

δ-Methyl-α-benzylthioglucoside (PACSU), i, 1243.

Methyl-β-bromoallylaniline, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1401.

Methylbromoethylmaleic anhydride (KÜSTER), i, 922.

Methyl-β-bromo-α-methoxyethylmaleinimide (KÜSTER and HEESS), i, 998.

β-Methylbutane, α-bromo- (DEWAEL and WECKERING), i, 3.

bromo derivatives, and their derivatives (MERESHKOVSKI), i, 1033.

γ-Methyl-Δα-buten-γ-ol (CLAISEN), i, 277.

β-Methyl-Δβ-buten-α-ol, γ-bromo-, and its acetate (MERESHKOVSKI), i, 1033.

2-α-Methyl-Δβ-butenyl-*p*-cresol, phenylcarbamate (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.

***o*-α-Methyl-Δβ-butenylphenol**, and its phenylcarbamate (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.

Methyl-*n*-butylacetoacetic acid, ethyl ester (POWELL), i, 8.

Methylbutylal (ADAMS and ADKINS), i, 784.

1-Methyl-2-butylindazolium iodides (v. AUWERS and PFUHL), i, 1101.

α-Methylbutylmalonic acid, and its ethyl ester (DEWAEL and WECKERING), i, 3.
β-Methylbutylmalonic acid (DEWAEL and WECKERING), i, 3.
Methyl*iso*butylnonylcarbinol (THOMS and AMBRUS), i, 790.
3-Methyl-5-*iso*butylpyrazoline, and its derivatives (LOCQUIN and HEILMANN), i, 837.
β-Methylbutyronitrile, catalytic reduction of (RUPE and HODEL), i, 275.
d-α-Methyl-*n*-butyryl-1-leucine, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
β-Methylcamphenilan (NAMETKIN and BRIUSOVA), i, 1078.
β-Methylcamphenilol, and its derivatives (NAMETKIN and BRIUSOVA), i, 1078.
β-Methylcamphenilone, and its derivatives (NAMETKIN and BRIUSOVA), i, 1078.
Methylcarbamide, action of phenylcarbimide on (BILTZ and BECK), i, 1393.
3-Methyl-3-*iso*carboline (ARMIT and ROBINSON), i, 1172.
Methylchlorobenzylindazolium iodides (v. AUWERS and PFUHL), i, 1101.
Methyl α-chloroethyl ketone, phytochemical reduction of (SANTOMAURO), i, 203.
Methylchlorohæmin, action of chlorine on (KÜSTER and HUTTENLOCHER), i, 992.
4-Methylchroman-4-ol (ARNDT, PUSCH, and SCHWARZ), i, 1304.
2-Methylcinchoninic acid, 3-amino-, and its methyl ester and their acetyl derivatives (GULLAND and ROBINSON), i, 1187.
d-Methylconhydrinone, and its derivatives (HESS and GRAU), i, 426.
5-Methylcoumaran-3-one-*p*-dimethylaminoanil (FRIES and BARTENS), i, 567.
6-Methylcoumaric acid, and its salts (THOMPSON and EDEE), i, 1442.
6-Methylcoumarin, and its derivatives (THOMPSON and EDEE), i, 1442.
4-Methylcoumarin, 3-bromo-7-hydroxy- (FRIES and NÖHREN), i, 954.
3-Methylcoumarone, 6-hydroxy-, derivatives of (FRIES and NÖHREN), i, 954.
6′-Methyl-3(3′-coumaryl)-benzfuran-2-carboxylic acid. See 3(3′-Coumaryl)-6′-methylbenzfuran-2-carboxylic acid.
7-Methyl-4-coumaryl-*p*-dimethylaminophenylethylene. See 7-Methyl-4-β-dimethylaminostyrylcoumarin.
7-Methyl-4-coumaryl-3′-methoxy-4′-hydroxyphenylethylene. See 7-Methyl-4-*p*-hydroxy-*m*-methoxystyrylcoumarin.
7-Methyl-4-coumaryl-*p*-methoxyphenylethylene. See 7-Methoxy-4-*p*-methoxystyrylcoumarin.
Methylcreatinine picrate (GREENWALD), i, 839.
Methyl-*p*-cresol, *oo′-di*hydroxy-, derivatives of (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 544.
ε-Methyl-Δ$^{\delta\zeta}$-decadiene (GRIGNARD and DUBIEN), i, 112.
ε-Methyl-Δ$^{\zeta}$-decen-ε-ol (GRIGNARD and DUBIEN), i, 111.
δ-Methyldextrose, and its phenylosazone (PASCU), i, 1242.
3-Methyldibenzyl, 6-hydroxy-, and its phenylurethane (SCHORIGIN), i, 1404.
N-Methyldibenzylphthalimidine (WEISS and FREUND), i, 139.
7-Methyl-4:3′-dicoumaryl, and bromo- and chloro-derivatives (DEY and ROW), i, 149.
Methyldihydrochelerythrine (GADAMER and STICHEL), i, 286.
Methyldihydrodeoxytetrahydro-α-methylmorphimethine methiodide (SPEYER and KOULEN), i, 59.
1-Methyl-Δ^{1}-dihydronaphthalene (v. AUWERS), i, 241.
1-Methyl-3:4-dihydronaphthalene (SCHROETER, ZADEK, and HOFFMANN), i, 678.
9-Methyl-9:10-dihydrophenanthrene-10-carboxylic acid, and its methyl ester (WINDAUS, JENSEN, and SCHRAMM), i, 19.
1-Methyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester, ψ-cyanide (MUMM), i, 965.
N-Methyldihydrothebenine hydriodide (SPEYER and ROSENFELD), i, 961.
Methyl-β-8(3:4-dimethoxy-5:6-methylenedioxy)phenanthrenylethylamine, and its hydrochloride (OSADA), i, 283.
7-Methyl-4-β-dimethylaminostyrylcoumarin (DEY and ROW), i, 953.
N-Methyldiphenylacetamide (VAN ALPHEN), i, 83.
N-Methyldiphenylamine-6-carboxylic acid, 2′-amino-, and its acetyl derivative, and 2′-nitro- (BURTON and GIBSON), i, 154.
3-Methyldiphenylmethane, 6:4′-*di*hydroxy-, and its derivatives (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1263.
Methyldiphenylmethyl*di*chloroamine, crystallography of (FISHER), ii, 942.
γ-Methyldipropionylmethane, and its copper salt (MORGAN and TAYLOR), i, 634.

o-**Methyldisalicoylimide**, silver salt (ANSCHÜTZ, RIEPENKRÖGER, and KUCKERTZ), i, 667.
Methyldi-*p*-tolylmethane, chloro- (SOMMELET), i, 803.
9-Methyldodecahydrocarbazole methiodide (v. BRAUN and SCHÖRNIG), i, 1450.
γ-Methyl-Δγ-dodecene (THOMS and AMBRUS), i, 789.
Methylenebenzoylpyruvic acid, diethyl ester, and its derivatives (GAULT and FUNKE), i, 37.
Methylenebisdimethyldihydroresorcinol, disodium derivative (RADULESCU and GEORGESCU), i, 820.
Methylenebisphenyldihydroresorcinol, disodium derivative (RADULESCU and GEORGESCU), i, 820.
Methylenebistelluriacetone *di*chloride (MORGAN and DREW), i, 531.
Methylenebistelluritrichloride (MORGAN and DREW), i, 531.
Methylene-blue, photographic action of (EGGERT and REITSTÖTTER), ii, 509.
photolysis of (BAUR), ii, 1082.
adsorption of, by charcoal (MECKLENBURG), ii, 530.
oxidation-reduction with (CLARK, COHEN, and GIBBS), ii, 1164.
reduction of, by dextrose (KNECHT and HIBBERT), ii, 605.
decolorisation of, by mixtures of phosphates, acetaldehyde, and glycine (HAEHN and PÜLZ), i, 858.
mercury derivatives of (CHALKLEY), i, 1108.
polychrome, preparation of (PROESCHER and KRUEGER), i, 597.
determination of, iodometrically (SABALITSCHKA and ERDMANN), ii, 908.
Methylenecitric acid, derivatives of (NAU, BROWN, and BAILEY), i, 1379.
*endo***Methylenedehydropiperidazine**, compound of cuprous chloride and (DIELS, BLOM, and KOLL), i, 977.
Methylenedicarbamic acid, *iso*propyl ester (DATTA and CHATTERJEE), i, 892.
Methylenedihydropyridines (KOENIGS, KÖHLER, and BLINDOW), i, 833; (MUMM), i, 964.
3-Methylene-2:5-diketopiperazine (BERGMANN, MIEKELEY, and KANN), i, 1134.
3-(3′:4′-Methylenedioxybenzyl)oxindole (WINDAUS and EICKEL), i, 33.
3:4-Methylenedioxy-γ-bromo-β-methoxypropylbenzene (SCHMIDT, BARTHOLOMÉ, and ASMAS), i, 136.
3:4(?2:3)-Methylenedioxy-9:10-dihydrophenanthrene-9-carboxylic acid, and its derivatives (WINDAUS and EICKEL), i, 33.
2:3-Methylenedioxydihydroprotoberberine, and its salts (HAWORTH, PERKIN, and PINK), i, 1170.
6:7-Methylenedioxydihydro*iso*quinoline, and its 1-benzoyl derivative, methiodides of (HAWORTH, PERKIN, and RANKIN), i, 1314.
6:7-Methylenedioxy-2′:3′-dimethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH and PERKIN), i, 968.
Methylenedioxy-2:4-distyrylbenzopyrylium chlorides, *tri*hydroxy- (HEILBRON, WALKER, and BUCK), i, 695.
4:5-Methylenedioxyhomophthalamic acid (HAWORTH and PINK), i, 929.
4:5-Methylenedioxyhomophthalimide (HAWORTH and PERKIN), i, 929.
2:3-Methylenedioxyoxydihydro*iso*protoberberine (HAWORTH, PERKIN, and PINK), i, 1169.
2:3-Methylenedioxyoxyprotoberberines (HAWORTH, PERKIN, and PINK), i, 1169.
7:8-Methylenedioxy-11-phenylindenoquinoline, and its derivatives (ARMIT and ROBINSON), i, 1171.
2:3-Methylenedioxyprotoberberine, salts of (HAWORTH, PERKIN, and PINK), i, 1170.
3′:4′-Methylenedioxystilbene, 4-nitro-2-amino-, and 2:4-*di*nitro- (GULLAND and ROBINSON), i, 1188.
3′:4′-Methylenedioxy-2-styryl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.
2:3-Methylenedioxytetrahydroprotoberberines, and their salts (HAWORTH, PERKIN, and PINK), i, 1169.
3-Methylene-6-methyl-2:5-diketopiperazine (BERGMANN, MIEKELEY, and KANN), i, 1134.
γ-Methylene-Δδ-octene (GRIGNARD and DUBIEN), i, 112.
3:6-*endo*Methylene-1:2-piperidazine, and its salts and derivatives (DIELS, BLOM, and KOLL), i, 976.
*endo***Methylenepiperidazine-1-carboxylic acid**, methyl ester, and its picrate (DIELS, BLOM, and KOLL), i, 976.
3:6-*endo*Methylene-1:2-piperidazine-1:2-dicarboxylic acid, ethyl ester (DIELS, BLOM, and KOLL), i, 976.
1-Methylene-1:2:3:4-tetrahydronaphthalene, and its ozonide (SCHROETER, ZADEK, and HOFFMANN), i, 678.
3:6-*endo*Methylene-3:4:5:6-tetrahydro-1:2-pyridazine (DIELS, BLOM, and KOLL), i, 977.

3:6-*endo*Methylene-1:2:3:6-tetrahydro-1:2-pyridazine-1:2-dicarboxylic acid, ethyl ester, and its dibromide (DIELS, BLOM, and KOLL), i, 976.

Methylethoxybenzaldehydes (SONN and PATSCHKE), i, 1280.

6-Methyl-2-ethoxymethylene*cyclo*hexanone (v. AUWERS, BAHR, and FRESE), i, 310.

***β*-Methyl-*β*-ethylacrylic acid.** See *β*-Methyl-Δ^{α}-pentenoic acid.

1-Methyl-2-ethylbenzene, formation of, from 2-methyl-3-ethyl-Δ^{2}-*cyclo*hexenone (BLAISE and MONTAGNE), i, 1072.

***β*-Methyl-*α*-ethylbutenoic acid** (KON, SMITH, and THORPE), i, 510.

3-Methyl-2-ethylcoumaran (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.

***ββ*-Methylethylglutarylfluorescein** (DUTT and THORPE), i, 141.

***ββ*-Methylethylglutarylrhodamine** (DUTT and THORPE), i, 142.

2-Methyl-3-ethyl-Δ^{2}-*cyclo*hexen-1-one (BLAISE and MONTAGNE), i, 836.
conversion of, into 1-methyl-2-ethylbenzene (BLAISE and MONTAGNE), i, 1071.

Methylethylindazoles, and their picrates (v. AUWERS and LOHR), i, 73.

1-Methyl-2-ethylindazolium salts (v. AUWERS and PFUHL), i, 1101.

Methyl ethyl ketone, condensation of aldehydes with (RYAN and CAHILL), i, 558.
action of calcium hydride on (PORLEZZA and GATTI), i, 788.
condensation of, with vanillin (ICHIKAWA), i, 1156.

6-Methyl-6-ethylphenoxarsonium salts (AESCHLIMANN), i, 706.

Methyl-1-ethylpyrazoles, chloro-, and their perchlorate (v. AUWERS and NIEMEYER), i, 1177.

4-Methyl-5-ethylpyrazoline, and its derivatives (LOCQUIN and HEILMANN), i, 837.

2-Methyl-4-ethylpyridine (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 431.

2-Methyl-5-ethylpyridine, 6-amino- (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 301.

4-Methyl-3-ethylpyridine, synthesis of (KOENIGS and HOFFMANN), i, 298.

***N*-6-Methyl-2:3-ethylpyridylpyrrole** (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 1329.

4-Methyl-2-ethylpyrrole-5-carboxylic acid, ethyl ester (FISCHER and KLARER), i, 578.

***as*-Methylethylsuccinylfluorescein** (DUTT and THORPE), i, 141.

***as*-Methylethylsuccinylrhodamine** (DUTT and THORPE), i, 142.

Methylethyltetrahydroindazoles, and their picrates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.

6-Methyl-4-ethylthio-chroman-4-ol and **-chromene** (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

2-Methyl*iso*flavone, 7-*mono*- and 5:7-*di*-hydroxy-, and their derivatives (BAKER and ROBINSON), i, 1299.

5-Methyl-*o*-*trans*-fluoracenedione (RADULESCU and GEORGESCU), i, 1287.

Methyl*iso*formo-*p*-bromoanilide (FARROW and INGOLD), i, 155.

6-Methyl-2-formyl*cyclo*hexanone (v. AUWERS, BAHR, and FRESE), i, 310.

6-Methyl-2-formyl*cyclo*hexenol (v. AUWERS, BAHR, and FRESE), i, 310.

***γ*-Methylfructoside**, fission of, by invertase (SCHLUBACH and RAUCHALLES), i, 1243.

Methylfuran, 2-chloro-, preparation of, from 2-furylcarbinol (GILMAN and VERNON), i, 53.

Methylfurfuraldehyde, hydroxy-, determination of (TROJE), ii, 1210.

Methylgalactoside (HAWORTH, RUELL, and WESTGARTH), i, 117.

***α*-Methylgentobioside**, rotation of (HUDSON), i, 636.

6(?)-Methyl-*d*-glucose, and its osazone (HELFERICH and BECKER), i, 11.

***α*-Methylglucoside** chlorohydrins, salts of (HELFERICH, SPROCK, and BESLER), i, 792.

***α*-Methyl-*d*-glucoside**, derivatives of (HELFERICH and BECKER), i, 10.

***β*-Methylglucoside**, hydrolysis of (JOSEPHSON), i, 1359.

***α*- and *β*-Methylglucosides**, solution volume and refraction constants of (RIIBER), i, 8.

***α*-Methylglutaric acid**, dianilide, di-*β*-naphthylide and di-*p*-toluidide of (v. AUWERS), i, 892.

***α*-Methylglutaric acid**, bromo-, chloro-, hydroxy-, and iodo-, and their salts and derivatives (INGOLD), i, 358.

Methylglyoxal, condensation of thiocarbamide and (SJOLLEMA and SEEKLES), i, 1175.

Methylglyoxal, amino-, acetyl derivative, osazone (MANN and POPE), i, 374.

Methylglyoxalase (MEYERHOF), i, 1507.

1-Methylglyoxaline, chloro- (SONN, HOTES, and SIEG), i, 157.

2-Methylglyoxaline, 4(5)-nitro-5(4)-thiol-, and its ammonium salt (BHAGWAT and PYMAN), i, 1175.
4(5)-Methylglyoxaline, 2-amino-, and its picrate (BURTLES and PYMAN), i, 1326.
Methylglyoxime, and amino- and chloro-, methyl ethers and derivatives of (AVOGADRA and TAVOLA), i, 1040.
Methylguanidine, acetyl and benzoyl derivatives, and their salts (GREENWALD), i, 840.
nitrate (FROMM, BARRENSCHEEN, FRIEDER, PIRE, and KAPELLER), i, 596.
β-Methyl-Δαγ-heptadiene (GRIGNARD and DUBIEN), i, 42.
β-Methylheptane-ββδ-diol (GRIGNARD and DUBIEN), i, 112.
γ-Methylheptan-β-ol, and its acetate (POWELL), i, 8.
γ-Methylheptan-β-one, and its semicarbazone, and δ-hydroxy- (POWELL), i, 7.
β-Methyl-Δγ-hepten-β-ol (GRIGNARD and DUBIEN), 111.
β-Methyl-Δβ-hepten-δ-ol, and its allophanate (GRIGNARD and DUBIEN), i, 112.
β-Methyl-Δβ-hepten-ζ-ol, benzoate of (HELFERICH and FRIES), i, 1039.
Methylheptenone, oxidation of, with ozone (VERLEY), i, 406.
β-Methyl-Δγ-hepten-ε-one, and its semicarbazone (THOMS and KAHRE), i, 788.
γ-Methyl-Δγ-hepten-β-one, and its semicarbazone (POWELL), i, 7.
β-Methylhexaldehyde, and its semicarbazone (DEWAEL and WECKERING), i, 3.
γ-Methylhexane, α-bromo- and α-chloro- (DEWAEL and WECKERING), i, 3.
1-Methyl-3:4-*cyclo*hexanediol ethyl ether (KÖTZ and HOFFMANN), i, 910.
γ- and **δ-Methylhexanols**, and their derivatives (DEWAEL and WECKERING), i, 3.
Methyl*cyclo*hexanols, surface tension and vapour pressure of, and their mixtures with benzene (WEISSENBERGER and SCHUSTER), ii, 648.
1-Methyl-3-*cyclo*hexanol-4-acetic acid, lactone (KÖTZ and HOFFMANN), i, 911.
1-Methyl-3-*cyclo*hexanol-4-malonic acid, and its derivatives (KÖTZ and HOFFMANN), i, 911.
1-Methyl*cyclo*hexan-4-one, chlorination of (GODCHOT and BEDOS), i, 258.
1-Methyl*cyclo*hexan-6-one, methylation of, with benzaldehyde (HALLER and CORNUBERT), i, 1071.
2-Methyl*cyclo*hexanone, derivatives of (HALLER and CORNUBERT), i, 1071.
2-Methyl*cyclo*hexanone, 2:6-*di*bromo-, action of alkalis on (CUSMANO), i, 818.
2-cyano-, and its derivatives (v. AUWERS, BAHR, and FRESE), i, 312.
2- and **6-Methyl*cyclo*hexanones**, 2-cyano-, and their derivatives (v. AUWERS, BAHR, and FRESE), i, 311.
6-Methyl-Δ¹-*cyclo*hexene, 2-amino-1-cyano-, and its derivatives (v. AUWERS, BAHR, and FRESE), i, 312.
β- and **γ-Methylhexoic acids**, derivatives of (DRWAEL and WECKERING), i, 3.
3-Methyl*cyclo*hexylacetic acid, ethyl ester (BECHERER), i, 665.
β- and **δ-Methylhexylamine**, and their derivatives (DEWAEL and WECKERING), i, 3.
3-Methyl*cyclo*hexylethyl alcohol (BECHERER), i, 665.
1-Methyl-2-*cyclo*hexyl*cyclo*hexane (GARLAND and REID), i, 1281.
1-Methyl-2-*cyclo*hexyl*cyclo*hexanol (GARLAND and REID), i, 1281.
2-Methyl*cyclo*hexylhydroxylamine (VAVON and BERTON), i, 807.
1-Methyl*cyclo*hexylidene-4-acetic acid, rotatory dispersion of (RICHARDS and LOWRY), ii, 632.
3-Methyl*cyclo*hexylideneanthranilic acid, and its methyl ester (PERKIN and SEDGWICK), i, 64.
1-Methyl-2-*cyclo*hexylidene*cyclo*hexanol (GARLAND and REID), i, 1281.
1-Methyl-6-*cyclo*hexylidene-Δ¹-*cyclo*hexene (GARLAND and REID), i, 1281.
α-3-Methyl*cyclo*hexylpropionic acid, and 1-hydroxy-, and their ethyl esters (BECHERER), i, 665.
β-3-Methyl*cyclo*hexylpropyl alcohol (BECHERER), i, 665.
Methyl*cyclo*hexylsemicarbazides (VAVON and BERTON), i, 807.
4-Methylhydrindene, and *tri*bromo- (KRUBER), i, 1138.
4-Methylhydrindenesulphonic acid, and its salts and amide (KRUBER), i, 1138.
Methylhydrobenzoins, optically active, dehydration of (MCKENZIE and ROGER), i, 25.
1-Methyl-4-*p*-hydroxybenzylhydantoin-3-acetic acid, and its derivatives (HAHN and RENFREW), i, 581.
Methylhydroxyethylfumaric acid, derivatives of (KÜSTER), i, 922.
Methylhydroxyethylmaleic acid, preparation of (KÜSTER and GRÄSSNER; KÜSTER), i, 922.
Methylhydroxyglyoxime, metallic salts of (PONZIO and RUGGERI), i, 1041.
7-Methyl-4-*p*-hydroxy-*m*-methoxystyrylcoumarin (DEY and ROW), i, 953.

1-Methyl-3-hydroxymethylene*cyclo*-hexan-4-one, derivatives of (v. AUWERS, v. SASS, and WITTEKINDT), i, 1181.

5-Methyliminazoline, 2:5-*di*amino-, tetrabenzoate (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 595.

Methylindazoles, and their derivatives, and *di*bromo-, *tri*bromo-, and iodo- (v. AUWERS and LOHR), i, 74.

Methylindazoles, 4-nitro- (v. AUWERS and FRESE), i, 1102.

5-Methylindazole-2-carboxylic acid, ethyl and methyl esters (v. AUWERS and LOHR), i, 74.

7-Methyl*iso*indigotin, and its derivatives (WAHL and FAIVRET), i, 588.

7-Methylindirubin (WAHL and FAIVRET), i, 588.

2-Methylindole, 3-chloroacetyl derivative (KALLER & Co.), i, 297.

picryl derivatives (KORCZYŃSKI and KIERZEK), i, 973.

2-Methylindole, 3-cyano- (SEKA), i, 67.

5-Methylindole-3-aldehyde (ROBSON), i, 298.

5-Methylindolylidenehydantoin (ODDO), i, 298.

2-Methylindolyl-2′-methylindolidene-methane, metallic derivatives (KUNZ and STÜHLINGER), i, 1319.

α-Methylindyl-α-methylindolidene-methane, derivatives of (PFEIFFER, RHEINBOLDT, and WOLF), i, 412.

2-Methylindyl-2-methylindolidene-phenylmethane-*o*-carboxylic acid, potassium salt (ODDO), i, 588.

7-Methylisatan (WAHL and FAIVRET), i, 588.

4- and 6-Methylisatin (MAYER and SCHULZE), i, 1315.

7-Methylisatin, derivatives of (WAHL and FAIVRET), i, 588.

Methylisatoic anhydride (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.

Methylisatoid, silver derivative (HANTZSCH), i, 701.

Methylitamalic acid, barium salt (INGOLD), i, 358.

Methylketolephthalein. See Di-2-methylindylphthalide.

Methylketole-yellow. See 2-Methylindyl-2-methylindolidenephenylmethane-*o*-carboxylic acid, potassium salt.

Methyl ketones, formation of, from triglycerides and fatty acids by moulds (STÄRKLE), i, 205.

Methyl-lichenin (SCHMID), i, 1386.

Methylmaltoside, and its hepta-acetyl derivative (FREUDENBERG, v. HOCHSTETTER, and ENGELS), i, 635.

Methylmercuric hydrogen carbonate and mercaptan (KOTEN and ADAMS), i, 236.

*tri*nitrobenzoate (KHARASCH and GRAFFLIN), i, 1107.

2-Methyl-1-methylenebenzthiazoline (KÖNIG and MEIER), i, 705.

6(?)-Methyl-α-methyl-*d*-glucoside (HELFERICH and BECKER), i, 10.

Methylmorphimethines (SPEYER and KOULEN), i, 59.

2-Methylnaphthalene, 6-amino-, 5-amino-6-hydroxy-, 6-hydroxy-, 5-nitro-6-hydroxy-, and 5-nitroso-6-hydroxy-, and their derivatives (DZIEWOŃSKI, SCHOENÓWNA, and WALDMANN), i, 1056.

amino-, bromo-, nitroamino-, and nitro-derivatives, and their derivatives (VESELY and KAPP), i, 246.

1-bromo-4-nitro- (VESELY and KAPP), i, 804.

2-Methylnaphthalene-6-sulphonic acid, derivatives of (DZIEWOŃSKI, SCHOENÓWNA, and WALDMANN), i, 1057.

2-Methyl-5:6-naphthaquinone (DZIEWOŃSKI, SCHOENÓWNA, and WALDMANN), i, 1057.

α-Methyl-β-naphthoic acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.

Δ^1-α-Methyl-β-naphthoic acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.

2-Methylnaphthols, and bromo- (VESELY and KAPP), i, 246.

2-Methyl-α-naphthylamine, 5-bromo- and its acetyl derivative and 4-nitro- (VESELY and KAPP), i, 246.

5-nitro-, and its acetyl derivative (VESELY and KAPP), i, 804.

***N*-Methylnicotone** (KARRER and WIDMER), i, 1084.

***N*-Methylniquine** and its derivatives (SUSZKO), i, 1449.

3-Methyl-1-*o*-nitrobenzoylpyrrole (v. AUWERS and DANIEL), i, 1181.

Methylnitrobenzylindazolium iodides (v. AUWERS and PFUHL), i, 1101.

1-Methylnitrouracil triacetylxyloside (LEVENE and SOBOTKA), i, 1464.

Methyl *n*-nonadecyl ketone (MORGAN and HOLMES), i, 514.

δ-Methyl-Δ^{ϵ}-nonadiene (GRIGNARD and DUBIEN), i, 112.

δ-Methyl-Δ^{ϵ}-nonen-δ-ol (GRIGNARD and DUBIEN), i, 111.

Methyl nonyl ketone (SCHIMMEL & Co.), i, 417.

Methyl ε-nonyl ketone (HESS and BAPPERT), i, 349.
Methyl *n*-octadecyl ketone (MORGAN and HOLMES), i, 514.
γ-Methyl-Δ$^{\beta\delta}$-octadiene (GRIGNARD and DUBIEN), i, 112.
10-Methyloctahydroacridine, and its picrate (PERKIN and SEDGWICK), i, 65.
3-Methyloctahydroindole, picrate of (v. BRAUN and BAYER), i, 429.
γ-Methyloctane-γε-diol (GRIGNARD and DUBIEN), i, 112.
β-Methyloctanols (THOMS and KAHRE), i, 788.
β-Methyloctan-ζ-one, and its semicarbazone (THOMS and KAHRE), i, 788.
γ-Methyl-Δγ-octen-ε-ol (GRIGNARD and DUBIEN), i, 112.
γ-Methyl-Δ$^{\delta}$-octen-γ-ol (GRIGNARD and DUBIEN), i, 111.
β-Methyl-Δγ-octenones, and their semicarbazones (THOMS and KAHRE), i, 788.
Methyl orange (*helianthin*), formula of (THIEL), ii, 37.
ionisation of (KOLTHOFF), ii, 296.
5-Methyloxazolidine, 2-imino-5-chloro-, and its derivatives (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 595.
5-Methyloxazoline, 2-amino-5-hydroxy-, tribenzoate (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 595.
Methyl*iso*pelletierine (HESS and GRAU), i, 425.
1-Methyl*cyclo*pentan-5-one, methylation of, with benzaldehyde (HALLER and CORNUBERT), i, 1070.
β-Methyl-Δβ-pentenal phenylhydrazone (v. AUWERS and KREUDER), i, 1454.
α-Methyl-Δγ-pentenoic acid (BHIDE and SUDBOROUGH), i, 1128.
β-Methyl-Δα- and -Δβ-pentenoic acids, and their derivatives (KON and LINSTEAD), i, 506.
γ-Methyl-Δβ-penten-δ-one, β-hydroxy- (KAUFMANN and LIEPE), i, 1241.
4-γ-Methyl-Δα-pentenoyl-4′-dimethylaminoazobenzene, and its hydrochloride (THOMS and KAHRE), i, 789.
γ-Methylpentinen-γ-ols, and their esters (RUPE and VONAESCH), i, 499.
9-Methylphenanthrene, synthesis of, and its picrate (WINDAUS, JENSEN, and SCHRAMME), i, 19.
Methylphenazine, hydroxy- (KEHRMANN and CHERPILLOD), i, 303.
Methylphenoxazine-*o*-quinone, condensation of, with *o*-aminophenol and *o*-diamines (KEHRMANN and WILD), i, 444.
5-Methylphenylene-1:3-diacetic acid, and its derivatives (v. BRAUN and ENGEL), i, 382.
***o*-Methylphthalimidine** (GRIFFITHS and INGOLD), i, 1191.
6-Methylpicolinic acid, derivatives of (MEYER), i, 836.
6-Methyl-1:2-piperidazine-1:2-dicarboxylic acid, 3-chloro-, ethyl ester (DIEL, BLOM, and KOLL), i, 976.
Methylprasindone, salts of (KEHRMANN and CHERPILLOD), i, 303.
1-Methyl*cyclo*propane-1:2-dicarboxylic acids, and their derivatives (INGOLD), i, 358.
3-Methyl*cyclo*propane-1:2-dicarboxylic acid, 2:3-*di*bromo-, methyl ethyl ester (GOSS, INGOLD, and THORPE), i, 550.
Methylpropargylaniline, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i. 1401.
Methylpropargylcyanamide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.
β-Methyl-Δβ-propene, α-bromo- (MEREJKOVSKI), i, 878.
3-Methyl-Δ^{2}-*cyclo*propene-1:2-dicarboxylic acid, esters of (GOSS, INGOLD, and THORPE), i, 549.
Methyl-Δ$^{\alpha}$-propinenyl ketone (YVON), i, 514.
5-Methylpropiophenone, 2-hydroxy-, oxime and semicarbazone (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
Methyl*iso*propylanthracene picrate (PHILLIPS), i, 45.
1:4-Methyl*iso*propylanthraquinone, and *di*nitro- (PHILLIPS), i, 45.
***o*-2:5-Methyl*iso*propylbenzoylbenzoic acid** (PHILLIPS), i, 45.
Methyl-*n*-propylglycerol. See Heptane-βγδ-triol.
1-Methyl-4-*iso*propyl*cyclo*hexanol-malonic acid, ethyl ester lactone (KÖTZ and HOFFMANN), i, 911.
2-Methyl-2-*n*-propyl*cyclo*hexanone, derivatives of (HALLER and CORNUBERT), i, 1071.
2-Methyl-5-*iso*propyl*cyclo*hexylacetic acid, 1-hydroxy-, ethyl ester (BECHERER), i, 665.
2-Methyl-5-*iso*propyl*cyclo*hexylethyl alcohol (BECHERER), i, 665.
2-Methyl-5-*iso*propyl*cyclo*hexylidene-1-acetic acid, sodium salt and ethyl ester (BECHERER), i, 665.

α-2-Methyl-5-*iso*propyl*cyclo*hexylidenepropionic acid, and its ethyl ester (BECHERER), i, 665.
α-2-Methyl-5-*iso*propyl*cyclo*hexylpropionic acid, 1-hydroxy-, ethyl ester (BECHERER), i, 665.
β-2-Methyl-5-*iso*propyl*cyclo*hexylpropyl alcohol (BECHERER), i, 665.
Methylpropylindazolium salts (v. AUWERS and PFUHL), i, 1101.
Methyl propyl ketones, chloro-oximino- (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
Methylpropylnonylcarbinols (THOMS and AMBRUS), i, 789.
γ-2-Methyl-5-*iso*propylphenylpropinene (BERT, DORIER, and LAMY), i, 1374.
3-Methyl-5-*iso*propylpyrazoline, and its derivatives (LOCQUIN and HEILMANN), i, 837.
3-Methyl-4-*n*-propyl-5-pyrazolone (HIRST, MACBETH, and TRAILL), i, 1251.
3-Methylpyrazole-1-carboxyl chloride (v. AUWERS and DANIEL), i, 1181.
Methylpyrazole-1-carboxylamides, and 4-bromo- (v. AUWERS and DANIEL), i, 1181.
3-Methylpyrazole-1-carboxylic acid, esters (v. AUWERS and DANIEL), i, 1180.
Methylpyrazolines, and their derivatives (FREUDENBERG and STOLL), i, 71.
1-Methyl-5-pyrazol-3-one (v. AUWERS and MAUSS), i, 1179.
Methylpyridine, 2-thiol-, and its salts (KOENIGS and GEISSLER), i, 166.
2-Methylpyridine, 4:6-*di*chloro-5-cyano- (SPÄTH and KOLLER), i, 1446.
4-hydroxy-, and its 6-carboxylic acid (COLLIE and BISHOP), i, 974.
3-Methylpyridine, 2-amino- (TSCHITSCHIBABIN; SEIDE), i, 1328.
2-chloro-, 2-hydroxy-, and nitroamino-, and their derivatives (SEIDE), i, 72.
2-Methylpyridine-5-carboxylamide, 4:6-*di*hydroxy- (SPÄTH and KOLLER), i, 1446.
1-Methyl-2-pyridone, 3-nitro- (TSCHITSCHIBABIN and KONOVALOVA), i, 1329.
1-Methyl-4-pyridoneimine, and its salts (TSCHITSCHIBABIN and OSSETROVA), i, 1328.
1-Methyl-2-pyridylnitroimine (TSCHITSCHIBABIN and MENSCHIKOV), i, 437.
1-Methyl-2-pyridylnitroimine, 3- and 5-nitro- (TSCHITSCHIBABIN and KONOVALOVA), i, 1329.
N-Methyl-2-[2-pyridyl]pyrrole, and its picrate (TSCHITSCHIBABIN and BYLINKIN), i, 1174.
1-Methyl-2-pyrimidine, 5-nitro-, and its salts (TSCHITSCHIBABIN and KONOVALOVA), i, 1329.
4-Methylpyrimidine-5-carboxylic acid, 2-amino-, and its ethyl ester (MITTER and PALIT), i, 1320.
Methylpyriminazole, and its chloroplatinate (TSCHITSCHIBABIN), i, 1328.
2-Methyl-4-quinazolone, 3-amino-, propionyl derivative, and 3-*m*-nitroamino-, benzoyl derivative (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1323.
2-Methylquinoline (*quinaldine*), salts of (TRÖGER and DUNKER), i, 433.
2-Methylquinoline, 4-chloro-, derivatives of (FISCHER, DIEPOLDER, and WÖLFEL), i, 439.
γ-2-Methylquinoline-3-butyric acid, 4-hydroxy- (PATERSON and PLANT), i, 1147.
N-Methyl-β-*iso*quinotoxin (SUSZKO), i, 1449.
Methyl-red, ionisation of (KOLTHOFF), ii, 296.
N-Methyl*apo*safranone, and its salts (KEHRMANN and CHERPILLOD), i, 303.
Methylsuccinimide, derivatives of, and *N*-chloro-, and *N*-hydroxy- (CHERBULIEZ and SULZER), i, 1252.
Methyltartaric acid, synthesis of (GOEBEL), i, 1038.
Methyltetrahydroacridone (PERKIN and SEDGWICK), i, 64.
7-Methyltetrahydroanthranil, *C*-amino-, and its derivatives (v. AUWERS, BAHR, and FRESE), i, 312.
Methyltetrahydrobenz-3:4- and -4:5-*iso*oxazoles, and 5-amino-derivative of the former (v. AUWERS, BAHR, and FRESE), i, 310.
5-Methyl-4:5:6:7-tetrahydroindazole, and its picrate (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.
7-Methyl-4:5:6:7-tetrahydroindazole, 3-amino-, and its salts and derivatives, and 3-bromo- (v. AUWERS, BAHR, and FRESE), i, 312.
5-Methyltetrahydroindazole-2-carboxylamide (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.
7-Methyl-4:5:6:7-tetrahydroindazole-2-carboxylamide, 3-amino- (v. AUWERS, BAHR, and FRESE), i, 311.
7-Methyltetrahydroindazolenaphthatriazine (v. AUWERS, BAHR, and FRESE), i, 313.
1-Methyl-1:2:3:4-tetrahydronaphthalene, 1:2-*di*hydroxy- (v. AUWERS), i, 241.
Methyl-β-8-(3:4:5:6-tetramethoxy)-phenanthrenylethylamine, and its hydrochloride (OSADA), i, 283.

p-**Methylthiobenzamide** (SCHÖNBERG, ABELSDORFF, ANTONOFF, and KIRCHRATH), i, 557.
4-Methylthiochroman-4-ol (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.
6-Methylthiochromanone, and 3-*mono*- and 3:3-*di*-bromo-, and their derivatives (ARNDT), i, 1309.
* salts of (ARNDT and PUSCH), i, 1304.
Methylthiochromanones, and their derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
4-Methyl-Δ^3-thiochromene (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.
6-Methylthiochromonol, derivatives of, and 2-bromo-2-chloro-, and 2:2-*di*-chloro- (ARNDT), i, 1311.
6-Methylthiocoumarin, and its mercurichloride (THOMPSON and EDEE), i, 1442.
6-Methylthioflavanone, 3-*mono*- and 3:3-*di*-bromo-, and their derivatives (ARNDT), i, 1309.
6-Methyl-1-thioflavone, and 3-bromo-, 2:3-*di*bromo-, and their derivatives (ARNDT), i, 1309.
5-Methyl-2-thiohydantoin, and its derivatives (SJOLLEMA and SEEKLES), i, 1175.
m-**Methylthiolphenylmethylsulphone** (TWIST and SMILES), i, 895.
5-Methylthiol-3-phenyl-2-tetradecyl-2:3-dihydro-1:3:4-thiodiazole (LANDA), i, 1039.
6-Methylthiol-*m*-toluic acid (ARNDT), i, 1311; (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
5-Methylthionaphthen-2-aldehyde, 3-hydroxy-, and its derivatives (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306.
2-Methylthiophen, and nitro- (CHRZASZCZEWSKA), i, 956.
4-Methylthiophen-2:3:5-tricarboxylic acid (SEKA), i, 1299.
Methyl *p*-tolyl ketone, chloro-oximino- (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
1-Methyl-1:2:3-triazole-4:5-dicarboxylic acid, and its methyl ester (GRISCHKEVITSCH-TROCHIMOVSKI and KOTKO), i, 1104.
Methyl-tribenzoyl-*α*-methyl-*d*-glucoside (HELFERICH and BECKER), i, 10.
8-Methyl-Δ^8-tridecene (THOMS and AMBRUS), i, 790.
6-Methyl-2.3:5-triketopiperazine (BERGMANN, MIEKELEY, and KANN), i, 1134.
Methyltrimethylammonium iodide, hydroxy-, acetyl derivative, and iodo-, action of, on the nervous system (HUNT and RENSHAW), i, 861.
Bz-**3-Methyltryptophan**, synthesis of (ROBSON), i, 297.
5-Methylumbelliferone-4-acetic acid (MÜLLER), i, 1443.
1-Methyluracil xyloside and triacetylxyloside (LEVENE and SOBOTKA), i, 1464.
Methyluracils, alkylated, action of formaldehyde on (SCHMEDES), i, 435.
Methylurethane, nitroso-, reaction of pyrocatechol tannins with (VOGEL), ii, 827.
1-Methyluric acid, oxidation of, in alkaline solution (PIAUX), i, 165.
γ-Methylvaleryl chloride, α-bromo- (ABDERHALDEN and ROSSNER), i, 975.
γ-Methylvalerylpiperazine, 1:4-*di*bromo- (ABDERHALDEN and ROSSNER), i, 975.
Methylvanillin, preparation of (BRINER, v. TSCHARNER, and PAILLARD), i, 1069.
Methylvasicine, hydroxy- (SEN and GHOSE), i, 958.
Methylvinylcarbinol, resolution and rotation of, and its esters (KENYON and SNELLGROVE), i, 771.
Methylvinylmaleic anhydride (KÜSTER), i, 922.
Methyl-*d*-xylosides, rotation of (HUDSON), i, 232.
Mica, hydrolysis of (ZEMIATTSCHENSKI), ii, 814.
orientation of ammonium iodide on (ROYER), ii, 270.
Micas, classification of (HALLIMOND), ii, 819.
Mica group (WINCHELL), ii, 592.
Microbes (*micro-organisms*), effect of toxicity of the medium on life-period of (PAVLOV), ii, 958.
action of the electric current on (KLEIBER), i, 1509.
reduction by (FERRO), i, 340.
energy balance in growth of (TERROINE, TRAUTMANN, and BONNET), i, 1117.
decomposition of amino-acids and proteins by (WAKSMAN and LOMANITZ), i, 867.
in soils, effect of hydrogen-ion concentration on (RIPPEL), i, 220.
liberation and fixation of iodine by (v. FELLENBERG and GEILINGER), i, 339.
utilisation of paraffin by (TAUSSON), i, 479.

Microbes (*micro-organisms*), fermentation of sugars by (KLUYVER and DONKER), i, 1215.
formation of plant vitamins by (MOCKERIDGE), i, 106.
Microsiphoneæ, utilisation of nitrogen by, in soils (GUITTONEAU), i, 106, 341.
Microtome for cutting gels (FRICKE), ii, 965.
Milk, action of hydrogen ions in coagulation of (COSMOVICI), i, 608.
arsenic in, after injection of salvarsan (FORDYCE, ROSEN, and MYERS), i, 189.
bacteriolytic power of (J. and M. BORDET), i, 616.
effect of heat on solubility of calcium and phosphorus compounds of (BELL), i, 998.
separation of the Schardinger enzyme from (HOPKINS and DIXON), i, 1506.
perhydridase of (SBARSKY and MICHLIN), i, 472.
inorganic phosphates in (VLADESCU), i, 1114.
phosphorus compounds in (KAY), i, 998.
effect of replacement of proteins by urea in diet on production of (MORGAN, WINDHEUSER, and OHLMER), i, 217.
xanthine oxydase of (THURLOW), i, 743.
cows', constituents of (BLEYER and KALLMANN), i, 184.
influence of sunlight on properties of (LUCK), i, 211.
precipitation of calcium from (ROTHWELL), i, 1350.
citric acid in (KIEFERLE, SCHWAIBOLD, and HACKMANN), i, 855.
yellowish-green colouring matter of (BLEYER and KALLMANN), i, 457.
cows' and human, phosphorus content of (HESS and HELMAN), i, 1204.
vitamins in (PRINGLE), i, 1018.
dried and evaporated, vitamin content of (HARTWELL) i, 751.
Milk-agar, use of, in bacterial investigations (SLOBODSKA-ZAYKOVSKA), i, 1510.
Milk-serum, organic phosphorus compounds in (PFYL and SAMTER), i, 1114.
Milkweed. See *Asclepias syriaca.*
Millon's base, decomposition of the iodide of (PETRIKALN), ii, 630.
Mineral sulphides, electrosynthesis of sols of (V. HAHN), ii, 522.
Mineral waters. See under Water.
Minerals, density of (PANICHI), ii, 64.
absorption of oxygen and water by (KURNAKOV), ii, 767.
transformation of, by replacement of gels (LINDGREN), ii, 392.
of the mica group (WINCHELL), ii, 592.
determination of the age of (KIRSCH), ii, 320.
fusion mixture for separation of (CLERICI), ii, 594.
"**Misch metal**," cerium-free, preparation of (THOMPSON and KREMERS), ii, 580.
Mists from chemical reactions (REMY and RUHLAND; REMY and KOCH), ii, 107.
Mixtures, binary, influence of chemical constitution on the thermal properties of (PASCAL), ii, 953.
vapour pressure of (BROWN), ii, 377.
Molecular association (ROCARD), ii, 1045.
of organic liquids (LANGE), ii, 840.
and the equation of state (JÄRVINEN), ii, 865.
diameter, calculation of (SIRK), ii, 184.
field, determination of (JONES), ii, 16, 91, 92.
and molecular volume (BATSCHINSKI), ii, 932.
symmetry and optical activity (DARMOIS), ii, 1119.
Molecules, structure of (MÜLLER), ii, 363; (CABRERA), ii, 1107.
formation and decomposition of (PÓLÁNYI and WIGNER), ii, 1077.
refraction and electron constraint in (SMYTH), ii, 843, 1019.
magnetic properties of (WILSDON), ii, 641.
collisions between (FRANCK), ii, 836.
hydration of (FRICKE), ii, 36.
anisotropy of (RAMANATHAN), ii, 478.
diameter of (SIRK), ii, 364.
in isomerides (WÖHLISCH), ii, 269.
determination of cross-section areas of (MACK), ii, 1124.
activation of (DHAR), ii, 214.
dipolar, electric moment of (EBERT), ii, 262.
polyatomic polar, configuration of (HUND), ii, 479.
Molybdenum, *K*-series spectrum of (ALLISON and DUANE), ii, 250; (RICHTMYER and SPENCER), ii, 1101.
wave-length of Kα rays of (COMPTON and WOO), ii, 1128.
Röntgen ray spectra of (ALLISON), ii, 724; (ALLISON and ARMSTRONG), ii, 1015.
X-ray absorption coefficient of (WARBURTON and RICHTMYER), ii, 1103.
pure, electrical properties of (GEISS and VAN LIEMPT), ii, 638.

Molybdenum, electron emission from (DUSHMAN, ROWE, EWALD, and KIDNER), ii, 345.
critical potential in (PETRY), ii, 1017.
temperature scale and melting point of (WORTHING), ii, 759.
Molybdenum alloys, chemical resistance of (GUERTLER and LIEPUS), ii, 1146.
with aluminium and nickel and with nickel and tin (PFAUTSCH), ii, 536.
with chromium and nickel (SIEDSCHLAG), ii, 298.
with nickel and silicon (PFAUTSCH), ii, 298.
Molybdenum compounds, complex (SCAGLIARINI), ii, 891.
tervalent (WARDLAW and PARKER), i, 893.
Molybdenum *di*bromide, and its derivatives (LINDNER and HELWIG), ii, 421.
*di*chromate (CALCAGNI), ii, 891.
halides, action of, with ammonia and with potassamide in liquid ammonia (BERGSTROM), ii, 1083.
*trio*xide, volatility of, and its formation from the sulphide (BRINTON and STOPPEL), ii, 72.
*penta*oxide (WARDLAW and NICHOLLS), ii, 817.
selenide (MOSER and ATYNSKI), ii, 583.
Molybdenyl chloride (WARDLAW and WORMELL), ii, 61.
Molybdic acid, complex compounds of, with pyrocatechol and pyrogallol (FERNANDES), i, 912, 1061.
Molybdates, isomorphism of (ZAMBONINI and LEVI), ii, 1133.
Dithiomolybdates (TER MEULEN), ii, 584.
Molybdosulphites of the rare earths (CANNERI and FERNANDES), ii, 888.
Molybdovanadates (CANNERI), ii, 891.
Molybdenum organic compounds:—
Molybdic acid, compounds of organic acids with (HONNELAITRE), i, 509.
alkyl and aryl ammonium salts (KRAUSE and KRAUSKOPF), i, 908.
Molybdenum determination and separation:—
determination of, colorimetrically (TER MEULEN), ii, 330; (WENDEHORST), ii, 718.
determination of, as trioxide (HARTMANN), ii, 1206.
separation of, from vanadium (STOPPEL, SIDENER, and BRINTON), ii, 718.
Molybdomalic acid, ammonium salt, effect of hydroxy compounds on rotation of (DARMOIS and HONNELAITRE), ii, 184.
Molybdosulphites and **Molybdovanadates**. See under Molybdenum.
Monascus purpureus, colouring matter from (HIBINO), i, 1118.
Monocotyledons, starch-free, carbohydrate enzymes of (CHAPMAN), i, 215.
Monosaccharides, constitution of (HIRST and ROBERTSON), i, 364.
condensation of, with dilute mineral acids (LEVENE and ULPTS), i, 1042.
degradation of mercaptals of (PACSU), i, 515.
Monotropitin, enzymic hydrolysis of (BRIDEL), i, 615.
Monotropitoside, preparation and properties of (BRIDEL and PICARD), i, 1027.
Montanic acid, montanyl ester (FARGHER and HIGGINBOTHAM), i, 880.
Mordanting, theory of (ELÖD), ii, 531.
Morinidin chloride (WILLSTÄTTER and SCHMIDT), i, 54.
and its 3:2′:4′-trimethyl ether and perchlorate (PRATT and ROBINSON), i, 826.
Morphine, and its derivatives, physiological action of (ZAMPARO), i, 1116.
arsenious tartrate (DEBUCQUET), i, 1090.
determination of, by titration with silicotungstic acid (SAS), ii, 1011.
Morphine alkaloids (WIELAND and KOTAKE), i, 1448.
structure of (WIELAND and KOTAKE), i, 1090.
Mosses, respiration and imbibition in (MAYER and PLANTEFOL), i, 1120.
Mother-of-pearl, structure of (SHAXBY), ii, 93.
Moulds, formation of citric and gluconic acids by (BUTKEVITSCH), i, 341.
formation of methyl ketones by (STÄRKLE), i, 205.
phosphorus metabolism of (SCHNÜCKE), i, 204.
utilisation of quinic acid by (BUTKEVITSCH), i, 1511.
decomposition of uric acid by (MORRIS and ECKER), i, 478.
Mucic acid, and its salts (KHOTINOKA and EPIFANOVA), i, 783.
nephropathic action of (ROSE and DIMMETT), i, 733.
Mucilage from plants (KOMATSU and UEDA), i, 762.

Mullite, formation of, from cyanite, andalusite, and sillimanite (GREIG), ii, 987.
crystal structure of sillimanite and (NAVIAS and DAVEY), ii, 1127.
Muscarine in fungi (GUTH), i, 1247.
Muscle, effect of ions on the functions of (ABRAHAM and KAHN), i, 728; (LANGE and MAYER; DEUTICKE), i, 729.
synthesis of carbohydrates in (MEYERHOF, LOHMANN, and MEIER), i, 727.
re-synthesis of carbohydrates in (JANSSON and JOST), i, 1354.
relation between pancreas and carbohydrate metabolism of (FOSTER), i, i, 1495.
production of carbon dioxide by (LIPSCHITZ and MEYER), i, 603.
carnosine in, in relation to excretion of iminazole (HUNTER), i, 459.
contraction of (GARNER), i, 607.
function of creatine in (TIEGS), i, 1003.
formation of lactic acid in (FURUSAWA), i, 849.
creatine content of (REISSER and HAMANN), i, 860.
influence of polyneuritis on (KUDRJAVZEVA), i, 329.
influence of ions on the decomposition of glycogen in (WEBER), i, 1004.
changes of glycogen and phosphates in (v. EULER, MYRBÄCK, and KARLSSON), i, 744.
effect of insulin on oxidation in (AHLGREN; NITZESCU and COSMA), i, 482.
effect of calcium on the synthesis of lactacidogen in (EMMRICH and LANGE), i, 728.
effect of sodium salts on the synthesis of lactacidogen in (EMBDEN, KAHLERT, and LANGE), i, 728.
lactic acid in, during fatigue (HENTSCHEL), i, 728.
oxidation of lactic acid in (v. SZENT-GYÖRGYI), i, 708.
killed by insulin, lactic acid in (BAUR and KÜHN), i, 482.
isoelectric points of proteins of (WÖHLISCH and SCHRIEVER), i, 1488.
colloidal properties of proteins of (WEBER), i, 995.
sugars in juice of (CONSTANTINO), i, 720.
cod's, autolysis of (CALLOW), i, 469.
fatigued, phosphate metabolism in (ANDREWS), i, 729.
Muscle, frog's, formation of acetaldehyde in (NEUBERG and GOTTSCHALK), i, 859.
action of fluorides on the activity and metabolism of (EMBDEN and HENTSCHEL), i, 727.
striated, effect of narcosis on (LANGE and MAYER), i, 735.
plain, physiology of (TSUBURA), i, 1004.
smooth, action of narcotics on (JOACHIMOGLU), i, 735.
Muscovite, orientation of ammonium iodide crystals on the surface of (ROYER), ii, 110.
Muscular exercise, supply and utilisation of oxygen in (FURUSAWA), i, 993.
effect of, on respiration and lactic acid (FURUSAWA, HILL, LONG, and LUPTON), i, 92; (LYTHGOE and PEREIRA; PEREIRA), i, 1341.
effect of, on composition of urine (LILJESTRAND and WILSON; WILSON, LONG, THOMPSON, and THURLOW), i, 1115.
Mustard, white. See *Sinapis alba*.
Mutarotation (RIIBER), i, 8; (RIIBER, ESP, and BERNER), i, 635; (RIIBER, SÖRENSEN, and THORKELSEN), i, 773; (LOWRY; LOWRY and RICHARDS), i, 886; (KUHN and JACOB), ii, 49.
kinetics of (v. EULER, ÖLANDER, and RUDBERG), ii, 876.
Mycorrhyza, activity of enzymes in (MELIN and HELLBERG), i, 745.
Myogen, isoelectric point and stability of (WEBER), i, 995.
Myoporum laetum (ngaio), constituents of (McDOWALL), i, 1521.
Myosin, isoelectric point and solubility of (WEBER), i, 995.
Myricetin, synthesis of (KALFF and R. ROBINSON), i, 423; (DEAN and NIERENSTEIN), i, 951.
5:7:3′:4′:5-pentamethyl ether (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
Myristaldehyde *p*-nitrophenylhydrazone (STEPHEN), i, 1131.
Myristic acid, hydroxylamine salt (OESPER and BALLARD), i, 1233.
thallous salt (HOLDE and TAKEHARA), i, 1233.
3-hydroxybenzaldehyde-2-mercuric ester (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1152.

N.

3′-β-Naphthacoumaryl-4-α-naphthapyrone (DEY and ROW), i, 149.

β-Naphthacridine-12-carboxylic acid, 10-amino-, acetyl derivative (SAFTIEN), i, 1318.
1:6-Naphthadiquinoline, and its sulphate (ARMIT and ROBINSON), i, 1172.
Naphthalanil, *o*-amino-, and its derivatives (CHAKRAVARTI), i, 162.
α-Naphthaldehyde *p*-nitrophenylhydrazone (STEPHEN), i, 1131.
Naphthalene, structure of (FUSON), i, 253; (LESSER, KRANLPUHL, and SAD), i, 1424.
constitution and nitration of (ODELO), i, 804.
molecular heat and viscosity of solutions of (DE KOLOSOVSKI), ii, 1163.
boiling point of (FINCK and WILHELM), ii, 759.
surface tension of solutions of, in benzene (SCHECHTMANN), ii, 1148.
solubility of, in tetrachloroethane (COHEN, DE MEESTER, and MOESVELD), ii, 190, 852.
pyrogenic decomposition of, in presence of aluminium and nickel oxides (IPATIEV and KIJUKWIN), i, 241.
derivatives, hydrogenated, formation and spectrochemistry of (v. AUWERS and MÖLLER), i, 402; (v. AUWERS), i, 815.
analysis of, and its sulphonic acids (CALCOTT, ENGLISH, and DOWNING), ii, 73.
Naphthalene, 1:3:4-*tri*amino-, and 3-nitro-1:4-*di*amino-, acetyl derivatives (PANIZZON-FAVRE), i, 145.
2:7-*di*hydroxy-, derivatives of (LESSER, KRANLPUHL, and SAD), i, 1426.
2-iodo-5- and -8-nitro- (CHUDOŽILOV), i, 903.
Naphthalenes, hydrogenated (STRAUS, BERNOULLY, and MAUTNER), i, 1155.
Naphthalenes, *tri*amino-, and their hydrochlorides and *di*nitro- (FINZI), i, 701.
bromonitro- (VESELÝ and CHUDOŽILOV), i, 1056.
Naphthalene series, hydrogenation in (ROWE and TARBETT), i, 317.
1-Naphthaleneazo-2-hydroxynaphthalene, 1′-amino-2′:4′-*di*hydroxy- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 989.
α-Naphthaleneazo-*ar*-tetrahydro-α-naphthylamine (ROWE and TARBETT), i, 317.
Naphthalene-3-carboxylic acid, 2-hydroxy-, constitution of (LESSER, KRANLPUHL, and SAD), i, 1424.
Naphthalenedisulphonic acids, benzyl-ψ-thiocarbamide salts (CHAMBERS and SCHERER), i, 127.
Naphthalene-2-sulphoiodide (GIBSON, MILLER, and SMILES), i, 1137.
Naphthalene-2-sulphonic acid, metallic salts, and their solubilities (EPHRAIM and PFISTER), i, 896.
Naphthalene-3-sulphonic acid, 1-cyano-, and its salts (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1426.
Naphthalene-5-sulphonic acid, 1-chloro-, metallic salts, and their solubilities (EPHRAIM and PFISTER), i, 897.
Naphthalenesulphonic acids (AMBLER, LYNCH, and HALLER), i, 126.
arylamine salts (FORSTER and KEYWORTH), i, 126.
benzyl-ψ-thiocarbamide salts (CHAMBERS and SCHERER), i, 127.
α- and β-Naphthalenesulphonylalanines, and their salts (COLLES and GIBSON), i, 137.
2-Naphthalenethiolsulphonic acid, 6-methoxy-*m*-tolyl and 2:4-xylyl esters (GIBSON, MILLER, and SMILES), i, 1137.
Naphthalic acid, preparation of (WHISTON), i, 140.
1:8-Naphthalic acid, derivatives of (MASON), i, 33, 34.
1:8-Naphthalyl chloride, preparation properties and derivatives of (MASON), i, 34.
3-Naphthamido-*p*-cresols, 5-chloro-, and 5-chloro-3:5′-bromo-, and their derivatives (RAIFORD and LANKELMA), i, 810.
Naphthaphenanthrazine, amino-, acetyl derivative (PANIZZON-FAVRE), i, 145.
Naphthaphenazine, 3-hydroxy-, and its acetyl derivative (KEHRMANN and CHERPILLOD), i, 303.
3- and 4-hydroxy- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 304.
2:3-*di*hydroxy-, and its diacetyl derivative (KEHRMANN and SCHEDLER), i, 441.
αβ-Naphthaphenazinesulphonic acids (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 304.
Naphthaphenfluorindine (KEHRMANN and SCHEDLER), i, 442.
αβ-Naphthaphenoxarsine, 7-chloro- (AESCHLIMANN), i, 706.
α-Naphthapyrone-4-*p*-dimethylaminophenylethylene. See 4-*p*-Dimethylaminostyryl-α-naphthapyrone.
α-Naphthapyrone-4-*p*-methoxyphenylethylene. See 4-*p*-Methoxystyryl-α-naphthapyrone.
β-Naphthaquinol monohydrate (STRAUS, BERNOULLY, and MAUTNER), i, 1155.

α-Naphthaquinoline-6:7-dicarboxylic acid (STEWART), i, 975.
α-Naphthaquinone, action of magnesium phenyl bromide on (FRANSSEN), i, 1146.
derivatives of (SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES), i, 413.
1:4-Naphthaquinone, 2:3-*di*amino-, derivatives of (FRIES and BILLIG), i, 938.
2-nitro-, attempted synthesis of (PANIZZON-FAVRE), i, 144.
Naphthaquinones, action of organomagnesium compounds on (FRANSSEN), i, 1146.
β-Naphthaquinone-1-*p*-acetamidophenylimine (LANTZ and WAHL), i, 820.
1:4-Naphthaquinone-4-anil, 5- and 6-amino-, acetyl derivatives (SANDER), i, 982.
1-β-Naphthaquinone-1-anisylimine (LANTZ and WAHL), i, 820.
β-Naphthaquinonearylimines (LANTZ and WAHL), i, 820, 1159.
1:4-Naphthaquinonediphenylimine, 2-hydroxy- (LANTZ and WAHL), i, 820.
β-Naphthaquinone-1-*o*-methoxyanil (LANTZ and WAHL), i, 1159.
Naphthaquinonyl thiosulphates, potassium salts (HELLER), i, 315.
α-1:4-Naphthaquinonyl-3-acetoacetic acid, 2-amino-, acetyl derivative, ethyl ester (FRIES and BILLIG), i, 940.
Naphtharhodamines (MASON), i, 34.
β-Naphthathioflavone (SCHÖNBERG, ROSENBACH, KRÜLL, and OSTWALD), i, 1300.
Naphthazinesulphonic acids, colouring matters from (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 1330.
Naphthenic acids (TANAKA and NAGAI; TANAKA, NAGAI, and ISHIDA), i, 252.
from Nishiyama petroleum (TANAKA and NAGAI), i, 1271.
conversion of, into ketones (ZELINSKI and RJACHINA), i, 39.
1′:2′-Naphthiminazole-2-benzoic acid (CHAKRAVARTI), i, 162.
Naphthiminazoletrimethyl*cyclo*pentanecarboxylic acids (CHAKRAVARTI and GUPTA), i, 981.
α-Naphthimino*iso*thio-α-naphthamide (ISHIKAWA), i, 1149.
3-Naphthoacetamide, 2-hydroxy-, and its acetyl derivative (LESSER, KRANLPUHL, and SAD), i, 1425.
Naphthoic acid, hydroxy-, alkali vanadyl salts (ROSENHEIM and MONG), i, 1412.
α-Naphthoic acid, 6-amino-, and its acetyl derivative (DZIEWOŃSKI, SCHOENÓWNA, and WALDMANN), i, 1057.
β-Naphthoic acid, 1-bromo-2-hydroxy-, and 2-hydroxy-, salts and derivatives of (LESSER, KRANLPUHL, and SAD), i, 1425.
7-bromo-3-hydroxy-, and its derivatives (CHEMISCHE FABRIK GRIESHEIM-ELEKTRON), i, 599.
α-Naphthol, reaction of phenylcarbylamide with (PASSERINI), i, 1298.
detection and determination of, in β-naphthol (CALLAN), ii, 444.
α-Naphthol, 6-amino-, acetyl derivative (SANDER), i, 982.
5-bromo- (FUSON), i, 254.
6- and 7-bromo- (FUSON), i, 540.
2-nitro-4-amino-, acetyl derivative (PANIZZON-FAVRE), i, 145.
β-Naphthol, catalytic dehydration of methyl alcohol and (PLÜSS), i, 1410.
derivatives of, with chloral hydrate and dimethylaniline (SAKOSCHANASKY), i, 1061.
determination of, oxidimetrically (TÄUFEL and WAGNER), ii, 1007.
α- and β-Naphthols, distinction between (ZAMPARO), ii, 444.
and their derivatives, molecular compounds of (WEISSENBERGER, SCHUSTER, and MAYER), ii, 766.
additive compounds of, with ketones (PFEIFFER, GOEBEL, and ANGERN), i, 271.
β-Naphtholazobenzene-*p*-sulphonic acid. See Orange-II.
β-Naphthol-4-carboxylic acid, preparation of (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1426.
α- and β-Naphtholcoumareins (SEN and SIRCAR), i, 554.
β-Naphthol-6-sulphonic acid, metallic salts, and their solubilities (EPHRAIM and PFISTER), i, 897.
Naphthoxanthen, 8-hydroxy- (SEN and SARKAR), i, 813.
1-Naphthoxyacetyl bromide (FRIES and PUSCH), i, 569.
α-Naphthoyl chloride, 5-bromo- (RAIFORD and LANKELMA), i, 810.
β-1-Naphthoylacrylic acid (BOGERT and RITTER), i, 816.
1:2(1′:8′)-Naphthoylenebenziminazole (CHAKRAVARTI), i, 162.
1:2(1′:8′)-Naphthoylene-4-methylbenziminazole (CHAKRAVARTI), i, 162.
1:2(1′:8′)-Naphthoylene-1:3-naphthiminazole (CHAKRAVARTI), i, 162.

1-Naphthoylformanilideanil, 2-hydroxy- (Saftien), i, 1318.
2-Naphthoylformic acid, 1-hydroxy-, and 2-hydroxy-, anilide (Fries and Pusch), i, 569.
3-α- and -β-Naphthoylperylenes, 4:10-*di*chloro- (Zinke, Funke, Matscher, Wolfbauer, and Lorber), i, 1436.
αβ-Naphth*iso*thiazole-3-carboxylic acid, and its derivatives (Stolte, Giesel, and Badstübner), i, 1466.
Naphthyl thiosulphates, *di*hydroxy-, potassium salts (Heller), i, 315.
α-Naphthyl ethyl ether, 4-iodo- (Tanaka), i, 1061.
α- and β-Naphthyl benzyl ethers (v. Braun and Reich), i, 1405.
α-Naphthyl groups, migration of (Luce), i, 263.
α-Naphthylamine *di*chloroacetate (Doughty), i, 805.
α-Naphthylamine, 4-bromo- and 4-chloro-3-nitro- (Panizzon-Favre), i, 145.
β-Naphthylamine, catalytic reduction of (Hara), i, 536.
hydroferricyanide (Cumming), i, 122.
α- and β-Naphthylamines, *m*-nitrobenzenesulphonamides (Marvel, Kingsbury, and Smith), i, 245.
β-α- and -β-Naphthylaminobenzylmalonic acids, ethyl esters (Wayne and Cohen), i, 550.
α-Naphthylaminocamphor, phototropism of, in chloroform (Singh), ii, 195.
2-β-Naphthylamino-3-hydroxy-1:4-naphthaquinone (Fries and Billig), i, 939.
3-Naphthylamino-5-keto*iso*oxazoles (Worrall), i, 308.
3-Naphthylamino-5-ketopyrazoles (Worrall), i, 308.
2-β-Naphthylamino-1:4-naphthaquinone, 3-chloro-2-*N*-nitroso- (Fries and Billig), i, 939.
1-α- and -β-Naphthylaminonaphthylamines (Levi and Faldino), i, 171.
2-α- and -β-Naphthylamino-5-phenyl-1:3:4-thiodiazines, and their derivatives (Bose), i, 1466.
2-Naphthylbenztriazole, α-amino-, α-hydroxy-, and β-nitroso- (Elbs), i, 165.
α- and β-Naphthyl benzyl ketones (Luce), i, 264.
1:4-Naphthylene dibenzoate (Panizzon-Favre), i, 145.
1:2-Naphthylenediamine, 4-amino-, acetyl derivative (Panizzon-Favre), i, 145.
aminoazines from (Kehrmann and Safar), i, 1331.
1:4-Naphthylenedihydraziuetetracarboxylic acid, ethyl and methyl esters (Stollé and Adam), i, 1469.
β-Naphthyl-3:4-*di*hydroxy-α-naphthylsulphone, and its derivatives (Hinsberg), i, 1062.
1-Naphthylimino-β-naphthaquinone (Société Anonyme des Matières Colorantes), i, 413.
3-β-Naphthyl-2-methyl-*lin*-naphthiminazole-4:9-quinone (Fries and Billig), i, 939.
2-β-Naphthyl-4-methylpyrimidine-5-carboxylic acid, and its ethyl ester (Mitter and Palit), i, 1320.
***N*-(1')-Naphthylnaphthalimide**, 2'-amino- (Chakravarti), i, 162.
β-Naphthyl-1-β-naphthaquinonylsulphone, and its derivatives (Hinsberg), i, 1062.
Naphthylnaphthylenediamines, and their derivatives (Levi), i, 436, 1186.
β-Naphthyl-4-nitropiaseleneazonium chloride (Battegay and Véchot), i, 1468.
α- and β-Naphthylquinoxalines, hydroxy derivatives (Fries and Pusch), i, 569.
5-α-Naphthyl-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole (Guha and Rây), i, 703.
α-Naphthyl-*p*-tolylsulphone (Gilman, Beaber, and Myers), i, 1057.
6-Naphthyl-1:3:5-triazine, 2:4-*di*amino-6-*p*-hydroxy- (Society of Chemical Industry in Basle), i, 441.
Naphthyridine group, syntheses in the (Gulland and Robinson), i, 1186.
Narcosis (Lange and Mayer), i, 735.
mineral composition of blood in (Blanchetière and Cardot), i, 455.
action of, on smooth muscle (Joachimoglu), i, 735.
Narcotine, salts, dissociation of, and extraction of the alkaloid from solutions (Fabre and Parinaud), i, 962.
Natural water. See under Water.
Nebulium, spectrum of (Rosseland), ii, 3; (Lemon), ii, 1099.
Neodymium, preparation and properties of (Kremers), ii, 588.
pole-effect in spectrum of (Mohr), ii, 612.
Röntgen ray spectrum of (Gleditsch and Botolfsen), ii, 612.
Neodymium oxide, spectrum of (Nichols), ii, 259.
sulphate, double salts of thallous sulphate and (Zambonini and Caglioti), ii, 1185.

Neodymium potassium sulphate (ZAMBONINI and CAGLIOTI), ii, 222, 315.
Neoline, and its derivatives (SCHULZE and BERGER), i, 283.
Neon, spectrum of (CHILDS), ii, 339; (GOUDSMIT), ii, 450; (BURNS; DORGELO), ii, 1099.
reversal of rays in the spectrum of (BUISSON and JAUSSERAN), ii, 333.
absorption spectra of, and of its mixtures with argon and helium (MEISSNER), ii, 1099.
arc spectrum of, and its ionisation potentials (HERTZ), ii, 723.
spark spectrum of (L. and E. BLOCH and DÉJARDIN), ii, 334.
ultra-violet spectrum of (LYMAN and SAUNDERS), ii, 911.
Zeeman effect with (BACK), ii, 341.
electrical properties of (MCCALLUM and FOCKEN), ii, 641.
ionisation potential of (HERTZ and DE VISSER), ii, 339.
in vacuum tubes (RIDING and BALY), ii, 925.
atomic field of (JONES), ii, 253.
emission of light by mixtures of solid nitrogen and (VEGARD, ONNES, and KEESOM), ii, 474.
isotherms of (HOLBORN and OTTO), ii, 851.
absorption in (MEISSNER; JORDAN), ii, 337.
Neopelline (SCHULZE and BERGER), i, 283.
Neosine, detection of (FLÖSSNER and KUTSCHER), i, 327.
Nephelometer, new (KINGSLAKE), ii, 821.
Nephelometry (KLEINMANN), ii, 389.
Nephritis, nitrogenous substances in urine in (MOSONYI), i, 1491.
Nernst filaments, construction of (GRIFFITH), ii, 896.
Nerves, production of carbon dioxide by (PARKER), i, 849.
frogs', excretion of carbon dioxide by (PARKER), i, 1353.
Nervone (KLENK), i, 1346.
Nervous system, formation of ammonia in (WINTERSTEIN and HIRSCHBERG), i, 607.
effect of arsonium, phosphonium, and sulphonium compounds on (HUNT and RENSHAW), i, 861.
central, glycogen and cerebroside metabolism of (WINTERSTEIN and HIRSCHBERG), i, 1495.
Nessler's reagent, preparation of (RICHMOND), ii, 327; (FREDERICK), ii, 435.
without potassium iodide (WINKLER), ii, 713.
Neurosyphilis (MYERS and CORBITT; CORNWALL and MYERS), i, 611.
Neutral-red, toxicity of (POLITZER), i, 197.
Neutral salt action and electrical field of ions (DEBYE and MCAULAY), ii, 171.
Newt, small water. See *Triton tæniatus*.
Ngaio. See *Myoporum laetum*.
Ngaiol, and its derivatives (MCDOWALL), i, 1521.
Ngaione, and its derivatives (MCDOWALL), i, 1521.
Nickel, occurrence of, in arable soils (BERTRAND and MOKRAGNATZ), i, 492.
occurrence of, in soils, plants, and animals (MCHARGUE), i, 1023.
spectrum of (BECHERT), ii, 1014.
arc spectrum of (WALTERS), ii, 335; (BECHERT and SOMMER), ii, 913.
line spectrum of (WORTHING and RUDY), ii, 1102.
spark spectrum of (L. and E. BLOCH), ii, 727.
pure, magnetic properties of (MALCOLM), ii, 371.
films, magnetic properties of (SORENSEN), ii, 82.
magnetic anisotropy of (FORRER), ii, 486, 639.
non-magnetic films of (OSEEN), ii, 734; (INGERSOLL and DE VINNEY), ii, 846.
magnetisation of iron and (DE WAARD; PESCHARD), ii, 751.
magnetisation of iron, cobalt, magnetite, and (ASHWORTH), ii, 944.
magnetostrictive effects in (MCCORKLE), ii, 487.
pure, electrical properties of (GEISS and VAN LIEMPT), ii, 638.
films, electrical conductivity and Hall effect in (RIEDE), ii, 355.
electro-deposition of (EMELIANOVA), ii, 676.
quantitative deposition of, from oxalate electrolytes (FRÖLICH), ii, 604.
conductivities of (SCHOFIELD), ii, 273.
critical potential in electron emission from (PETRY), ii, 1017.
current-potential curves for (LIEBREICH and WIEDERHOLT), ii, 404.
polarisation of (TRIANDAFIL), ii, 405.
passivity of (ROTHMUND, EISENKOLB, and STEINHERZ), ii, 131; (EISENKOLB), ii, 1165.
atomic heat of (RODEBUSH and MICHALEK), ii, 949.
heat of adsorption of hydrogen on (FORESTI), ii, 692.

Nickel, transformation of, at the Curie point (DEL REGNO), ii, 372.
solubility of, in water containing carbon dioxide (ROBL), ii, 231.
electrolytic solution of, in sulphuric acid (ROLLET), ii, 799.
physical state and catalytic activity of (GAUGER), ii, 1072.
catalytic reduction with (FELDMANN), i, 1263.
catalytic reduction of acetaldehyde with (NEGOSHI), i, 1375.
catalytic, promoter action of thoria on (RUSSELL and TAYLOR), ii, 1071.
effect of thiophen on the action of (KUBOTA and YOSHIKAWA), ii, 805.
inactivation of, by impurities (ARMSTRONG and HILDITCH), ii, 562.
colloidal, sols of, in benzene and toluene (HATSCHEK and THORNE), ii, 197.
reduced, composition of (KUBOTA and YOSHIKAWA), ii, 1174.
catalytic action of (KOMATSU and YUKITOMO), i, 687; (KOMATSU and TANAKA), i, 905.
catalytic activity of reduced copper, thoria, and (KOMATSU and MASUMOTO), ii, 1071.
in the animal organism (BERTRAND and MÂCHEBŒUF), i, 719.
Nickel alloys with aluminium and molybdenum and with molybdenum and tin (PFAUTSCH), ii, 536.
with carbon and iron (KASE), ii, 973.
with chromium and molybdenum (SIEDSCHLAG), ii, 298.
with copper (CHEVENARD), ii, 851.
oxidation of (PILLING and BEDWORTH), ii, 689.
with iron (DELORAINE), ii, 639; (GRENET), ii, 973.
magnetic properties of (YENSEN), ii, 372.
thermomagnetic properties of (PESCHARD), ii, 651.
effect of tension on magnetic properties of (BUCKLEY and McKEEHAN), ii, 945.
expansion coefficients of (HONDA and OKUBO), ii, 104.
temper colours of (TAMMANN and SIEBEL), ii, 1169.
with molybdenum and silicon (PFAUTSCH), ii, 298.
Nickel compounds in vegetables (BERTRAND and MOKRAGNATZ), i, 873.
Nickel salts, rotatory dispersion of (ROBERTS), ii, 478.
Nickel chloride, magnetic properties of (WOLTJER; WOLTJER and ONNES), ii, 1038.
Nickel hydroxide, magnetic properties of (VEIL), ii, 412.
solution and precipitation of, in water (VEIL), ii, 183.
precipitation of, electrometrically (BRITTON), ii, 1203.
nitrate, action of phosphorus on (SCHMOSS), ii, 889.
*sub*oxide (LEVI and TACCHINI), ii, 424.
oxide, reduction of, by hydrogen (BENTON and EMMETT), ii, 216.
effect of chlorine on catalysis by (BOSWELL and BAYLEY), ii, 215.
selenide (MOSER and ATYNSKI), ii, 583.
sulphate, hydrated, solubility of (TANCOV), ii, 852.
Nickel organic compounds:—
with diacetyldioxime (PANETH and THILO), i, 1132.
Nickel detection, determination, and separation:—
detection and determination of (FEIGL and CHRISTIANI-KRONWALD), ii, 330; (SOULE), ii, 603.
determination of (JÄRVINEN), ii, 602.
determination of, as dioxide (MOSER and MAXYMOWICZ), ii, 1206.
determination of, in presence of iron and cobalt (WEELDENBURG), ii, 72.
separation of cobalt, manganese, zinc, and (LEMARCHANDS), ii, 242.
separation of, from iron (ARDAGH and BROUGHALL), ii, 603.
separation of iron and, in presence of chromium (ROUSSEAU), ii, 441.
separation of zinc and (KLING and LASSIEUR), ii, 439.
Nickel wire, magnetic spectrum of (ARKADIEV), ii, 82.
Nicotine, rotation of (PATTERSON and FULTON), ii, 1120.
configuration of, and its oxidation (KARRER and WIDMER), i, 1084.
adsorption of, by calcium salts (CHAPIN), i, 697.
separation of, from ammonia, and its decomposition by enzymes (FODOR and REIFENBERG), i, 1519.
Nicotinic acids, derivatives of (MEYER), i, 836.
α-Nicotyrine. See *N*-Methyl-2-[2-pyridyl]pyrrole.
Niobium, arc spectrum of (MEGGERS), ii, 167.
Niobium carbide and nitride (FRIEDERICH), ii, 374.
nitride (FRIEDERICH and SITTIG), ii, 420.
oxide, visible radiation of (NICHOLS), ii, 350.

Niobium detection, determination, and separation :—
detection and determination of, and its separation from tantalum (POWELL and SCHOELLER), ii, 1096.
determination of, and separation from iron (PIED), ii, 442.
Niquine, and *di*bromo-, and their derivatives, and *N*-nitroso- (SUSZKO), i 1449.
Nitella, adsorption of dyes by cell sap of (IRWIN), i, 1363.
Niton (*radium emanation*), radioactive constant of (CURIE and CHAMIÉ), ii, 8.
decay constant of (BASTINGS), ii, 621.
ionisation potential of (GLOCKLER), ii, 1105.
rate of transformation of (CURIE), ii, 463.
number of ions produced by, in a spherical volume (MUND), ii, 732.
action of, on hydrocarbons (MUND and KOCH), i, 625.
perfusion experiments with calcium and (ZWAARDEMAKER, FEENSTRA, and STEYNS), i, 193.
effect of, on growth of rats (CHICK and TAZELAAR), i, 211.
Nitrates. See under Nitrogen.
Nitration (SCHAARSCHMIDT, BALZERKIEWICZ, and GANTE), i, 532; (KLEMENC and SCHÖLLER), ii, 212.
at high temperatures, apparatus for (KRANZ and KOPECKY), ii, 319.
new method of (SCHAARSCHMIDT), i, 128.
with nitrates (MENKE), i, 386, 655.
with mixed nitrosulphonic and fuming nitric acids (VARMA and KULKARNI), i, 238.
Nitric acid. See under Nitrogen.
Nitrides, preparation and properties of (FRIEDERICH and SITTIG), ii, 419.
Nitrification by bacteria in acid solutions (GAARDER and HAGEM), i, 480.
in soils (GIBBS, BATCHELOR, and MAGNUSON), i, 1030.
Nitriles, synthesis of (HARA and KOMATSU), i, 893.
catalytic reduction of (ROSENMUND and JORDAN), i, 245; (GRIGNARD and ESCOURROU), i, 931.
action of magnesium organic compounds on (BRECKPOT), i, 14; (BRUYLANTS), i, 15; (CHRISTIAEN), i, 23; (ECTORS), i, 138; (JASPERS), i, 936.
condensation of thioamides with (ISHIKAWA), i, 917, 1149.
Nitrites. See under Nitrogen.
α-**Nitro-acids**, aliphatic, action of hydrazine hydrate on halogen derivatives of (MACBETH and TRAILL), i, 628.
Nitro-alcohols, aliphatic (TRÉNEL and WILKENDORF), i, 112.
Nitroamide, catalytic decomposition of (BRÖNSTED and DUUS), ii, 982.
Nitroamino-groups, determination of (LEHMSTEDT and ZUMSTEIN), ii, 1201.
Nitro-compounds, physical properties of (DESVERGNES), i, 1056; ii, 490.
reduction of, by calcium hydride (DURAND and HOUGHTON), i, 646.
action of sulphites and hydrogen sulphites on (RASCHIG), i, 289.
aromatic, ionisation of, in liquid ammonia (FIELD, GARNER, and SMITH), ii, 792.
reduction of (WEST), i, 535; (VESELÝ and CHUDOŽILOV), i, 654.
Nitrogen, structure and valency of (WAHL), ii, 937.
atomic, and its arc spectrum (COMPTON), ii, 910; (KIESS), ii, 911.
atom, asymmetric (WEDEKIND and UTHE), i, 536, 1059; (WEDEKIND), i, 678.
tervalent, asymmetric compounds of (HESS and GRAU), i, 425.
nuclei, ejection of protons from (BLACKETT), ii, 256.
spectrum of (MERTON and PILLEY), ii, 333.
band spectrum of (HULTHÉN and JOHANSSON; JOHNSON), ii, 11; (LINDAU), ii, 11, 625; (FASSBENDER), ii, 350; (MERTON and PILLEY; BIRGE and HOPFIELD), ii, 737.
infra-red emission spectrum of (PFUND), ii, 11.
line spectrum of (CROZE), ii, 77, 166.
ionised, line spectrum of (FOWLER), ii, 250.
spark spectrum of (KIESS), ii, 4.
solid, luminescence of (MCLENNAN, ii, 88; (VEGARD), ii, 630.
and its mixtures with neon (VEGARD, ONNES, and KEESOM), ii, 474.
fluorescence radiation of (OLDENBERG), ii, 1116.
magnetic susceptibility of (GLASER), ii, 82.
diamagnetism of, at low pressures (GLASER), ii, 642.
electrical properties of (MCCALLUM and FOCKEN), ii, 641.
heat of dissociation of (EUCKEN), ii, 207.

Nitrogen, molecular heat of (SCHREINER), ii, 97.
reproduction of electrical conditions of the afterglow of (CAMERON), ii, 172.
temperature-entropy diagram for (RODEBUSH, ANDREWS, and TAYLOR), ii, 492.
isotherms of (HOLBORN and OTTO), ii, 851.
absorption of, in water (BECKER), ii, 106.
solubility of, in liquid ammonia (LARSON), ii, 852.
fixation of, by the electric arc process (KARRER), ii, 987.
Haber equilibrium for (GILLESPIE), ii, 532.
as sodium cyanide (GUERNSEY and SHERMAN), ii, 889.
in soils (WINTERS), i, 767; (TRUFFAUT and BEZSSONOFF), i, 1227.
in soils of the Punjab (LAUDER and ALI), i, 1524.
explosion of mixtures of acetylene and (GARNER and SAUNDERS), ii, 627.
attempts to prepare a new chloride of (NOYES), ii, 988.
reaction of hydrogen with, in presence of mercury vapour (NOYES), ii, 573.
sources of available, for higher plants (BIALOSUKNIA), i, 1366.
residual, distribution of, in the organism (MADSEN), i, 718.
excretion of, in urine (SCHIMIZU; TAKANOSU), i, 185.
effect of ethyl acetate and other substances on (BYLSMA), i, 1356.
Nitrogen *tri*chloride, heat of formation of (NOYES and TULEY), ii, 644.
iodide, composition of (RASCHIG), ii, 147.
*mon*oxide (*nitrous oxide*), solubility of, in electrolytes (MANCHOT, JAHRSTORPER, and ZEPTER), ii, 282.
thermal and catalytic decomposition of (HINSHELWOOD and PRICHARD), ii, 310.
adsorption of, by glass (BANGHAM and BURT), ii, 657.
catalytic decomposition of, on gold (HINSHELWOOD and PRICHARD), ii, 567.
solid, structure of (DE SMEDT and KEESOM), ii, 484.
*di*oxide (*nitric oxide*), preparation of (NOYES), ii, 993.
electrical formation of (SCHWAB and LOEB), ii, 150.
Nitrogen *di*oxide (*nitric oxide*), rate of oxidation of (LATSHAW and PATRICK; HASCHE and PATRICK), ii, 681.
oxidation reactions with (KLEMENC), ii, 407.
dissociation equilibria of compounds of ferrous salts with (MANCHOT and HAUNSCHILD), ii, 298; (MANCHOT and LINKH), ii, 317.
formation of nitrous acid from nitric acid and (ABEL and HARASTY), ii, 139.
action of sodium ethoxide on (HESS), i, 58; (TRAUBE), i, 110.
analysis of, colorimetrically (WHITE and TOLMAN), ii, 682.
detection of (EEGRIWE), ii, 156.
*isodi*oxide (RASCHIG), ii, 146.
per- or *tetr*-oxide, adsorption of, by silica gels (RAY), ii, 191.
action of, on copper (KLEMENC and SCHROTH), ii, 228.
action of, on hydrocarbons (SCHAARSCHMIDT), ii, 227.
additive compounds of olefines and (SCHAARSCHMIDT and HOFMEIER), i, 877.
*pent*oxide, decomposition of (HUNT and DANIELS), ii, 801.
thermal decomposition of (HIRST), ii, 554.
velocity of decomposition of (WHITE and TOLMAN), ii, 682.
reactions of, with organic compounds (HAINES and ADKINS), i, 801.
Nitrosonitrogen *tri*oxide (HASCHE), ii, 988.
Nitrogen oxides, compressibility of (BATUECAS), ii, 497.
reduction of, in presence of sulphuric and sulphurous acids (GRAIRE), ii, 227.
determination of, by absorption (SCHLESSING), ii, 599.
determination of, in air and in combustion products of coal gas (FRANCIS and PARSONS), ii, 713.
Nitric acid (KLEMENC and SCHÖLLER), ii, 212.
constitution of (HANTZSCH and WOLF), ii, 634.
synthesis of (PASCAL), ii, 566.
vapour pressure of solutions of (TAYLOR), ii, 767.
action of, on metals (DHAR), ii, 315.
formation of nitrous acid from nitric oxide and (ABEL and HARASTY), ii, 139.

Nitrogen:—
Nitric acid, reduction of, by stannous and titanous chlorides (COBLENS and BERNSTEIN), ii, 804.
Nitrates, formation of, in soils (RUSSEL, JONES, and BAHRT), i, 1031.
detection of (MARVEL and DU VIGNEAUD), ii, 240; (VÁGI), ii, 599; (HAHN), ii, 1095; (HAHN and JAEGER), ii, 1199; (EKKERT), ii, 1200.
detection of, by the diphenylamine reaction (EKKERT), ii, 1093.
determination of (HIBBARD), ii, 240.
Pernitric acid (POLLAK), ii, 407.
Nitrous acid, decomposition of, by light and by catalysts (MUKERJI and DHAR), ii, 691.
reactions of sulphurous acid with (RASCHIG), ii, 146.
Nitrites, oxidation of (REINDERS and VLÈS), ii, 308.
Tromsdorff reagent for (COQUILLAT), ii, 328.
detection of (VÁGI), ii, 599; (HAHN and JAEGER), ii, 1199; (EKKERT), ii, 1200.
detection of, colorimetrically (NOVELLI), ii, 900.
Nitrogen *tetra*selenide and *tetra*sulphide (VAN VALKENBURGH and BAILAR), ii, 993.
*per*sulphide (USHER), ii, 581.
Nitrogen organic compounds, spectrochemistry of (v. AUWERS and KRAUL), ii, 847.
availability of, in pot experiments (CROWTHER), i, 1371.
heterocyclic, synthesis of (MINUNNI), i, 1175.
Nitrogen determination:—
determination of, by Kjeldahl's method (FLEURY and LEVALTIER), ii, 434.
determination of, by modified Kjeldahl methods (FLEURY and LEVALTIER; SHAW), ii, 65; (MARKLEY and HANN), ii, 824.
determination of, microchemically (ROSE), ii, 900.
determination of, in blood (OSBORN), i, 323.
determination of, in explosives (MARQUEYROL, CHENEL, FRIEDERICH, FLORENTIN, KOEHLER, and LORIETTE), ii, 599.
determination of, in nitrates, by Kjeldahl's method (MARGOSCHES, SCHEINOST, and WOYNAR; MARGOSCHES and SCHEINOST), ii, 1094.
determination of, in oil, coke, and proteins (TER MEULEN), ii, 599.
Nitrogen determination:—
determination of, in organic compounds (HESLINGA), ii, 65; (TER MEULEN), ii, 66.
determination of, in proteins (MAIN and LOCKE), i, 997.
determination of distribution of, in proteins (GORTNER and SANDSTROM), ii, 908.
inhibition of bumping in determination of, in soils (HANCE), i, 1032.
amino-, determination of, in bacterial metabolism (PARSONS and STURGES), i, 1509.
Nitroglauberite (FOOTE), ii, 786.
Nitro groups, replacement of benzoyl groups by (ELION), i, 44.
Nitroimino groups, determination of (LEHMSTEDT and ZUMSTEIN), ii, 1201.
Nitronium salts (HANTZSCH and WOLF), ii, 635.
Nitroprussic acid, sodium salt, action of, on acetone and acetaldehyde (VAN URK), ii, 162.
Nitrosochlorination (RHEINBOLDT and SCHMITZ-DUMONT), i, 1131.
Nitroso compounds, constitution of (GOLDSCHMIDT and CHRISTMANN), i, 649.
action of sulphites and hydrogen sulphites on (RASCHIG), i, 239.
Nitroso groups, influence of, in aromatic substitution (INGOLD), i, 646.
Nitrosonitrogen. See under Nitrogen.
Nitrososulphites. See Dinitrososulphonates under Sulphur.
Nitrosulphonic acid, nitration with a mixture of fuming nitric acid and (VARMA and KULKARNI), i, 238.
Nitrosyl chloride, formation of (TRAUTZ and SCHUETER), ii, 552.
velocity of formation of (TRAUTZ and GERWIG), ii, 878.
photochemical decomposition of (BOWEN and SHARP), ii, 695.
condensations with (SCHAARSCHMIDT and RAECK), i, 380.
reactions with (RHEINBOLDT and SCHMITZ-DUMONT), i, 1131.
Nitrous acid. See under Nitrogen.
Nitroxyl bromide and chloride, preparation of, and their reactions with Grignard reagents (ZUSKINE), ii, 587.
Nobili's rings, colours of (CHUCKUBUTTI), ii, 744.
Nonaldehyde, *i*-hydroxy-, and its derivatives (HELFERICH and SCHÄFER), i, 7.
Nonanediols, and their di-*p*-nitrobenzoates (PIERCE and ADAMS), i, 825.
Nona-oxymethylene diacetates (STAUDINGER and LÜTHY), i, 361.

Non-electrolytes, relation of, to rare gases in melting and boiling points (CARLSOHN), ii, 1044.
Δβ-Noninene (BOURGUEL), i, 770.
Non-metals, relations between hydrides and alkyl compounds of (v. GROSSE), ii, 843.
Nonodilactone (BENNETT), i, 883.
Nonoic acid, sodium salt, effect of sodium hydroxide on surface tension of (HARKINS and CLARK), ii, 857.
Nopinene, oxidation of, with permanganate (BRUS), i, 47.
Nor-*m*-hemipinic acid, ethylimide of (SPÄTH and DOBROWSKY), i, 1085.
Northebenine, cyano- (SPEYER and ROSENFELD), i, 962.
Novocaine, determination of, colorimetrically (CHERAMY), ii, 247.
Novocaine, bromo- (FREJKA and VITHA), i, 663, 1416.
Nuclei, mechanism of staining of (FEULGEN and VOIT), i, 1477.
Nucleic acid, determination of, in animal tissues (JAVILLIER and ADAMS), i, 996.
Nucleic acids, alkaloidal salts of (PEISER), i, 1477.
Nucleosides, dissociation constants of, and their relation to nucleic acid (LEVENE and SIMMS), i, 1478.
synthetic (LEVENE and SOBOTKA), i, 1463.
Nucleotides (IZUMI), i, 174.
dissociation of constants of, and their relation to nucleic acid (LEVENE and SIMMS), i, 1478.
plant, in animal tissues (JONES and PERKINS), i, 182.
Nutrient solutions, effect of bacteria on (BLEYER), i, 746.
Nutrition of aquatic animals (KŘIŽENECKÝ and PODHRADSKÝ), i, 612.
Nux vomica, determination of alkaloids in (SABALITSCHKA and JUNGERMANN), ii, 608.

O.

Oak, tannins from (FEIST and BESTEHORN), i, 566.
Oats, nutrients for culture of (JONES and PEMBER), i, 1030.
culture of, with nitrogen, phosphorus, and potassium (PEMBER and MACLEAN), i, 1121.
Oat bran, insulin-like substance in extracts of (BODEN, NEUKIRCH, and WANKELL), i, 483.
Octadecahydrodecacyclene (DZIEWOŃSKI and SUSZKO), i, 242.
Octaethylcellobiose, acetolysis of (HESS and SALZMANN), i, 1383.
Octahydroacridine, and amino-, and nitro-, and their derivatives (PERKIN and SEDGWICK), i, 63.
***s*-Octahydroanthracene**, and its salts and derivatives, and 9-thiol- (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 129.
action of aluminium chloride with (SCHROETER, VAN HULLE, GLUSCHKE, STIER, and MÜLLER), i, 125.
***s*-Octahydroanthracene-9-sulphinic acid**, sodium salt (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 130.
1-*s*-Octahydroanthracenylcarbamide (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 130.
1:2:3:4:5:6:7:8-Octahydrocarbazole, constitution of (v. BRAUN and SCHÖRNIG), i, 1449.
Octahydrodecacyclene (DZIEWOŃSKI and SUSZKO), i, 242.
Octahydroindene, preparation and dehydrogenation of (ZELINSKI and BORISSOV), i, 122.
Octahydronaphthalene (ZELINSKI and GAVEDOVSKAJA), i, 123.
***s*-Octahydrophenanthrene**, and 1-hydroxy-, and their derivatives (SCHROETER, VAN HULLE, and MÜLLER), i, 131.
***s*-Octahydrophenanthrene-9-carboxylic acid**, and its silver salt (SCHROETER, VAN HULLE, and MÜLLER), i, 131.
***s*-Octahydrophenanthrene-9-sulphonic acid**, salts and derivatives of (SCHROETER, VAN HULLE, and MÜLLER), i, 131.
Octahydrophenazine, and its derivatives (GODCHOT), i, 436.
Octahydroretene (VESTERBERG and BORGE), i, 252.
α- and β-Octahydrotrianhydrostrophanthidins (JACOBS and COLLINS), i, 567.
***n*-Octaldehyde** *p*-nitrophenylhydrazone (STEPHEN), i, 1131.
Octa-oxymethylene diacetate (STAUDINGER and LÜTHY), i, 361.
Δγ-Octinene (BOURGUEL), i, 770.
***n*-Octoic acid**, 3-hydroxybenzaldehyde-2-mercuric ester (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1154.
***n*-Octoylglycine**, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
Octyl alcohol, substitution of hydroxyl group of, by halogen (MCKENZIE and TUDHOPE), i, 226.
***sec.*-Octyl ether** (SENDERENS), i, 113.

Odorants (THOMS), i, 788.
Oidium lactis, action of, on tyrosine and its derivatives (KOTAKE, CHIKANO, and ICHIHARA), i, 746.
Oil, behaviour of oleic acid and, on water (CARRIÈRE), ii, 287.
Oils, action of ultra-violet light on (HESS and WEINSTOCK), i, 212.
surface tensions of aqueous solutions against (HOWARD and SOLLMAN), ii, 109.
acid value of (SOMAZZI), ii, 828.
hydrogenation of (LUSH), ii, 411.
iodine super-number of (MARGOSCHES, FRIEDMANN, SCHEINÖST, and TSCHÖRNER), i, 883.
animal marine, constituents of (ANDRÉ and CANAL), i, 1373.
drying, "oxynes" in (EIBNER and MUNZING), i, 1036.
essential. See Oils, vegetable.
fatty, polymerisation of (MARCUSSON), i, 356, 1234.
drying of (EIBNER and PALLAUF), i, 777.
iodine value of (MARGOSCHES, FRIEDMANN, and TSCHÖRNER), i, 629.
lecithin in (BOEDTKER), i, 1114.
fluorescent, coating of photographic plates with (HARRISON), ii, 930.
lubricating, heat of wetting of (BACHMANN and BRIEGER), ii, 510.
surface tension of (GRUNMACH and SCHWEIKERT), ii, 31.
marine, catalytic hydrogenation of (RICHARDSON, KNUTH, and MILLIGAN), i, 229.
vegetable (SCHIMMEL & Co.), i, 417.
formation of, in plants (FRANCESCONI, MANFREDI, and ASTENGO), i, 759; (POPOVICI), i, 1123.
extracted from flowers (v. SODEN), i, 1123.
fatty degeneration caused by (v. GRAEVENITZ), i, 195.
antiseptic action of (SCHÖBL), i, 1006.
growth-promoting and calcifying properties of, after exposure to light (STEENBOCK and BLACK), i, 1020.
detection of ethyl phthalate in (THOMS), ii, 1008.
determination of cineole in (CASH and FAWSITT), ii, 75.
determination of phenols in (RETI), ii, 604.
Australian, germicidal values of (PENFOLD and GRANT), i, 614.
from Calabria, constituents of (LA FACE), i, 564.
Oils, vegetable, Indian, constituents of (SIMONSEN), i, 565, 1164; (RAO), i, 565, 687; (RAO and SIMONSEN), i, 687; (RAO, SUDBOROUGH, and WATSON), i, 1164.
from Travancore (MOUDGILL), i, 565, 823, 945, 1293.
determination of iodine–bromine numbers of (KÖPKE), ii, 246; (WINKLER), ii, 446, 1009.
determination of nitrogen in (TER MEULEN), ii, 599.
Oil emulsions, reversible (SEIFRIZ), ii, 779.
Oil gas, compressed, hydrocarbons from (LEWIS-DALE), i, 769.
Oleanolic acid (VAN DER HAAR), i, 50.
Olefines, isomerisation in (BRUYLANTS), i, 493.
catalytic reduction of (KERN, SHRINER, and ADAMS), i, 625.
action of nitrogen tetroxide on (SCHAARSCHMIDT and HOFMEIER), i, 877.
Oleic acid, preparation, properties, and salts of (LAPWORTH, PEARSON, and MOTTRAM), i, 355.
synthesis of (G. M. and R. ROBINSON), i, 354.
behaviour of oil and, on water (CARRIÈRE), ii, 287.
oxidation of (LAPWORTH and MOTTRAM), i, 1129, 1234.
ammonium salt, elasticity and viscosity of (HATSCHEK), ii, 862.
calcium salt (KLIMONE, v. MOLTINI, and BENEDIK), i, 506.
solubility of (HARRISON), ii, 190.
sodium salt, surface tension of (JOHLIN), ii, 1054.
surface tension of aqueous solutions of (DU NOÜY), ii, 109.
thallium salt (HOLDE and SELIM), i, 504.
3-hydroxybenzaldehyde-2-mercuric ester (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1154.
Δ^{α}-Oleic acid, configuration of (SEMERIA), i, 5.
Oleyl acetate and benzoate (HELFERICH and SCHÄFER), i, 7.
***N*-Oleylpropylenediamine** (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
Olives, Palestine, constituents of, and their oil (MENCHIKOWSKY), i, 1521.
Olive oil, oxidation of organic compounds in (WALKER), i, 990.
Olive resin (REINITZER), i, 146.
Onion, toxins in scales of (WALKER, LINDEGREN, and BACHMANN), i, 872.

Ooporphyrin, conversion of, into hæmatoporphyrin (FISCHER and LINDNER), i, 992.
Opianic acid, condensation of, with phenols (JACOBSON and ADAMS), i, 272.
Opium alkaloids, extraction of (KANEWSKAJA), i, 153.
picrates of (MAPLETHORPE and EVERS), i, 1166.
detection of (DAVID), ii, 1010.
Optical activity and molecular dissymmetry (DARMOIS), ii, 1119.
and polarity of substituent groups (RULE and SMITH), ii, 1120.
potential (READ and MCMATH), i, 1126.
constants of matter (DARWIN), ii, 2.
inversion, Walden's (LEVENE and MIKESKA), i, 5; (SENTER and WARD), i, 31, 1128; (MCKENZIE and TUDHOPE), i, 226; (KENYON, PHILLIPS, and TURLEY), i, 507; (TERRY and EICHELBERGER), i, 631.
phenomena, quantum theory of (SLATER), ii, 478.
rotatory power, and size of atoms (BRAUNS), ii, 633.
screening constants (MENZIES), ii, 831.
superposition, studies in (PATTERSON and BUCHANAN), i, 115.
Optically active compounds, chemical constitution and rotatory power of (RUPE and KOPP), i, 274; (RUPE and VONAESCH), i, 499; (RUPE and RINDERKNECHT), i, 533.
Orange II, derivatives of, with sulphites (BUCHERER and STICHEL), i, 1338.
Oranges, insulin-like substances in (FISHER and MCKINLEY), i, 1016.
protein from (SMITH), i, 619.
navel, glucosides of (HALL), i, 760.
Valencia, constituents of the juice of (HALL and WILSON), i, 1521.
Orange juice, antiscorbutic value of (LIOTTA), i, 1365.
effects of lemon juice and of, on calcification (KORENCHEVSKY and CARR), i, 211.
Orchids, loroglossin from (DELAUNEY), i, 487.
Orcinol dimethyl ether, 2:6-*di*bromo- (WAGENHOFER), i, 550.
Orcinol, 2:4-*di*bromo-, and its salts (WAGENHOFER), i, 550.
Ordosite (LACROIX), ii, 429.
Organs, extraction of alkaloids from (FABRE), i, 719.
animal, method of testing therapeutic powders from (JAVILLIER, ALLAIRE, and GROG), ii, 1012.
Organic compounds, structure of, from Röntgen ray crystal analysis (MARK), i, 1.
formation of, from inorganic compounds in light (BAUDISCH), ii, 1082.
ultra-red spectrochemistry of (BONINO), ii, 1032.
ultra-violet absorption spectra of (MARCHLEWSKI and MOROZ), ii, 353.
rotatory dispersion of (LOWRY and RICHARDS), ii, 265; (LOWRY and CUTTER), ii, 356; (RICHARDS and LOWRY), ii, 632, 934; (CUTTER, BURGESS, and LOWRY), ii, 743.
fluorescence of (MOIR), ii, 261.
electron displacement in (LUCAS and JAMESON), i, 2; (LUCAS, SIMPSON, and CARTER), i, 769; (LUCAS and MOYSE), i, 770.
thermochemistry of (PARKS and KELLEY), ii, 949.
heats of combustion of (KHARASCH and SHER), ii, 636.
thermal data of (PARKS), ii, 491.
repulsive action of various groups in (BÖESEKEN), ii, 1031.
lability of halogen atoms in (MACBETH and TRAILL), i, 628, 782.
influence of hydrogen and halogens on the properties of (VAN ARKEL and DE BOER), ii, 758.
stability of (BOLIN), ii, 411.
reactivity of atoms and groups in (NORRIS and ASHDOWN), i, 626.
catalytic hydrogenation of, with platinum oxide (PIERCE and ADAMS), i, 824; (HECKEL and ADAMS), i, 909; (CAROTHERS and ADAMS), ii, 693.
liberation of hydrogen from (DICKSON), i, 1033.
autoxidation of (STAUDINGER), i, 897, 898.
adsorption of, by charcoal (RICHARDSON and ROBERTSON), ii, 383.
decomposition of (SCHÖNBERG), i, 557.
action of chlorine monoxide on (GOLDSCHMIDT and SCHÜSSLER), i, 497.
acidic, colour changes in salt formation by (KEHRMANN), i, 435.
aliphatic, spreading of, on surface of water (CARY and RIDEAL), ii, 1046, 1047, 1048.
complex, reactivity of (REIHLEN, ILLEG, and WITTIG), i, 232.
isomeric, solubility of (ANDREWS; KOHMAN), ii, 1052; (KOHMAN and ANDREWS), ii, 1053.
long-chain, Röntgen ray spectra of (SHEARER), ii, 938.

Organic compounds, proof of identity of (MURMANN), ii, 719.
elementary analysis of (ŠVÉDA and PROČKE), ii, 719.
determination of arsenic in (NEWBERY), ii, 901.
determination of carbon in (WHITE and HOLBEN), ii, 240; (DESGREZ and VIVARIO; SIMON), ii, 436; (WILDE and LOCHTE), ii, 600.
determination of carbon, hydrogen, and nitrogen in (HESLINGA), ii, 65.
determination of halogens in (BUSCH), ii, 823.
determination of nitrogen in (TER MEULEN), ii, 66.
determination of oxygen in (TER MEULEN), ii, 156.
separation of, by means of adsorption (FODOR and ROSENBERG), ii, 1060.
Organic radicals. See under Radicals.
Organic reactions, course of (MÜLLER), ii, 414.
Organic syntheses, physico-chemical study of (MATIGNON), ii, 1068.
Organism, animal, synthesis of amino-acids in (MCGINTY, LEWIS, and MARVEL), i, 100.
electrolytes in the (KRAUS, ZONDEK, ARNOLDI, and WOLLHEIM), i, 198.
metabolism of mineral salts in the (SASAKI), i, 331.
human, water–salt content of, in relation to acid–base balance (OEHME and PAAL), i, 326.
Organo-metallic compounds, fluorides of (KRAUSE and V. GROSSE), i, 378.
Ornithine, behaviour of, in the liver (FELIX and ROTHLER), i, 859.
Orobanches, blackening of, during drying (BRIDEL and CHARAUX), i, 488.
p-**Orsellinic acid** (WAGENHOFER), i, 550.
Orthoboric acid. See under Boron.
Orthocarbonic acid, ethyl ester, hydrolysis of (SKRABAL and BALTADSCHIEVA), ii, 139.
Osmium chloride, compounds of carbon monoxide with (MANCHOT and KÖNIG), ii, 232.
*tetr*oxide (V. WARTENBERG), ii, 231.
boiling point of (V. WARTENBERG), ii, 276.
compounds of (KRAUSS and WILKEN), ii, 894.
Osmium organic compounds, complex base of (TSCHUGAEV and FRITZMANN), i, 1395.
Osmosis in various gels (YUMIKURA), i, 735.
See also Electro-endosmosis.
Osmotic equilibria of systems with a semi-permeable membrane (SCHREINEMAKERS), ii, 975.
Osmotic pressure, determination of, by the solubility method (APPLEBEY and DAVIES), ii, 964.
relation of, to adsorption (PÓLÁNYI), ii, 290.
of colloids (BJERRUM), ii, 111.
electrolytes of high molecular weight (HAMMARSTEN), ii, 195.
Ovariectomy, salts in blood after (BLANCHETIÈRE), i, 1207.
Ovary, preparation of hormone from (DICKENS, DODDS, and WRIGHT), i, 1513.
lipoids of the (YAMAUCHI; LANG), i, 457.
Over-potential, theory of (HEYROVSKÝ), ii, 675.
Overvoltage (KNOBEL), ii, 211, 212; (BIRCHER, HARKINS, and DIETRICHSON), ii, 211; (NEWBERY), ii, 405; (SMITS), ii, 547.
influence of colloids on (MARIE and LEJEUNE), ii, 115.
effect of hydrogen-ion concentration on (HERASYMENKO), ii, 675.
effect of surface condition on (KNOBEL), ii, 547.
cathodic, and passivity (LIEBREICH and WIEDERHOLT), ii, 44.
hydrogen (HARKINS and ADAMS), ii, 301.
on alloys (FISCHER), ii, 44.
at arsenic cathodes (GRUBE), ii, 43.
of lead cathodes (GLASSTONE), ii, 43, 301.
of mercury cathodes (GLASSTONE), ii, 133.
Ox, constituents of extracts of testicles of (MÜLLER), i, 854.
Oxacyanines (KÖNIG and MEIER), i, 705.
p-**Oxadiazphospholes** (AUTENRIETH and BÖLLI), i, 1468.
Oxalacetic acid, fermentation of (NEUBERG and GORR), i, 837.
behaviour of, with animal organs (MAYER), i, 736.
Oxalenediuramidoxime, use in, in detection and determination of nickel (FEIGL and CHRISTIANI-KRONWALD), ii, 330.
Oxalic acid, dissociation constants of (BRITTON), ii, 977.
adsorption of, by oxides (KOZAKEVITSCH), ii, 855.
photochemical decomposition of, in uranyl sulphate solution (ANDERSON and ROBINSON), ii, 415.
esterification of, with phenols (FEIGL and KOBILIANSKY), i, 1235.

Oxalic acid, reaction of ethers with (WASER and SANDER), i, 536.
oxidation of, by hydrogen peroxide (HATCHER and HOLDEN), ii, 684.
catalysis of the reaction of permanganates with (RIDLEY), ii, 689.
additive compounds of sodium ethoxide and esters of (ADICKES), i, 1378.
decomposition of, by plants (PALLADIN and LOVTSCHINOVSKAJA), i, 1222.
Oxalic acid, aniline trihydrogen salt (RAMBECH), i, 385.
calcium salt, abnormal crystal forms of (BARDACH), i, 1114.
hydration of (AUMÉRAS), ii, 895.
action of sulphuric acid on (CARRIÈRE and VILON), ii, 206.
precipitation of, in presence of ammonium citrate (JAKÓB), ii, 69.
conversion of, into calcium carbonate in tissues (LOEPER, SCHULMANN, and TOUNET), i, 1497.
magnesium salt, occlusion of, by calcium oxalate (LEMARCHAND), ii, 385.
molybdenum salts (WARDLAW and PARKER), i, 893.
potassium salt, electrolysis of solutions of (JEFFERY), ii, 304.
effect of light on the reactions of bromine and iodine with (BERTHOUD and BELLENOT), ii, 141.
uranyl salt (COLANI), i, 1235.
urea salts, determination of, in fertilisers (SABALITSCHKA and KUBISCH), i, 347.
Oxalic acid, dinaphthyl and ditolyl esters (FEIGL and KOBILIANSKY), i, 1236.
ethyl and methyl esters, equilibria of, with phenols (KREMANN, ZECHNER, and DRAZIL), ii, 650.
Oxalic acid, detection of, in tissues (KLEIN and WERNER), i, 871.
separation of, in analysis of Group III metals (KESCHAN), ii, 1008.
Oxalpropionic acid, ethyl ester, thermal decomposition of (WATSON), ii, 556.
Oxalsuccinic acid, ethyl ester, thermal decomposition of (WATSON), ii, 556.
Oxalyl-4:4′-*di*aminodiphenylmethane (BUTLER and ADAMS), i, 1458.
Oxalyldibenzyl ketone, azines from (CHAKRAVARTI), i, 1330.
Oxalyldimalonic acid, ethyl ester (PANKOKE), i, 358.
α-Oxalyl-γ-phenyl-Δ$^{\beta}$-butenoic acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.
α-Oxalyl-γ-phenylbutyric acid, ethyl ester (v. AUWERS and MÖLLER), i, 403.
Oxazole-yellow (KÖNIG and MEIER), i, 705.
Oxazoline, 2-hydroxy-, benzoate (FROMM, BARRENSCHEEN, FRIEDER, PIRK, and KAPELLER), i, 595.
Oxeserine, derivatives of (POLONOVSKI and POLONOVSKI), i, 696.
Oxidation (ARMSTRONG), i, 1009.
mechanism of (WARBURG), i, 374; (WIELAND, HAUSSMANN, and LÖVENSKIOLD), ii, 1171.
in light (ECKERT), i, 413.
in oils (WALKER), i, 990.
with ozone (BRINER, v. TSCHARNER, and PAILLARD), i, 1069.
in sea water (HARVEY), ii, 1171.
anomalous protection against (SHEPPARD), ii, 1084.
negative catalysis of (DHAR), ii, 690.
equilibria in stages of (GRUBE and STAESCHE), ii, 893.
biological (MARK), i, 332; (NEILL and AVERY), i, 340.
as a function of temperature (CROZIER), i, 102.
liberation of energy in (AUBEL and WURMSER), i, 480.
influence of oxygen tension on (HAMBURGER and v. SZENT-GYÖRGYI), i, 709.
induced (DEY and DHAR), ii, 692; (JORISSEN and VAN DEN POL), ii, 879.
Oxidation-reduction (COHEN, GIBBS, and CLARK), i, 25; (CLARK), ii, 673; (CADY and TAFT), ii, 1073; (CLARK, COHEN, and GIBBS), ii, 1164.
new system of (HAEHN and PÜLZ), i, 858.
by blood pigments (LIPSCHITZ), ii, 1070.
Oxides, physico-chemical analysis of sols of (LOTTERMOSER, FRIEDRICH, HÜBNER, and SZABÓ), ii, 521.
effect of high temperatures on (RUFF), ii, 579.
acidic and basic, heating curves for mixtures of (DE CARLI), ii, 670.
amphoteric hydrated, molecular size of, in alkaline solution (JANDER and SCHULZ), ii, 528.
See also Metallic oxides.
α-Oxides, thermochemistry of (SWIENTOSLAWSKI), ii, 364.
***cis*-Oxidoethylenedicarboxylic acid**, conversion of, into *r*-tartaric acid (BÖESEKEN), i, 1237.
Oxidoethylene-αβ-dicarboxylic acids, and their salts (KUHN and EBEL), i, 780.

Oxidoethylene-αβ-dicarboxylic acids, action of yeast on (KUHN and EBEL), i, 1237.
Oxido-ketones, preparation of (WEITZ), i, 408.
Oximes, thermochemistry of (DORABIALSKA), ii, 208, 1140.
isomerism of (BRADY and MEHTA), i, 43; (BRADY and KLEIN), i, 674; (BRADY and BISHOP), i, 930.
tautomerism of (GRIFFITHS and INGOLD), i, 1190.
catalytic reduction of (ROSENMUND and JORDAN), i, 245; (GULEVITSCH), i, 653.
electrolytic reduction of (ISHIBASHI), i, 1382, 1431.
reduction of, with aluminium amalgam (MAZOUREVITCH), i, 1247.
sodium salts, distillation of, under reduced pressure (KOMATSU and HIRAIDZUMI), i, 934.
γ-Oximinovaleric acid, electrolytic reduction of (ISHIBASHI), i, 1382.
Oxindigo. See 3:3′-Diketo-$\Delta^{2,2'}$-dicoumaran.
Oxindole, condensation reactions of (MACBETH and CRAIK), i, 1315.
Oxindole-3-aldehyde, 5:7-*di*iodo-, and its derivatives (KALB and BERRER), i, 161.
Oxonic acid, cuprammonium salt (PIAUX), i, 593.
Oxonitin (MAJIMA and SUGINOME), i, 1447.
Oxonium *per*bromides (KEHRMANN and FALKE), i, 351.
Oxonium compounds, heats of formation of (TSCHELINCEV), ii, 480.
Oxyberberine, synthesis of (PERKIN, RÂY, and ROBINSON), i, 695.
Oxycellulose (HESS), i, 519.
nitrates (ATSUKI), i, 120.
Oxycelluloses (BIRTWELL, CLIBBENS, and RIDGE), i, 234.
Oxychelidonine (GADAMER and THIESSEN), i, 287.
Oxycodeinones, preparation of (MERCK, CHEMISCHE FABRIK), i, 1315.
Oxycyanogen (BIRCKENBACH and KELLERMANN), ii, 569.
Oxydase, xanthine (THURLOW), i, 743.
Oxyeseretholemethine, *N*-oxide, and its derivatives (POLONOVSKI and POLONOVSKI), i, 959.
Oxyeseriethine (POLONOVSKI and POLONOVSKI), i, 960.
Oxyeserine, and its derivatives (POLONOVSKI and POLONOVSKI), i, 293.
Oxyeserole-ethine (POLONOVSKI and POLONOVSKI), i, 960.
Oxyeserolene picrate (POLONOVSKI and POLONOVSKI), i, 960.
Oxygen, spectrum of (BUNGARTZ), ii, 609.
arc spectrum of (LOCKROW), ii, 1099.
K-absorption spectrum of (ROBINSON), ii, 614.
ultra-violet absorption spectrum of (SCHMIDT), ii, 336; (FÜCHTBAUER and HOLM), ii, 626.
band spectrum of (HOLLAND), ii, 1113.
ionised, line spectrum of (CROZE), ii, 166, 250.
dry, effect of ultra-violet light on (BAKER and CARLTON), ii, 1180.
atom, co-ordination number of (PICCARD), ii, 15.
liquid, dielectric constant of (BREIT and ONNES), ii, 631.
molecular heat of (SCHREINER), ii, 97.
heat of dissociation of (EUCKEN), ii, 207; (WULF), ii, 848.
temperature-entropy diagram for (RODEBUSH, ANDREWS, and TAYLOR), ii, 492.
isotherms of (HOLBORN and OTTO), ii, 851.
density of (BAXTER and STARKWEATHER), ii, 188.
absorption of, in gas analysis (FIESER), ii, 238.
absorption of, in water (WHITMAN and DAVIS; BECKER), ii, 106.
sorption of, by activated graphite (BANGHAM and STAFFORD), ii, 655.
solubility of, in silver (PARRAVANO and MALQUORI), ii, 769.
velocity of reaction of, with inorganic salt solutions (REINDERS and VLÈS), ii, 567.
activation of (JORISSEN and VAN DEN POL), ii, 52.
catalysis of the formation of water from hydrogen and (HOFMANN and DOLDE), ii, 139.
combination of hydrogen and, in presence of silver and gold (CHAPMAN, RAMSBOTTOM, and TROTMAN), ii, 310.
oxidation of metallic salts with (REINDERS and VLÈS), ii, 308.
exchange of, in blood (MURRAY and MORGAN), i, 1481.
respiration of, in muscular exercise (FURUSAWA), i, 993.
supply and utilisation of, during muscular exercise (LYTHGOE and PEREIRA; PEREIRA), i, 1341.
free, origin of, in air (TAMMANN), ii, 100.

Oxygen, univalent (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
Oxygen detection and determination:—
detection of (SCHMALFUSS), ii, 238; (SCHMALFUSS and WERNER), ii, 1198.
determination of, colorimetrically (EFIMOV), i, 481.
dissolved, determination of (FRIEND), ii, 326.
determination of, in aqueous solution, in presence of nitrous acid (ALSTERBERG), ii, 1198.
apparatus for determination of, in air (PLANTEFOL), ii, 902.
determination of, in iron (ROONEY), ii, 327.
determination of, in organic compounds (TER MEULEN), ii, 157.
Oxyhæmin, and its salts (HAMSIK), i, 845.
Oxyhæmocyanin, determination of, colorimetrically (PANTIN and HOGBEN), i, 1481.
Oxyhæmoglobin, crystalline, preparation of (THIVOLLE and ROCHE), i, 1111.
dissociation of, in tissues (CAMPBELL), i, 1481.
Oxylysine, and its derivatives (SCHRYVER, BUSTON, and MUKHERJEE), i, 794.
Oxynes (EIBNER and MUNZING), i, 1036; (EIBNER and RIED), i, 1377.
Oxy*iso*protoberberine (HAWORTH, PERKIN, and PINK), i, 1168.
Oxysanguinarine (GADAMER and THIESSEN), i, 287.
3-Oxythionaphthen, condensation reactions of (MACBETH and CRAIK), i, 1315.
3-Oxy(1)thionaphthen glucoside (*thioindican*) (CRAIK and MACBETH), i, 1296.
Oysters, shell-growth in (ORTON), i, 1002.
Ozone (SCHWAB), ii, 149.
formation of, in incandescent capillaries (RIESENFELD), ii, 989.
electrolytic preparation of (MALQUORI), ii, 62.
production of (WARBURG and RUMP; WARBURG), ii, 706.
altitude of, in the atmosphere (CABANNES and DUFAY), ii, 998.
in flames (v. WARTENBURG), ii, 147; (RIESENFELD), ii, 148.
absorption of radiation by, in the atmosphere (FABRY), ii, 627.
photochemical decomposition of, in presence of chlorine (ALLMAND), ii, 1079.
photochemical and thermal decomposition of (GRIFFITH and MCKEOWN), ii, 1080.
Ozone, thermal decomposition of (GRIFFITH and MCKEOWN), ii, 1168.
destruction of, by various reagents (SMITH), ii, 890.
oxidation with (BRINER, EGGER, and PAILLARD), i, 274; (BRINER, v. TSCHARNER, and PAILLARD), i, 1069.
action of, on inorganic colloids (RIESENFELD and HAASE), ii, 988.
determination and solubility of (WARTENBERG and PODJASKI), ii, 1198.
Ozonides, constitution of (STAUDINGER), i, 897.
Ozoniser, laboratory (SMITH), ii, 896.

P.

Palladium, and its amalgam in British Guiana (HARRISON; HARRISON and BOURNE), ii, 593.
arc spectrum of (BEALS), ii, 1015.
Röntgen ray spectrum of (ALLISON), ii, 724.
polarisation of, in alkaline solution (JIRSA), ii, 45.
physical state and catalytic activity of (SMITH), ii, 1072.
adsorption of hydrogen by (LAMBERT and GATES), ii, 785.
Palladium alloys with copper and with gold, structure of (HOLGERSSON and SEDSTRÖM), ii, 20.
with silver, adsorption of hydrogen by (KRUGER and SACKLOVSKY), ii, 1125.
Palladium oxide, catalytic reduction with (KERN, SHRINER, and ADAMS), i, 625.
selenide (MOSER and ATYNSKI), ii, 584.
Palladium organic compounds:—
Palladium dimethylglyoxime (COOPER), ii, 827.
Palladium determination and separation:—
determination of (ZSCHIEGNER), ii, 443.
separation of platinum and (KRAUSS and DENEKE), ii, 1005.
Palladium black, structure of (OSAWA), ii, 747.
Palm kernel oil (ARMSTRONG, ALLAN, and MOORE), i, 504.
Palm tree, American, fats from (ANDRÉ and GUICHARD), i, 1124.
Palmatrubine, and its salts (FEIST and DSCHU), i, 830.
Palmitaldehyde *p*-nitrophenylhydrazone (STEPHEN), i, 1131.

Palmitic acid, latent and specific heats of (PARKS and KELLEY), ii, 949.
latent heat of fusion of (STRATTON and PARTINGTON), ii, 25.
metallic salts (KLIMONE, v. MOLTINI, and BENEDIK), i, 506.
calcium salt, solubility of (HARRISON), ii, 190.
sodium salt, equilibria of sodium chloride, water, and (McBAIN and LANGDON), ii, 537.
emulsifying power of (YAJNIK and ILAHI), ii, 968.
thallium salt (HOLDE and SELIM), i, 504.
Palmitylacetic acid, ethyl ester (LEVENE and HALLER), i, 890.
Palmitylacetoacetic acid, ethyl ester (LEVENE and HALLER), i, 890.
***N*-Palmitylpropylenediamine** (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
α-Paltreubyl alcohol (VESTERBERG), i, 1062.
Pancreas, effect of ingestion of food on activity of (SEVRINGHAUS and SMITH), i, 727.
effect of removal of, on excretion (BIERRY and RATHERY), i, 856.
relation between carbohydrate metabolism of muscle and (FOSTER), i, 1495.
urinary diastase in diseases of (HANSEN), i, 856.
enzymes of (WALDSCHMIDT-LEITZ and HARTENECK), i, 1360.
hæmoleucolysin from (BELFANTI), i, 326.
nucleic acid from (JORPES), i, 182.
Pancreatic juice, activation of (LISBONNE), i, 615.
by enterokinase (SETH), i, 202.
Papain, lipase from (SANDBERG and BRAND), i, 1009.
proteolytic activity of (FABRE and FROSSARD), i, 863.
Papaverine nitrite, preparation of (BOEHRINGER SOHN), i, 427.
Paracetaldehyde, action of, on proteins and lipins (COOPER), i, 91.
Paracetaldehyde, *di*bromo- (STEPANOV, PREOBRASCHENSKI, and SCHTSCHUKINA), i, 1240.
Parachloralose (CHEVALIER and CHERBULIEZ), i, 467.
Parachor and chemical constitution (SUGDEN, REED, and WILKINS), ii, 936; (SUGDEN and WHITTAKER), ii, 937.
Paraffin, photographic action of *H*-particles from (BLAU), ii, 1111.
utilisation of, by micro-organisms (TAUSSON), i, 479.
Paraffins, cracking of (WILLIAMS-GARDNER), i, 1229.
ignition of mixtures of air and (WHEELER), ii, 408.
*cyclo*Paraffins, structure of (WIGHTMAN), i, 894.
Paraffin wax, melting point of (BJERREGAARD), i, 769.
decomposition of (WATERMAN and PERQUIN), ii, 1125.
Paraldehyde. See Paracetaldehyde.
Paralinoleic acid (HASHIMOTO), i, 1234.
Paramagnetism, theories of (CABRERA), ii, 173.
and the electron configuration of atoms (JACKSON), ii, 732.
of salts (COTTON-FEYTIS), ii, 945.
of substances with an odd number of electrons (TAYLOR and LEWIS), ii, 945.
Parathyroids, extracts of, and their activity (HJORT, ROBISON, and TENDICK; COLLIP), i, 1364.
hormone from (COLLIP; COLLIP, CLARK, and SCOTT), i, 754; (COLLIP and CLARK), i, 1017.
Particles, electric charge on (SEXL; DERIEUX), ii, 832.
recorder for measuring distribution of, in sedimentation (LAMBERT and WIGHTMAN), ii, 1194.
charged, action of, in liquids (BURTON and CURRIE), ii, 531.
α-Particles, model for (HARGREAVES), ii, 835.
enumeration of (APPLETON, EMELÉUS, and BARNETT), ii, 10.
disintegration of atoms by (KIRSCH), ii, 923.
capture and loss of electrons by (HENDERSON), ii, 922.
scattering of, by elements (RUTHERFORD and CHADWICK), ii, 1109.
ionisation of gases by (GURNEY), ii, 256.
stopping power of gases for (FOWLER; KRONIG), ii, 834.
distinction between *H*-particles and (KARA-MICHAILOVA), ii, 621.
***H*-Particles**, retrograde (KIRSCH), ii, 621.
distinction between α-particles and (KARA-MICHAILOVA), ii, 621.
Paschen-Back effect (RUNGE), ii, 341.
Passivity (BECKER and HILBERG), ii, 405; (RUSSELL; GERDING and KARSSEN), ii, 406.
and anodic behaviour of metals (SBORGI), ii, 550.
and cathodic overvoltage (LIEBREICH and WIEDERHOLT), ii, 44.
of metals, influence of anions on (ROTHMUND, EISENKOLB, and STEINHERZ), ii, 131.

Pearlite, structure of ferrite and cementite in (BELAIEW), ii, 768.
Pechmann colouring matters, constitution and formation of (BOGERT and RITTER), i, 255.
Pectic substances in plants (O'DWYER), i, 1225; (NORRIS and SCHRYVER), i, 1226.
Pectin, coagulation of (KOPACZEWSKI), i, 872.
hydrolysis of (SMOLEWSKI), i, 216.
Pectinogen (NORRIS and SCHRYVER), i, 1226.
Pelargonidin chloride, and its 3:3′-dimethyl ether (PRATT and ROBINSON), i, 826.
Pellagra, prevention and causation of (GOLDBERGER and TANNER), i, 1517.
Peneus setiferus (shrimp), amino-acids in muscle of (JONES, MOELLER, and GERSDORFF), i, 1348.
Pentachlororuthenious acid. See under Ruthenium.
Pentadecaldehyde, derivatives of (LANDA), i, 1038.
Pentadecylidenehydrazine benzoyl and *m*-nitrobenzoyl derivatives (LANDA), i, 1039.
Pentaerythritol *tetra*nitrate, crystalline structure of (KNAGGS), ii, 748.
1:3:3′:4′:5′-Pentamethoxybenzoylcoumaranone, 2:4-*di*bromo- (DEAN and NIERENSTEIN), i, 953.
1:3:3′:4′:5′-Pentamethoxybenzylcoumaranone (DEAN and NIERENSTEIN), i, 952.
1:3:3′:4′:5′-Pentamethoxybenzylidenecoumaranone, and 2:4-*di*bromo-, *di*bromide (DEAN and NIERENSTEIN), i, 952.
2:4:6:3′:4′-Pentamethoxydiphenylpropane, isomerides of (DRUMM, O'REILLY, and RYAN), i, 1268.
2:4:6:3′:4′-Pentamethoxy-αα-diphenyl-Δα-propene, and its dibromide (DRUMM, O'REILLY, and RYAN), i, 1268.
1:3:3′:4′:5′-Pentamethoxyflavanone (DEAN and NIERENSTEIN), i, 952.
3:5:7:2′:4′-Pentamethoxyflavylium salts (PRATT and ROBINSON), i, 826.
2:2:3:6:8-Pentamethylbenzopyran (CLAISEN), i, 278.
αα′-Pentamethylene*di*iminodiphenyldiacetic acid, nickel salt (SCHLESINGER), i, 1250.
Pentamethylene*di*thiocarbamic acid, salts of (WHITBY and MATHESON), i, 644.
Pentamethylguanidinium salts (LECHER, GRAF, and GNÄDINGER), i, 1393.
Pentamethyl*leuco*sulphur-blue (BINZ and RÄTH), i, 446.
Pentane, βγ-*di*chloro- (BOURGUEL), i, 770.
*cisc*yclo**Pentane**, 1:3-*di*amino-, and its derivatives (DIELS, BLOM, and KOLL), i, 977.
*cyclo*Pentane-1-carboxylic acid, 1-hydroxy-, compound of boric acid and (HERMANS), i, 501.
*cyclo*Pentane-1′-carboxylylanilino*cyclo*pentane-1-carboxylic acid, 1:1′-hydroxy-, lactone (PLANT and FACER), i, 1271.
Pentane-ββδ-diol, compound of boric acid and (HERMANS), i, 501.
*cisc*yclo**Pentanediol**, potassium borates of (HERMANS), i, 501.
Pentanolones, and their phenylosazones (SCHMIDT and ASCHERL), i, 364.
Penta-oxymethylene diacetate (STAUDINGER and LÜTHY), i, 361.
Δβ-Pentene, action of hydrogen bromide on (LUCAS and MOYSE), i, 770.
Δβ-Pentene, γ-chloro- (BOURGUEL), i, 364.
Δδ-Pentenol (HELFERICH and SCHÄFER), i, 7.
Δβ-Penten-δ-ol (CLAISEN), i, 278.
o-**Pentenyl-*p*-cresol** (CLAISEN), i, 278.
o-**Pentenylxylenol** (CLAISEN), i, 278.
Δα-Pentinene-γδ-diol, ε-chloro- (LESPIEAU), i, 1376.
Δα-Pentinen-γ-ol, δε-*di*chloro-, derivatives of (LESPIEAU), i, 1375.
Pentosans, determination of (KLINGSTEDT), ii, 720.
determination of, in wood (GIERISCH), i, 1122.
Pentoses in plants (ENGLIS and HALE), i, 618.
new reaction for (BERTRAND; DENIGÈS), i, 790.
detection of (THOMAS), ii, 604.
detection of, in plant glucosides (THOMAS and IMAS), ii, 1209.
*cyclo*Pentylideneazine, action of hydrochloric acid on (PERKIN and PLANT), i, 842.
Peppermint oil, influence of hydrogen-ion concentration in soil on composition of (H. and (MME.) H. DEEL), i, 622.
Esthonian, constituents of (WEIDERPASS), i, 687.
Pepsin, ionic nature of (NORTHROP), i, 864.
effect of reagents on activity of (HUGOUNENQ and LOISELEUR), i, 1198.
effect of temperature and reaction on the destruction and activity of (EGE), i, 743.

Pepsin, action of hydrochloric acid and, on proteins (VAN URK), i, 1507.
study of the action of, by peptisation of gold hydrosols (UHLENBRUCK), i, 742.
action of, on insulin (EPSTEIN), i, 1513.
hydrolytic and synthetic properties of (BORSOOK and WASTENEYS), i, 472.
synthesis of proteins by means of (WASTENEYS and BORSOOK), i, 102, 864.
determination of, in gastric juice (ROSTOCK), i, 1009; (BOAS, HIRSCH-MAMROTH, and RINDFLEISCH), i, 1213.
Peptase in leaves (BLAGOVESCHENSKI and BIELOZERSKI), i, 1009.
Peptidase, balance of, in man and animals (PFEIFFER and STANDENATH), i, 1361.
Peptides, hydrolysis of (LEVENE and SIMMS), i, 473.
transformations of (BERGMANN, MIEKELEY, and KANN), i, 1134.
action of alkalis on (LEVENE and PFALTZ), i, 1474.
Peptisation, theory of (SEN), ii, 666.
Peptones, hydrolysis of, with hydrochloric acid (YAITSCHNIKOV), i, 320.
Per-acids, formation of (FICHTER and STOCKER), i, 239.
Perbenzoic acid, preparation of (HIBBERT and BURT), i, 1147.
Perborates. See under Boron.
Perchlorates and **Perchloric acid**. See under Chlorine.
Perfumes in foods (BYLSMA), i, 1356.
Perhydridase of milk (SBARSKY and MICHLIN), i, 472.
Perhydroanthracene (SCHROETER, VAN HULLE, GLUSCHKE, STIER, and MÜLLER), i, 125.
Periodic system (PALMAER), ii, 90.
theory of (SOMMERFELD), ii, 177.
in relation to isotopes (SCHTSCHUKAREV), ii, 462.
of elements (ODDO), ii, 623.
Periodicity in electrochemical reactions (HEDGES and MYERS), ii, 680.
and unsaturated cyclic compounds (PETRENKO-KRITSCHENKO), ii, 1122.
"**Permalloy**" (DELORAINE), ii, 639.
"**Permalloys**," effect of tension on magnetisation and hysteresis of (BUCKLEY and MCKEEHAN), ii, 945.
Permanganates. See under Manganese.
Permanganic acid. See under Manganese.
Permeability (GYÖRGY), i, 322.
of cells (BROOKS), i, 1004; (CHODAT), ii, 521.
Permeability of membranes (BANCROFT and GURCHOT), ii, 110.
for electrolytes (MICHAELIS), ii, 1150; (FUJITA), ii, 1151.
of stereoisomerides (OKAGAWA), i, 711.
reversible (GANS), ii, 173.
Permutoid structure (KAUTSKY and HERZBERG), ii, 941.
Pernitric acid. See under Nitrogen.
Pernitroso compounds, action of potassium cyanide on (PASSERINI), i, 1290.
Perowskite, crystal structure of (LEVI and NATTA), ii, 1036.
Peroxides, fusion with, by the explosion method (MUEHLBERG), ii, 899.
organic, syntheses with (GELISSEN and HERMANS), i, 379, 545, 663, 664.
analogies between diazo compounds and (GELISSEN and HERMANS), i, 813.
determination of (RUPP and SIEBLER), ii, 432.
Peroxydases, influence of neutral salts on (SMIRNOV), i, 486.
hydrolysis of starch by (BIEDERMANN and JERNAKOFF), i, 11.
in dried seeds (COUPIN), i, 615.
Per-salts, determination of (RUPP and SIEBLER), ii, 432.
Perylene, and its derivatives (ZINKE, FUNKE, and PONGRATZ), i, 819; (ZINKE, FUNKE, MATSCHES, WOLFBAUER, and LORBER), i, 1436.
preparation of (COMPAGNIE NATIONALE DE MATIÈRES COLORANTES ET DE PRODUITS CHIMIQUES), i, 21.
derivatives of (ZINKE, LINNER, and WOLFBAUER), i, 383; (ZINKE, PONGRATZ, and FUNKE), i, 384.
Perylene, 1:12-*di*hydroxy- (ZINKE and HANSELMAYER), i, 564.
Perylene colouring matters (BADISCHE ANILIN- & SODA-FABRIK), i, 1290.
1:12-Perylenequinone (ZINKE and HANSELMAYER), i, 564.
Perylenetetracarboxylic acid, and its derivatives (KALLE & Co.), i, 406.
vat dyes from derivatives of (KALLE & Co.), i, 1334.
Perylenetetracarboxylic acid, *tetra*-chloro-, and its imide (KALLE & Co.), i, 1277.
Petroleum, helium in gas from (CLAY), ii, 1195.
sulphur compounds in (BIRCH and NORRIS), i, 628.
action of sodium hypochlorite on (BIRCH and NORRIS), i, 1229.
Niitsu, naphthenic acids from (TANAKA, NAGAI, and ISHIDA), i, 252.
Nishiyama, naphthenic acids from (TANAKA and NAGAI), i, 1271.

Petromyzon fluviatilis, detection of amino-acids and other constituents in (FLÖSSNER and KUTSCHER), i, 327.
Phanerogams, heterotrophic, chemistry of (ZELLNER), i, 1025.
Phase rule and moving boundaries (SMITH), ii, 399.
Phaseolus lunatus, enzymes of (ROSENTHALER), i, 1008.
Phaseolus radiatus, vitamin-*A* and albumin in germinating seeds of (DONATH), i, 483.
***o*-Phenacyloxybenzyl** bromide (FREUDENBERG, FIKENTSCHER, and HARDER), i, 420.
Phenanthraphenazinazine, and amino-, bromo-, bromonitro-, hydroxy-, and nitro- (SIRCAR and DUTT), i, 593.
Phenanthraphenazine-2:7-bis(1′-azo-2′-hydroxy-3′-naphthoic acid (SIRCAR and GUPTA), i, 984.
Phenanthraphenazine-2:7-bis(1′-azo-2′-naphthol (SIRCAR and GUPTA), i, 984.
Phenanthraquinol phenyl ether (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
Phenanthraquinone, action of, on aromatic aldehydes in presence of ammonia (SIRCAR and RAY), i, 980.
Phenanthraquinone, *di*amino-, *di*amino-*di*hydroxy-, and *tetra*hydroxy-, and their derivatives (BRASS and NICKEL), i, 273.
Phenanthraquinone colouring matters (SIRCAR and DUTT), i, 593; (SIRCAR and GUPTA), i, 983.
Phenanthraquinonetetrazonium *per*bromides (BRASS and NICKEL), i, 273.
Phenanthraquinonyl-3-azide, acid decomposition of (BRASS and NICKEL), i, 446.
Phenanthraquinonyl-3-diazonium *per*bromide (BRASS and NICKEL), i, 447.
Phenanthrazine (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
Phenanthrene, hydrogenation of (SCHROETER, VAN HULLE, and MÜLLER), i, 130.
action of aluminium chloride on a mixture of *m*-xylene and (SCHAARSCHMIDT, MAYER-BUGSTRÖM, and SEVON), i, 241.
Phenanthrene, 9-bromo-10-hydroxy- (GOLDSCHMIDT, VOGT, and BREDIG), i, 1435.
Phenanthrol, oxidation products of (GOLDSCHMIDT, VOGT, and BREDIG), i, 1435.
10-Phenanthryl *per*oxide, 9-bromo- (GOLDSCHMIDT, VOGT, and BREDIG), i, 1435.
Phenarsazinic acid, and its salts and derivatives (BURTON and GIBSON), i, 84.
Phenazine, 1-amino- and 1:3-*di*amino-, and their acetyl derivatives (KEHRMANN and PRUNIER), i, 304.
3-amino-7- and -8-hydroxy-, 3:7-*di*hydroxy-, 3-nitro-7- and -8-hydroxy-, and their derivatives (KEHRMANN and HAENNY), i, 1330.
2-hydroxy-, and its derivatives (KEHRMANN and CHERPILLOD), i, 303.
3-*p*-Phenetidino-5-keto*iso*oxazole (WORRALL), i, 308.
3-*p*-Phenetidino-5-ketopyrazole (WORRALL), i, 308.
Phenetole, 2:4:5-*tri*chloro- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 1145.
*tri*nitro-, and trinitroanisole, alcoholysis of (BRADY and HORTON), i, 1409.
***o*- and *p*-Phenetolesulphonylacetones**, and their derivatives (TRÖGER and BROHM), i, 1453.
3-*o*- and *p*-Phenetolesulphonyl-2-methylquinolines, and their salts and derivatives (TRÖGER and BROHM), i, 1453.
***p*-Phenetylcarbamide** (*dulcin*), constitution of (TÄUFEL and WAGNER), i, 841.
changes in the sweetening power of (THOMS), i, 538.
Phenol, ultra-violet absorption by benzoic acid and (KEPIANKA and MARCHLEWSKI), ii, 179.
heats of formation of aqueous solutions of (FERGUSON and HOPE), ii, 492.
surface tension of aqueous solutions of (GOARD and RIDEAL), ii, 510.
vapour pressure of aqueous solutions of (FERGUSON and FUNNELL), ii, 501.
vapour pressure of mixtures of, with various compounds (WEISSENBERGER, SCHUSTER, and SCHULER), ii, 649.
influence of another substance on the critical temperature of aqueous solutions of (DUCKETT and PATTERSON), ii, 381.
surface tension of aqueous solutions of (GOARD and RIDEAL), ii, 961.
salting-out of, from aqueous solution (HAFNER and KÜRTHY), ii, 283.
molecular state of, in benzene solution (PHILIP and CLARK), ii, 770.
equilibrium of salicylic acid, water, and (BAILEY), ii, 1064.
condensation of benzyl alcohol and (HUSTON), i, 249.

Phenol, condensation of carbon tetrachloride and (GOMBERG and SNOW), i, 660.
determination of, in blood (HAAS and SCHLESINGER), i, 334.
Phenol, *p*-amino-, sulphate, preparation of (HORII and KOMORI), i, 1410.
*tri*bromo-, and its derivatives (KOHN and STRASSMANN), i, 1264.
3-chloro-*mono*-, *-di*-, and *-tri*-nitro derivatives, and their derivatives (HODGSON and MOORE), i, 1144.
3-chloro*di*nitro- (SANÉ and JOSHI), i, 134.
2:4:5-*tri*chloro-, butyl carbinyl ethers of (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 1145.
thio-, action of anisilic and benzilic acids on (BISTRZYCKI and RISI), i, 1426.
Phenols, heats of solution of, in water (DE KOLOSOVSKI), ii, 540.
catalytic hydrogenation of (VAVON and BERTON), i, 806.
catalytic dehydration of mixtures of alcohols and (BRINER, PLÜSS, and PAILLARD), i, 248.
oxidation of (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1262.
molecular compounds of (WEISSENBERGER and PIATTI), i, 538, 539; (WEISSENBERGER and SCHUSTER), ii, 648, 765; (WEISSENBERGER SCHUSTER, and SCHULER), ii, 649; (WEISSENBERGER, SCHUSTER, and MAYER), ii, 766.
with 4:4′-dipyridylium dialkyl halides (EMMERT and ROH), i, 587.
binary systems of, with acids or esters (KREMANN, ZECHNER, and DRAZIL), ii, 650.
alkylation of (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656; (CLAISEN), i, 1410.
condensation of, with citric acid (MÜLLER), i, 1442.
condensation of diphenylformamidine with (SHOESMITH and HALDANE), i, 39.
nitrosation of (HODGSON and MOORE), i, 1408.
esterification of oxalic acid with (FEIGL and KOBILIANSKY), i, 1235.
preparation of mercury derivatives of (SACCHARIN-FABRIK AKTIEN-GESELLSCHAFT VORM. FAHLBERG, LIST & CO.), i, 1197.
mercuri compounds of (WELLCOME FOUNDATION, LTD., HENRY, and SHARP), i, 1154.
Phenols, monohydric, alkyl ethers of, and their halogen derivatives (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 1145.
polyhydric, association of (ROUYER), i, 911.
detection of, in plants (WARE), i, 1122.
determination of, in essential oils (RETI), ii, 604.
Phenols, amino-, catalytic reduction of (HECKEL and ADAMS), i, 909.
action of sulphuryl chloride on (ELLER and LORENZ), i, 537.
diazo derivatives, thermochemistry of (SWIENTOSLAWSKI and BLASZKOVSKA), ii, 1044.
o-amino-, migration from nitrogen to oxygen in (RAIFORD and LANKELMA), i, 809.
bromo- (KOHN and FINK), i, 133; (KOHN and JAWETZ), i, 135; (KOHN and WIESEN), i, 539; (KOHN and WEISSBERG), i, 655; (KOHN and GUTTMANN), i, 1263; (KOHN and LÖFF; KOHN and STRASSMANN; KOHN and MARBERGER), i, 1264; (KOHN and GRÜN), i, 1265.
2- and 3-bromo-4-nitroso-, and 2-iodo-4-nitroso- (HODGSON and MOORE), i, 1408.
nitro-, equilibria of, with camphor (EFREMOV), ii, 1160.
action of, with *p*-toluenesulphonyl chloride (SANÉ and JOSHI), i, 134.
phenylcarbamates of (BRADY and HARRIS), i, 1261.
determination of (DESVERGNES), ii, 447.
*tri*nitro-, determination of (DESVERGNES), ii, 447.
nitroamino-, detection of, in urine (DESVERGNES), i, 328.
nitroso-, reduction of, with alkali sulphides (POBAI-KOSCHITZ) i, 1060.
Phenolisatein (SEN and SIRCAR), i, 555.
Phenolmercurisulphonic acid (SACCHARIN-FABRIK AKTIEN-GESELLSCHAFT VORM. FAHLBERG, LIST & CO.), i, 1197.
Phenolphthalein, effect of alcohol and salts on dissociation of (RICHTER), ii, 237.
*iso*Phenolphthalein, and its derivatives (ORNDORFF and BARRETT), i, 35.
Phenolphthalin, detection of hydrocyanic acid with (STAMM), ii, 76.
*iso*Phenolphthalin, and its diacetate (ORNDORFF and BARRETT), i, 36.

Phenolresorcinolphthalein, and its derivatives (SEN and SIRCAR), i, 554.
Phenolsulphonephthalein, adsorption of, by charcoal and proteins (GROLLMAN), i, 1000.
effect of alkalis on colour of (HUBBARD and MEEKER), i, 1115.
diethyl and dimethyl ethers (ORNDORFF and SHAPIRO), i, 251.
determination of, in urine in jaundice (ABRAMSON), i, 329.
o- and *p*-**Phenolsulphonic acids**, action of nitrous acid on (RODIONOV and MATVEEW), i, 83.
2:3-*iso*Phenosafranine, and its salts (HOEHN), i, 938.
Phenoxarsine, 6-chloro- (TURNER and SHEPPARD), i, 705.
Phenoxarsines, chloro-, formation of, from phenoxyphenyldichloroarsines (ROBERTS and TURNER), i, 1339.
*di*chloro- (ROBERTS and TURNER), i, 1340.
Phenoxarsinic acids, chloro- (ROBERTS and TURNER), i, 1340.
Phenoxides, metallic, preparation of (ZETZSCHE, SILBERMANN, and VIRLI), i, 1411.
Phenoxyacetic acid, 2:4-*di*nitro- (CHRISTIANSEN), i, 817.
Phenoxyacetic acids, hyperthermic action of (MAMELI and FILIPPI), i, 466.
δ-(ε-Phenoxyamylamino)butylbenzamide hydrochloride (v. BRAUN and ZOBEL), i, 1455.
***o*-Phenoxybenzeneazo-β-naphthol** (TURNER and SHEPPARD), i, 706.
α-Phenoxybutyl alcohol (BAEKELAND and BENDER), i, 689.
ε-(δ-Phenoxybutylamino)amylbenzamide hydrochloride (v. BRAUN and ZOBEL), i, 1456.
δ-Phenoxybutylmalonic acid, and its ethyl ester, and α-bromo- (MARVEL, MACCORQUODALE, KENDALL, and LAZIER), i, 234.
α-Phenoxy-αβ-dibenzoylethylene (CONANT and LUTZ), i, 682.
9-Phenoxy-2:9-diethoxy-9:10-dihydroacridine (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 429.
β′-Phenoxydiethyl ether, β-chloro- (CRETCHER, KOCH, and PITTENGER), i, 627.
9-Phenoxy-2-ethoxyacridine (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 429.
ε-Phenoxyhexoic acid, α-bromo- (MARVEL, MACCORQUODALE, KENDALL, and LAZIER), i, 235.
m- and *p*-**Phenoxymethylbenzonitriles** (v. BRAUN and REICH), i, 1405.
***p*-Phenoxymethylbenzyl alcohol** (v. BRAUN and REICH), i, 1405.
***p*-Phenoxymethylbenzyl bromide** (v. BRAUN and REICH), i, 1405.
m- and *p*-**Phenoxymethylbenzylamines**, and their salts and derivatives (v. BRAUN and REICH), i, 1405.
Phenoxy-*P*-oxotetrahydrodiazphospholium (AUTENRIETH and BÖLLI), i, 1469.
Phenoxy-*P*-oxydihydrobenzodiazphospholium (AUTENRIETH and BÖLLI), i, 1468.
9-Phenoxy-10-phenanthryl *per*oxide (GOLDSCHMIDT, VOGT, and BREDIG), i, 1434.
***o*-Phenoxyphenylarsinic acid** (TURNER and SHEPPARD), i, 706.
Phenoxyphenylarsinic acids, and chloro- (ROBERTS and TURNER), i, 1440.
***o*-Phenoxyphenyl*di*chloroarsine** (TURNER and SHEPPARD), i, 706.
and its chloro-derivatives, conversion of, into chlorophenoxarsines (ROBERTS and TURNER), i, 1339.
Phenoxyphenyl*di*chloroarsines, chloro- (ROBERTS and TURNER), i, 1340.
Phenoxy-*p*-thiodihydrodiazphospholium (AUTENRIETH and MEYER), i, 990.
Phenyl allyl ether, *p*-oximinoamino-, acetyl derivative (KARRER, DIECHMANN, and HAEBLER), i, 243.
allyl ethers, transformation of (CLAISEN and TIETZE), i, 389.
benzhydryl sulphide (BISTRZYCKI and RISI), i, 1426.
benzoate, *m*-bromo- and 3:5-*di*bromo- (KOHN and FINK), i, 133.
benzyl ether, *s-tri*bromo-, and its nitro derivatives (HOLMES and INGOLD), i, 1142.
benzyl ether and sulphide, *o*-amino-, and *o*-nitro-, and their derivatives (SIEGLITZ and KOCH), i, 278.
β-chloroethyl sulphide, and *o*-nitro- (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.
cinnamyl and γ-phenylpropyl ethers (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.
4:4′-dimethoxybenzhydryl sulphide (BISTRZYCKI and RISI), i, 1426.
di-*p*-tolyl thiophosphate (AUTENRIETH and MEYER), i, 807.
groups, migration of *p*-anisyl and (TIFFENEAU and ORÉKHOV), i, 679.
hydrogen thiosulphate, 2:4-*di*hydroxy-, and its potassium salt (HELLER), i, 315.

Phenyl hydroxyphenylalkyl ethers (BAEKELAND and BENDER), i, 689.
o-iodobenzyl ether, *o*-iodo- (SIEGLITZ and KOCH), i, 278.
p-methylaminophenyl sulphide, and its derivatives (RIVIER and RICHARD), i, 1417.
α-methyl-Δ*β*-butenyl ether (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.
β-phenylethyl ether, *o*-amino-, *o*-hydroxy-, and *o*-nitro-, and their derivatives (SIEGLITZ and KOCH), i, 278.
*cyclo*propylmethyl ether (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.
Phenyl-4-acenaphthylmethane (LORRIMAN), i, 673.
Phenyl-4′-acenaphthylmethane-2-carboxylic acid (LORRIMAN), i, 673.
Phenyl-4-acenaphthylphthalide (LORRIMAN), i, 672.
Phenylacetaldehyde-ammonia (GRIGNARD and ESCOURROU), i, 931.
***β*-Phenylacetaldimine**, and its hydrochloride (GRIGNARD and ESCOURROU), i, 931.
3-Phenylacetamido-*p*-cresol, 5-chloro-, and its *p*-toluate (RAIFORD and LANKELMA), i, 810.
Phenylacetic acid, hydroxylamine salt (OESPER and BALLARD), i, 1233.
***d*- and *l*-Phenylacetic acids**, *α*-bromo- and *α*-chloro-, bornyl esters (MCKENZIE and SMITH), i, 822.
Phenylacetomethylamide, *o*-nitro- (NEBER, HARTUNG, and RUOPP), i, 1073.
Phenylaceto-*β*-phenylethylamide, *o*-amino- (GADAMER, OBERLIN, and SCHOELER), i, 576.
3-Phenylacetoxymethyl-6-methylbenzthiopyrone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.
***o*-Phenylacetyldeoxybenzoin** (WEISS and SONNENSCHEIN), i, 937.
Phenylalkylcyanoacetamides (THOMPSON, BEDELL, and BUFFETT), i, 699.
Phenylalkylhydantoins (THOMPSON, BEDELL, and BUFFETT), i, 699.
3-Phenyl-3-allyl-4:5-benzocoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.
3-Phenyl-3-allylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.
3-*α*-Phenylallyl-*p*-cresol, and its phenylcarbamate (CLAISEN and TIETZE), i, 389.
2-Phenyl-2-allyldiketohydrindene, spiran derivatives of (RADULESCU), i, 1159.
***o*-*α*-Phenylallylphenol**, and its phenylcarbamate (CLAISEN and TIETZE), i, 389.
***α*-Phenyl-*α*-allylsuccinamic acid**, ethyl ester (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.
***α*-Phenyl-*α*-allylsuccinimide** (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.
1-Phenyl-4-allylthiosemicarbazide, *o*-nitro- (GUHA and RAY), i, 1462.
Phenyl*tetra*aminobenzene, and its derivatives (KEHRMANN and STANOYÉVITCH), i, 1332.
2-Phenyl-4-aminomethylquinoline, and its salts (JOHN), i, 1317.
4-Phenyl-1-*o*-aminophenylthiosemicarbazide (GUHA and RAY), i, 1462.
Phenyl aminostyryl ketones, *per*chlorates of (PFEIFFER), i, 410.
Phenyl*iso*amyl*di*thiocarbamic acid, salts of (WHITBY and MATHESON), i, 644.
4-Phenyl-3-anisyl-2-anisylidene-5-methyl-Δ³-*cyclo*penten-1-one (RYAN and LENNON), i, 1282.
3-Phenyl-4-*p*-anisylcoumarin, 7-hydroxy-, and its acetyl derivative (BARGELLINI), i, 1442.
***β*-Phenyl-*β*-anisylethylamine**, *β*-hydroxy-, action of nitrous acid on (ORÉKHOV and ROGER), i, 262.
***αα*-Phenyl-*p*-anisylethylene** iodohydrin (TIFFENEAU and ORÉKHOV), i, 680.
***α*- and *β*-Phenylanisylfuroxanes** (MEISENHEIMER, LANGE, and LAMPARTER), i, 1075.
4-Phenyl-3-anisyl-5-methyl-Δ²-*cyclo*penten-1-one (RYAN and LENNON), i, 1282.
1-Phenyl-3-*p*-anisyl-5-methylpyrazole-4-carboxylic acid, and its ethyl ester (MINUNNI, LAZZARINI, and D'URSO), i, 1176.
Phenyl-*p*-anisyl-*α*-naphthylmethane (DILTHEY), i, 651.
Phenyl-*p*-anisyl-*α*-naphthylmethyl bromide and chloride (DILTHEY), i, 651.
Phenylanisylpyrazolines, acetyl derivatives, and 4-hydroxy- (FREUDENBERG and STOLL), i, 70.
Phenylarsenious oxide, 3-nitro-4-hydroxy- (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471.
Phenyl-1-arsenoxide-4-stibinoxide (CHEMISCHE FABRIK VON HEYDEN), i, 86.
Phenylarsinic acid, *p*-amino-, salts of, crystal structure of (GILTA), ii, 93.
action of pyruvic acid and, on aldehydes (ADAMS and JOHNSON), i, 319.

Phenylarsinic acid, *p*-amino-, benzoyl, aminobenzoyl, and nitrobenzoyl derivatives of, and their derivatives (KING and MURCH), i, 319.
3-amino-4-hydroxy-, 3-acetyl derivative, bismuth salt, action of, in syphilis (LEVADITI), i, 1005; (FOURNIER and SCHWARTZ), i, 1006.
4-amino-3-hydroxy-, action of carbonyl chloride on (CASSELLA & Co.), i, 172.
3-chloro-2-amino-4-hydroxy- and its acetyl derivative, and 3-chloro-2-nitro-4-hydroxy- (CASSELLA & Co.), i, 1471.
3-oximinoamino-4-hydroxy-, 3-acetyl derivative (KARRER, DIECHMANN, and HAEBLER), i, 243.
Phenylarsinic acids, *di*amino- and nitroamino-, benzoyl derivatives (HAMILTON and MAJOR), i, 990.
Phenyl-1-arsinic acid–3-stibinic acid, 4-hydroxy- (CHEMISCHE FABRIK VON HEYDEN), i, 86.
Phenylarsinodicarboxylic acid, ethyl ester (JOB, REICH, and VERGNAUD), i, 173.
Phenylazodiacetylsuccinic acid, *p*-amino-, acetyl derivative, ethyl ester (BÜLOW and BAUR), i, 1327.
Phenylbarbituric acid, bromo- (VOORHEES and SKINNER), i, 837.
2-Phenyl-1:3-benzdiazole, and its hydrochloride (GUHA and RAY), i, 1462.
***N*-Phenylbenzimidophenyl ether**, and its chloro-derivatives, molecular rearrangement of (CHAPMAN), i, 1400.
3-Phenylbenzopyran, bromohydroxy- and hydroxy-, and their derivatives (KAHIL and NIERENSTEIN), i, 53
2-Phenylbenzopyrylium chloride, 3:5:7-2-2′:4′-*penta*hydroxy-. See Morinidin chloride.
1-Phenylbenzoxazole, 1-*o*-hydroxy- (v. AUWERS and JORDAN), i, 265.
3-Phenyl-3-benzoylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.
Phenylbenzoyldiazomethane, reaction of carbon disulphide with (MEYER), i, 424.
1-Phenylbenzthiazole methiodide (CLARK), i, 841.
2-Phenylbenztriazole, *p*-amino-, *m*-amino-*o*-hydroxy-, *mm′-di*-bromo- and -chloro-*s*-*p*-hydroxy-, *di*bromo*di*hydroxy-, *p-mono*- and *op-di*-hydroxy-, and their derivatives (ELBS), i, 163.
1-Phenylbenztriazole-5-carboxylic acid, 7-amino-, and its acetyl derivative, and 7-nitro- (LINDEMANN and WESSEL), i, 1190.
3-Phenyl-3-benzyl-4:5-benzocoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
3-Phenyl-3-benzylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
Phenyl benzyl diketone, and its derivatives (MALKIN and ROBINSON), i, 559.
Phenylbenzyldimethylammonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 495.
Phenylbenzyldimethylarsonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 496.
α-Phenylbenzyl ethyl ketone, semicarbazone (LÉVY and LAGRAVE), i, 679.
Phenylbenzylglyoxal. See *αγ*-Diphenylpropan-*αβ*-dione.
Phenylbenzyl-*p*-hydroxytolylacetic acid, potassium salt (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
3-Phenyl-3-benzyl-5-methylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
α-Phenylbenzyl methyl ketone, semicarbazone (LÉVY and LAGRAVE), i, 679.
Phenylbenzylmethyl-(methylanilinoethyl)ammonium nitrate (WEDEKIND and UTHE), i, 536.
***d*-Phenylbenzylmethyl-*β*-phenylmethylaminoethylammonium nitrate**, decomposition of, by aniline in chloroform solution (WEDEKIND and UTHE), i, 1059.
α-Phenyl-*β*-benzyl-*β*-methylpropane (TROTMAN), i, 383.
***as*-Phenylbenzyl-*p*-phenylenediamine**, and its derivatives (DESAI), i, 388.
Phenyl *o*-benzylphenyl ketone (MAYER and FISCHBACH), i, 1076.
α-Phenyl-*β*-benzylpropane, *β*-bromo- (TROTMAN), i, 382.
α-Phenyl-*β*-benzylpropan-*β*-ol, γ-amino- (THOMAS and BETTZIECHE), i, 250.
Phenylbenzylpyrazoles, chloro- (v. AUWERS and MAUSS), i, 1179.
2-Phenyl-3-benzylquinoxaline (MALKIN and ROBINSON), i, 559.
Phenyl-bis-(3-hydroxy-4:4′-dicarbethoxy-5:5′-dimethyl-2:3′-dipyryl)-methane, and its derivatives (FISCHER and HEYSE), i, 78.
ω-Phenylbiuret, and its methyl derivatives (GATEWOOD), i, 805.
Phenyl *αβ-di*bromo-*α*-methoxy-*β*-phenylethyl ketone (MALKIN and ROBINSON), i, 559.
3-Phenylbromomethyl-6-methylbenzthiopyrone, and its pyridinium salt (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

2-Phenyl-6-bromo-4-methylquinoline, and its salts (JOHN and WEBER), i, 1452.

Phenyl-*p*-bromophenylformamidines, *N*-hydroxy-*N*- and -*N'*-*p*-chloro- (FARROW and INGOLD), i, 155.

Phenyl-*p*-bromophenyl-α-naphthylmethyl chloride (DILTHEY), i, 653.

Phenyl-*N*-*p*-bromophenylnitron, *o*-hydroxy- (BAMBERGER), i, 142.

Phenyl-*p*-bromophenyloxazolidines (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1064.

Phenylbromotolylcarbamide (BAMBERGER), i, 143.

Phenylbromotolylthiocarbamide (BAMBERGER), i, 143.

δ-Phenylbutinene (BERT, DORIER, and LAMY), i, 1373.

Phenylbutinoic acid (BOURGUEL), i, 770.

Phenyl-*n*-butylcyanamide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.

Phenyl butyl ketones, 2:4-*di*hydroxy- (SHARP & DOHME and DOHME), i, 541.

Phenyl*cyclo*butylmethylcyanamide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.

Phenylcarbamic acid, 2-chloro-4:6-*di*nitro-, ethyl ester (KNIPHORST), i, 907.

Phenylcarbamide, bromo*di*nitro-, chloro-*di*nitro-, and 2:4:6-*tri*nitro- (KNIPHORST), i, 906.

Phenylcarbamidomalonic acid, ethyl ester (GATEWOOD), i, 1189.

β-Phenyl-α-carbethoxyhydrazine-β-diphenylacetic acid (INGOLD and WEAVER), i, 580.

Phenylcarbimide, action of methylcarbamide on (BILTZ and BECK), i, 1393.

Phenylcarbylamine, action of α-naphthol with (PASSERINI), i, 1298.

Phenylchelerythrine, and its chloroaurate (GADAMER and STICHEL), i, 287.

Phenyl*di*chloroarsine, additive compound of aluminium chloride and (HUNT and TURNER), i, 844.

Phenyl-ββ'-*di*chlorodivinylarsine, and its derivatives (HUNT and TURNER), i, 844.

2-Phenylchloro-4-methylquinolines, and their salts (JOHN and WEBER), i, 1452.

1-Phenyl-5-*o*-chlorophenyl-3-methylpyrazoline (v. AUWERS and KREUDER), i, 1455.

Phenyl-4-chloropiaselenazonium chloride (BATTEGAY and VÉCHOT), i, 1467.

Phenyl *o*-chlorostyryl ketone, *o*-hydroxy-, and its acetyl derivative and their dibromides (RÖTHLISBERGER), i, 572.

Phenyl-β-chlorovinylchloroarsine (HUNT and TURNER), i, 843.

Phenylchromans. See Phenylbenzopyrans.

3-Phenylchroman-2-one, and its phenylhydrazone (KAHIL and NIERENSTEIN), i, 52.

Phenylcinchonic acid, β-hydroxyethyl ester (CRETCHER and PITTENGER), i, 1415.

α-Phenylcinnamylideneacetonitrile, photodimerides of (STOBBE and KUHRMANN), i, 253.

Phenyl cinnamylidenemethyl ketone, *p*-hydroxy-, glucoside (BARGELLINI and LEONE), i, 1284.

Phenylcitronellylacetic acid, and its derivatives (BECHERER), i, 664.

Phenylcitronellylamine, and its salts and derivatives (RUPE and RINDERKNECHT), i, 658.

Phenylcitronellylcarbinol (RUPE and RINDERKNECHT), i, 658.

***as*-Phenylcitronellylhydrazine**, and its derivatives (RUPE and RINDERKNECHT), i, 658.

3-Phenylcoumarin, 6-bromo-, 6-chloro-, 6:8-*di*chloro-, and 7-hydroxy-, and its acetyl derivative (DEY and ROW), i, 150.

4-Phenylcoumarin, 5:7:4-*p*-*tri*hydroxy-, and its triacetyl derivative (BARGELLINI), i, 1299.

3-Phenylcoumarone, 2-hydroxy-, potassium, and sodium derivatives (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.

γ-Phenylcrotonamide, α-hydroxy-, derivatives of (BOUGAULT), i, 921.

Phenylcyanamide, 2:4-*di*nitro- (GIUA and PETRONIO), i, 1396.

Phenyl-di-3(2-anilino-1:4-naphthaquinonyl)-amine (FRIES and BILLIG), i, 940.

Phenyl αα-di-*p*-anisylbenzyl ketone (TIFFENEAU and ORÉKHOV), i, 680.

α-Phenyl-ββ-dibenzylpropane (TROTMAN), i, 383.

Phenyldiethylallylammonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 495.

α-Phenyl-αα'- and **-αα'-diethylsuccinimides** (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 377.

α-Phenyl-α'α'-diethylsuccinonitrile, α-cyano- (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 377.

Phenyldihydrochelerythrine, and its chloroaurate (GADAMER and STICHEL), i, 287.
1-Phenyldihydrofluorenone, 3-hydroxy- (JONESCU), i, 1154.
Phenyldi-indonylcarbinol (RADULESCU and GEORGESCU), i, 1287.
1-Phenyl-3:5-di-indylpyrazole (ODDO), i, 297.
Phenyl-2-diketohydrindenylmethylmalonic acid, and its ethyl esters and lactones (JONESCU), i, 1154.
β-Phenyl-β-2-diketohydrindenylpropionic acid (JONESCU), i, 1154.
Phenyl-1:3-diketones, *o*-hydroxy-, action of ammonia on (WITTIG), i, 279.
1-Phenyl-3:5-diketopyrazolidines, nitro-, nitrophenylhydrazine derivatives of (VAN ALPHEN), i, 83.
Phenyl β:*p*-dimethoxystyryl ketone (MALKIN and ROBINSON), i, 559.
Phenyl 2:3-dimethoxystyryl ketone, *p*-hydroxy-, and its sodium salt (PFEIFFER, ARMBRUSTER, BACKES, and OBERLIN), i, 270.
2-Phenyl-6-dimethylamino-4-methylquinoline, and its salts (JOHN and WEBER), i, 1452.
Phenyl *p*-dimethylaminostyryl ketone, salts of (PFEIFFER), i, 410.
1-Phenyl-5:5-dimethyl-3-*iso*butenylpyrazoline (v. AUWERS and KREUDER), i, 1455.
3-Phenyl-3:5-dimethylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
κ-Phenyl-βζ-dimethyl-Δ$^{\alpha\eta}$-decadien-Δ$^{\iota}$-inene (RUPE and RINDERKNECHT), i, 533.
κ-Phenyl-βζ-dimethyl-Δ$^{\alpha\eta\iota}$-decatriene (RUPE and RINDERKNECHT), i, 533.
κ-Phenyl-βζ-dimethyl-Δ$^{\alpha}$-decene (RUPE and RINDERKNECHT), i, 533.
κ-Phenyl-βζ-dimethyl-Δ$^{\alpha}$-decen-Δ$^{\iota}$-inen-θ-ol (RUPE and RINDERKNECHT), i, 533.
4-Phenyl-2:6-dimethyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester, ψ-cyanide (MUMM), i, 925.
1-Phenyl-3-dimethylene-4-methylpyrazolone, and its hydrochloride (KÜSTER), i, 923.
***N*-Phenyl-*N'*:*S*-dimethyl-*N*-ethyl-ψ-thiocarbamide**, and its salts (LECHER), i, 1391.
2-Phenyl-4:5-dimethylglyoxaline, and its picrate (MORGAN and HICKINBOTTOM), i, 156.
1-Phenyl-3:5-di(2-methylindyl)pyrazole (ODDO), i, 297.
2-Phenyl-1:6-dimethylmethylenedihydropyridine, and *m*-nitro-, and their derivatives (MUMM), i, 965.
α-Phenyl-ββ-dimethylpentan-α-ol, and its phenylurethane (HALLER, BAUER, and RAMART), i, 261.
α-Phenyl-ββ-dimethyl-Δ-penten-α-ol, and its phenylurethane (HALLER, BAUER, and RAMART), i, 261.
1-Phenyl-3:5-dimethylpyrazole, *p*-nitro- (v. AUWERS and KREUDER), i, 1455.
5-Phenyl-1:3-dimethylpyrazoline, and its picrate (v. AUWERS and KREUDER), i, 1455.
3-Phenyl-1:2-dimethylpyrazolium iodide, 5-iodo- (v. AUWERS and MAUSS), i, 1179.
1-Phenyl-2:3-dimethyl-5-pyrazolones, *mono-* and *di*-chloro- (CHATTAWAY and STROUTS), i, 71.
4-Phenyl-1:6-dimethylpyridine-3:5-dicarboxylic acid, ethyl ester, methosulphate (MUMM), i, 964.
1-Phenyl-2:5-dimethylpyrrole, 3:4-*di*-iodo-, and 3:4-*di*nitro- (PIERONI and NOCENTINI), i, 1097.
1-Phenyl-2:5-dimethylpyrrole-3-carboxylic acid, 4-iodo-, and its silver salt (PIERONI and NOCENTINI), i, 1097.
2-Phenyl-4:8-dimethylquinoline, and its salts (JOHN and WEBER), i, 1452.
Phenyldimethyltetrahydroindazoles, and their *per*chlorates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.
2-Phenyl-6:6-dimethylthiopyranone (ARNDT, PUSCH, and SCHWARZ), i, 1304.
Phenyldi-α-naphthylmethyl acetate (SCHOEPFLE), i, 811.
Phenyldi-α-naphthylmethylamine (SCHOEPFLE), i, 811.
Phenyl 3:4-dioxymethylenestyryl ketone, 4-hydroxy-, glucoside (BARGELLINI and LEONE), i, 1284.
Phenyldiphenazineoxazine (KEHRMANN and BENER), i, 444.
***N*-Phenyldiphenylacetamide, *o*-nitro-** (VAN ALPHEN), i, 83.
3-Phenyl-5-diphenylmethyl-2-keto-2:3-dihydrofuro-3:4-diazole (VAN ALPHEN), i, 81.
Phenyldiphenylyl-α-naphthylcarbinol, additive compounds of (DILTHEY), i, 653.
Phenyldiphenylyl-α-naphthylmethyl bromide and methyl ether (DILTHEY), i, 653.
Phenyldi-*o*-tolylmethane-*o*-carboxylic acid (WEISS and KORBZYN), i, 560.
Phenyldiveratroharmyrine methosulphate (ARMIT and ROBINSON), i, 1172.
***o*-Phenylenecarbamide**, acetyl and benzoyl derivatives (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1324.

Phenylene-2-*p*-chlorophenyltriazolylene-glycollic acid, and its sodium salt (CHARRIER, GALLOTTI, and VITALE), i, 307.

***p*-Phenylenediamine**, electrolytic preparation of (NORRIS and CUMMINGS), i, 668.
oxidation of, by the action of hydrogen peroxide and formaldehyde (LÄTT), i, 1457.
in tissues (v. SZENT-GYÖRGYI), i, 93.

Phenylenediamines, compounds of carbon suboxide with (VAN ALPHEN), i, 81.

***o*- and *m*-Phenylenediamines**, hydroferricyanides of (CUMMING), i, 122.

***o*-Phenylenediphenyldiglycollolactone**, and its methyl ester (WEISS and SONNENSCHEIN), i, 938.

Phenyleneoxamide, salts and *O*-benzoyl derivative of (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1324.

Phenylene-2-phenyltriazolyleneglycollic acid, and its sodium salt (CHARRIER, GALLOTTI, and VITALE), i, 306.

***r*-Phenylethanolmethylamine**, *o-di*hydroxy-, hydrochloride (SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE), i, 136.

3-Phenylethoxymethyl-6-methylbenzthiopyrone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

2-Phenyl-8-ethoxy-4-methylquinoline, and its salts (JOHN and WEBER), i, 1452.

β-Phenylethylacetoacetic acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.

γ-(β-Phenylethyl)acetylacetone (v. AUWERS and MÖLLER), i, 404.

β-Phenylethyl alcohol, synthesis of (LEONARD), i, 913.

Phenylethylamine, condensation of, with *s*-dichlorodimethyl ether (SHORT), i, 387.

Phenylethylamine, chloro-*p*-hydroxy-, and its hydrochloride (ZEYNEK), i, 920.

β-Phenyl-γ-ethylamylene βγ-glycol (ROGER), i, 660.

Phenylethylbarbituric acid, dimethylamine salt (HOFFMANN, LA ROCHE & Co.), i, 300.

5-β-Phenylethylbarbituric acid (DOX), i, 301.

3-Phenyl-3-ethyl-4:5-benzocoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.

β-Phenylethylbenzoyl-*d*-ψ-ecgonine, and its hydrochloride (GRAY), i, 830.

δ-Phenyl-γ-ethylbutan-γ-ol, δ-amino-, and its hydrochloride and benzoyl derivative (THOMAS and BETTZIECHE), i, 250.

Phenylethylcarbamic acid, 4-bromo-2:6-*di*nitro-, esters of (KNIPHORST), i, 906.

α-Phenyl-β-ethylcarbamide, bromo-, and chloro- (KNIPHORST), i, 906.

2-β-Phenylethylchromone, 3:7-*di*hydroxy- (ROBINSON and SHINODA), i, 1301.

3-Phenyl-3-ethylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.

Phenylethyldimethylamine, *p*-amino- (KINDLER), i, 387.

2-β-Phenylethyl-4:4-dimethylhomophthalimide (HAWORTH, PERKIN, and PINK), i, 1168.

Phenylethylene, αβ-*di*thiocyano- (SÖDERBÄCK), i, 899.

5-β-Phenylethyl-5-ethylbarbituric acid (DOX), i, 301.

β-Phenylethylethylmalonic acid, and its ethyl ester (DOX), i, 300.

Phenylethyl*cyclo*hexylamines, and their salts (WIELAND and DRAGENDORFF), i, 1089.

Phenylethyl *n*-hexyl ketone (THIERFELDER and KLENK), i, 193.

***N*-β-Phenylethylhomophthalamic acid**, and its methyl ester (HAWORTH, PERKIN, and PINK), i, 1168.

2-β-Phenylethylhomophthalimide (HAWORTH, PERKIN, and PINK), i, 1168.

3-α-Phenylethylideneoxindole (WINDAUS, JENSEN, and SCHRAMME), i, 19.

Phenylethylketazine (MAZOUREVITCH), i, 1240.

β-Phenylethyl ketone, *o*-hydroxy-, and its salts (FREUDENBERG, FIKENTSCHER, and HARDER), i, 420.

β-Phenylethylmalonic acid, ethyl ester, and its amides (DOX), i, 300.

β-Phenylethylmethylamine (KINDLER), i, 387.

β-Phenylethyl methyl ketone, *m*-hydroxy-, and its derivatives (MURAI), i, 1158.

α-Phenyl-ββ-ethylnitrocarbamide 4-bromo-2:6-*di*nitro-, chloro*di*nitro-, and 2:4-*di*- and 2:4:6-*tri*-nitro- (KNIPHORST), i, 906.

α-Phenylethyloxindole (WINDAUS, JENSEN, and SCHRAMME), i, 19.

ε-Phenyl-γ-ethylpentan-γ-ol, δ-amino-, and its benzoyl derivative (THOMAS and BETTZIECHE), i, 251.

3-Phenyl-1-ethylpyrazole, and its picrate (v. AUWERS and SCHMIDT), i, 586.

Phenylethylpyrazoles, chloro- (v. AUWERS and MAUSS), i, 1179.
β-Phenylethylpyridine, 2-β-bromo-β-*o*-nitro-, hydrobromide (RÄTH and LEHMANN), i, 432.
α-Phenyl-α-ethylsuccinamic acid, ethyl ester (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.
α-Phenyl-α-ethylsuccinimide (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.
2-β-Phenylethyl-1:2:3:4-tetrahydro*iso*quinoline, and its hydrochloride (HAWORTH, PERKIN, and PINK), i, 1168.
Phenylethyl*di*thiocarbamic acid, salts of (WHITBY and MATHESON), i, 644.
1-Phenyl-4-ethyl-1:2:3-triazole (BERTHO), i, 840.
3-Phenylflavone, 7-hydroxy-, and its acetyl derivative (BAKER and ROBINSON), i, 1299.
5-Phenylfluoflavine (KEHRMANN and BENER), i, 443.
1-Phenylfluorenone, 3-hydroxy- (JONESCU), i, 1154.
Phenylfluorone, *p*-hydroxy-, and its acetyl derivative (GOMBERG and SNOW), i, 660.
9-Phenylfluorone, 9-*o*:*p*-*di*hydroxy- (SEN and SARKAR), i, 813.
Phenyl furfurylidenemethyl ketone, 4-hydroxy-, glucoside (BARGELLINI and LEONE), i, 1284.
Phenylgermanonic acid (MORGAN and DREW), i, 1197.
β-Phenylglutamic acid (HARINGTON), i, 1094.
β-Phenylglutaric acid, ethyl ester (SPRIGHT, STEVENSON, and THORPE), i, 32.
β-Phenylglutaric acid, α-amino-, benzoyl derivative, and α-oximino-, and its ethyl ester (HARINGTON), i, 1094.
α-*mono*- and αα′-*di*-bromo-, and their esters, and α-bromo-α′-hydroxy-, ethyl ester, lactone (HAERDI and THORPE), i, 924.
Phenylglycine, derivatives of (WESSELY), i, 1152.
Phenylglycine, *p*-hydroxy-, synthesis of (SHIMO), i, 1423.
Phenylglycine-*o*-carboxylic acid, 4-iodo- (KALB and VOGEL), i, 161.
Phenylglycol, potassium borate of (HERMANS), i, 501.
***N*-Phenylglycylglycine**, and its ethyl ester (WESSELY), i, 1152.
***N*-Phenylglycyl-*l*-tyrosine**, ethyl ester (WESSELY), i, 1152.
2-Phenylglyoxaline, *o*-, *m*-, and *p*-nitro-, and their salts and 4-carboxylic acids (PYMAN and STANLEY), i, 158.
4(5)-Phenylglyoxaline, 2-bromo-, 5(4)-bromo- and its salts, and 2:5(2:4)-*di*bromo- (FORSYTH and PYMAN), i, 700.
4(5)-Phenylglyoxaline-5(4)-carboxylic acid, and 2-thiol-, ethyl esters (FORSYTH and PYMAN), i, 700.
β-Phenylglyoxime, α-hydroxy-, and its derivatives (PONZIO), i, 1075.
Phenylglyoxylic acid, *p*-bromo-, and its methyl ester, and *p*-nitro-, xylylhydrazones of (BUSCH and v. BEUST), i, 400.
β-Phenyl-Δ$^{\alpha\gamma}$-heptadiene (GRIGNARD and DUBIEN), i, 112.
β-Phenylheptane-βδ-diol (GRIGNARD and DUBIEN), i, 112.
η-Phenyl-Δ$^{\beta\delta\zeta}$-heptatrien-α-al (VORLÄNDER, FISCHER, and KUNZE), i, 1068.
η-Phenyl-Δ$^{\beta\delta\zeta}$-heptatrienylmalonic acid (VORLÄNDER, FISCHER, and KUNZE), i, 1069.
β-Phenyl-Δγ-hepten-β-ol (GRIGNARD and DUBIEN), i, 111.
s-Phenylheptylhydrazine (MAZOUREVITCH), i, 1247.
α- and γ-Phenylhexa-βδ-diones, and their copper salts (MORGAN, DREW, and PORTER), i, 363.
9-Phenylhexahydrocarbazole, 11-nitro-10-hydroxy- (LINNELL and PERKIN), i, 63.
6-Phenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylic acid, ethyl ester (INGOLD and WEAVER), i, 581.
α-Phenyl-γ-hexanol, resolution and rotation of, and its salts and esters (HEWITT and KENYON), i, 914.
s-Phenyl*cyclo*hexylhydrazine (GOODWIN and BAILEY), i, 843.
Phenylhydantoins, *p*-hydroxy- (COGHILL and JOHNSON), i, 582.
3-Phenylhydantoin-[Δ$^{5:3'}$]-oxindole (HILL and HENZE), i, 306.
5-Phenylhydrazidouracil (LEVENE), i, 979.
Phenylhydrazine, compounds of carbon suboxide with (VAN ALPHEN), i, 83.
reaction of mercuric acetate with (VECCHIOTTI and CAPODACQUA), i, 1106.
acetyl derivative, bromination of (HUMPHRIES and EVANS), i, 1339.
Phenylhydrazine, *o*-amino-, and its derivatives (GUHA and RAY), i, 1461.
2:4-*di*bromo-, preparation of (HUMPHRIES and EVANS), i, 1339.
3:4-*di*bromo- (VOTOČEK and JIRŮ), i, 317.
o-nitro-, derivatives of (GUHA and RAY), i, 1462.

3-Phenylhydrazino-5-phenyl*iso*oxazole, 4-amino- and 4-nitroso- (RUGGERI), i, 79.

Phenylhydrazones, behaviour of, when dissolved in organic solvents (RASTELLI), i, 256.
reduction of (GOODWIN and BAILEY), i, 843.
action of chlorine on (HUMPHRIES, HUMBLE, and EVANS), i, 989.
influence of constitution on formation of pyrazolines from (v. AUWERS and KREUDER), i, 1456.

Phenyl 2-hydroxy-4:6-dimethoxystyryl ketone (PRATT and ROBINSON), i, 825.

Phenylhydroxyfurazan, and its derivatives (GASTALDI and REPOSSI), i, 988.

Phenylhydroxylamine, nitroso- (*cupferron*), salts of (AUGER, LAFONTAINE, and CASPAR), ii, 328.

Phenyl 2-hydroxy-3-methoxystyryl ketone, and its potassium salt, and acetyl derivative (PFEIFFER, ARMBRUSTER, BACKES, and OBERLIN), i, 270.

Phenyl 4-hydroxy-3-methoxystyryl ketone, 4-hydroxy-, glucoside (BARGELLINI and LEONE), i, 1283.

γ-Phenyl-α-hydroxymethylene-Δβ-butenoic acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.

γ-Phenyl-α-hydroxymethylenebutyric acid, ethyl ester (v. AUWERS and MÖLLER), i, 404.

2-Phenyl-8-hydroxy-4-methylquinoline, and its salts (JOHN and WEBER), i, 1452.

Phenyl 2-hydroxy-3-naphthyl ketone, and its potassium salt (LESSER, KRANLPUHL, and SAD), i, 1426.

3-Phenyl-5-*p*-hydroxyphenyl-4:5-dihydro*iso*oxazole, and its derivatives (VORLÄNDER and SCHOENEMANN), i, 269.

Phenyl β-*di*hydroxyphenylethyl ketones, *di*hydroxy- (CHAPMAN and STEPHEN), i, 669.

1-Phenyl-5-*o*-hydroxyphenyl-3-methylpyrazoline, *p*-nitro- (v. AUWERS and KREUDER), i, 1455.

3-Phenyl-5-*p*-hydroxyphenyl*iso*oxazole (VORLÄNDER and SCHOENEMANN), i, 269.

1-Phenyl-2:4:6-*tri*-*p*-hydroxyphenylpyridinium bromide (DILTHEY and SCHAEFER), i, 154.

1-Phenylhydroxyquinoxalone (KEHRMANN and BENER), i, 444.

Phenyl *p*-hydroxystyryl ketone, and *p*-hydroxy-, and their derivatives (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 267.

Phenyl-6-hydroxy-*m*-tolylmethane. See 3-Benzyl-*p*-cresol.

Phenyl β-hydroxyvinyl ketone, derivatives of (v. AUWERS and SCHMIDT), i, 585.

α-Phenyl-β-iminoethane. See β-Phenylacetaldimine.

2-Phenylimino-1:2:3:4-tetrahydro-1:3:4-benztriazine (GUHA and RÂY), i, 1462.

5-Phenylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, *p*-bromo- and *m*-chloro-, and their derivatives (GUHA and RÂY), i, 703.

Phenyl*cyclo*iminotoluquinone, and bromo- and chloro-derivatives (CHATTAWAY and PARKES), i, 985.

Phenylindandionyldi-indonylmethane (RADULESCU and GEORGESCU), i, 1287.

Phenylindandionylmethyl alcohol, and its derivatives (RADULESCU and GEORGESCU), i, 1286.

2-Phenylindazole, 5-chloro-, 5-chloro-3-cyano-, and 3-cyano-, 3-cyano-2-*p*-chloro-, and their oxides (HELLER and SPIELMEYER), i, 838.

2-Phenylindazole-3-carboxylic acid, and 2-*p*-chloro-, and 5-chloro- (HELLER and SPIELMEYER), i, 838.

2-Phenylindole, 2-*p*-hydroxy- (KORCZYŃSKI and KIERZEK), i, 978, 1098.

2-Phenyl-6-iodo-4-methylquinoline, and its salts (JOHN and WEBER), i, 1452.

***s*-Phenyl-5-iodo-*o*-tolylcarbamide** (HANN and BERLINER), i, 908.

Phenylmercuric *tri*nitrobenzoate (KHARASCH and GRAFFLIN), i, 1107.

Phenylmercury 2:4:6-trinitrophenyl (KHARASCH and GRAFFLIN), i, 1107.

Phenyl *p*-methoxybenzyl ketone (TIFFENEAU and ORÉKHOV), i, 680.

Phenyl *p*-methoxybenzyl diketone (MALKIN and ROBINSON), i, 559.

2-Phenyl-3-*p*-methoxybenzylquinoxaline (MALKIN and ROBINSON), i, 559.

Phenyl α-methoxy-β-hydroxyvinyl ketone, and its copper salt (MALKIN and ROBINSON), i, 827.

3-Phenylmethoxymethyl-6-methylbenzthiopyrone (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

2-Phenyl-8-methoxy-4-methylquinoline, and its salts (JOHN and WEBER), i, 1452.

Phenyl β-methoxystyryl ketone (MALKIN and ROBINSON), i, 559.

Phenyl *p*-methoxystyryl ketone, *p*-hydroxy-, and its salts (VORLÄNDER, HIEMESCH, SCHOENEMANN, SCHADE, and KUNZE), i, 267.

Phenyl *p*-methoxystyryl ketone, *p*-hydroxy-, glucoside (BARGELLINI and LEONE), i, 1283.
3-Phenyl-5-methyl-3-allylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.
4-Phenylmethylamino-1-methyl-2-methylene-1:2-dihydroquinoline (FISCHER, DIEPOLDER, and WÖLFEL), i, 438.
4-Phenylmethylamino-2-methylquinoline, and its picrate (FISCHER, DIEPOLDER, and WÖLFEL), i, 439.
1-Phenyl-2-methylbenziminazole-5-carboxylic acid, 7-nitro- (LINDEMANN and WESSEL), i, 1100.
3-Phenyl-3-methyl-4:5-benzocoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.
1-Phenyl-5-methylbenzthiazole, 4'-amino-, physiological action of (HUNTER), i, 702.
*per*bromide (HUNTER), i, 987.
1-Phenyl-4(or 6)-methyl-1:2:3-benztriazole, 7-nitro- (BRADY, HEWETSON, and KLEIN), i, 16.
ω-Phenyl-*ms*-methylbiuret (BILTZ and BECK), i, 1393.
ω'-Phenyl-ω-methylbiuret, ω-nitroso- (BILTZ and BECK), i, 1393.
α-Phenyl-β-methylbutane, β-bromo- (TROTMAN), i, 382.
α-Phenyl-β-methyl-Δ$^{\alpha}$-buten-γ-one, condensation of aldehydes with (RYAN and LENNON), i, 1282.
Phenyl γ-methyl-Δ$^{\alpha}$-butenyl ketone, and *p*-amino-, and its hydrochloride (THOMS and KAHRE), i, 789.
α-Phenyl-β-methylbutyronitrile (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.
Phenylmethylcarbinol, *o*-chloro- (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.
3-Phenyl-2-methylcoumaran (CLAISEN and TIETZE), i, 389.
3-Phenyl-3-methylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 147.
3-Phenyl-4-methylcoumarin, 7-hydroxy- (BAKER and ROBINSON), i, 1300.
Phenylmethyldipropargylammonium bromide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1401.
Phenyl-*Py*-*N*-methyldiveratro*iso*-harmyrine, and its methiodide (ARMIT and ROBINSON), i, 1172.
1-Phenyl-3-*mp*-methylenedioxyphenyl-5-methylpyrazole-4-carboxylic acid, and its ethyl ester (MINUNNI, LAZZARINI, and D'URSO), i, 1176.
Phenylmethylethylallylarsonium iodide (STEINKOPF and BESSARITSCH), i, 496.
3-Phenyl-5-methyl-3-ethylcoumaran-2-one (LÖWENBEIN, SIMONIS, LANG, and JACOBUS), i, 148.
4-Phenyl-6-methyl-2-ethylpyridine-3:5-dicarboxylic acid, ethyl ester, and its derivatives (MUMM), i, 966.
2-Phenyl-4-methyl-6-ethylquinoline, and its salts (JOHN and WEBER), i, 1452.
1-Phenyl-4-methylglyoxaline, 2-thiol- (BURTLES, PYMAN, and ROYLANCE), i, 697.
4-Phenyl-1-methylglyoxaline, 5-bromo-, and its picrate (FORSYTH and PYMAN), i, 700.
β-Phenylmethylglyoxime methyl ethers (AVOGADRO and TAVOLA), i, 1040.
1-Phenyl-5-methyl-3-*n*-hexylpyrazole-4-carboxylic acid (MINUNNI, LAZZARINI, and D'URSO), i, 1176.
3-Phenyl-1-methylhydantoylmethylamide, and 5-hydroxy- (GATEWOOD), i, 1188.
Phenylmethylketen oxides (STAUDINGER, DYCKERHOFF, KLEVER, and RUZICKA), i, 934.
2-Phenyl-4-methyl-β-naphthaquinoline (JOHN and NOZICZKA), i, 1451.
2-Phenyl-4-methyl-β-naphthaquinoline, hydroxy-, and its salts and derivatives (JOHN and WEBER), i, 1452.
3-Phenyl-2-methyl-*lin*-naphthiminazole, 4:9-*di*hydroxy-, and its diacetyl derivative (FRIES and BILLIG), i, 939.
3-Phenyl-2-methyl-*lin*-naphthiminazole-4:9-quinone (FRIES and BILLIG), i, 939.
Phenylmethylnitroamine, *tri*nitro- (*tetryl*), heat effusion of (RINKENBACH and HALL), ii, 207.
α-Phenyl-ββ-methylnitrocarbamide, 2:4-*di*nitro- (KNIPHORST), i, 907.
Phenylmethylnonylcarbinol (THOMS and AMBRUS), i, 790.
Phenylmethyl*iso*oxazole, *O*-alkyl ethers of (WEYGAND and FRIELING), i, 1288.
1-Phenyl-2-methylperimidine, 7-hydroxy-, and its hydrochloride (SANDER), i, 982.
α-Phenyl-β-methylpropane, β-bromo- (TROTMAN), i, 383.
Phenylmethyl-*n*-propylallylarsonium iodide (STEINKOPF and BESSARITSCH), i, 496.
3-Phenyl-4-methylpyrazole, 5-chloro-, and its hydrochloride (v. AUWERS and MAUSS), i, 1179.
Phenylmethylpyrazoles, and 4-bromo- (v. AUWERS and SCHMIDT), i, 586.
1-Phenyl-5-methylpyrazole-3:4-dicarboxylic acid, 1-*p*-amino-, and its acetyl derivative, and its ethyl ester (BÜLOW and BAUR), i, 1327.

5-Phenyl-1-methylpyrazoline hydrobromide, 4-bromo- (v. AUWERS and OTTENS), i, 1429.
Phenylmethylpyrazolines, and their derivatives (FREUDENBERG and STOLL), i, 70.
1-Phenyl-3-methyl-5-pyrazolone, *mono*- and *di*-chloro-, and their derivatives (CHATTAWAY and STROUTS), i, 71.
Phenylmethylpyrazol-5-ones (v. AUWERS and MAUSS), i, 1179.
1-Phenyl-3-methyl-5-pyrazolone-4-azobenzene, 2′:4′-*di*chloro- (CHATTAWAY and STROUTS), i, 72.
1-Phenyl-3-methyl-5-pyrazolone-4-azochlorobenzenes, 1-chloro-(CHATTAWAY and STROUTS), i, 71.
1-Phenyl-2-methylpyrrolidine, and its methiodide (WOLFF), i, 428.
2-Phenyl-4-methylquinolines, substituted (JOHN and NOZICZKA), i, 1451; (JOHN and WEBER), i, 1452.
2-Phenyl-4-methylquinolinecarboxylic acids, and their salts and derivatives (JOHN and WEBER), i, 1452.
Phenylmethylsulphone, derivatives of, and 3-nitro- (TWIST and SMILES), i, 895.
Phenylmethylsulphone, 4-*mono*- and 2:5-*di*-chloro- (MILLER and SMILES), i, 392.
Phenylmethyltetrahydroindazoles, and their perchlorates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1182.
Phenylmethyl*di*thiocarbamic acid, salts of (WHITBY and MATHESON), i, 644.
4-Phenyl-6-methylthio-chroman-4-ol- and -chromene (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.
1-Phenyl-4-methyl-1:2:3-triazole (BERTHO), i, 840.
Phenylnaphthafluorone, 2′:4′-*di*hydroxy- (SEN and SARKAR), i, 812.
12-Phenyl-$\alpha\beta$-naphthaphenazonium salts, 5:12-*m*-*di*amino-, and their acetyl derivatives (KEHRMANN and LISTVA), i, 1332.
Phenylnaphthaphenfluorindines (KEHRMANN and SCHEDLER), i, 442.
2-Phenyl-$\alpha\beta$-naphthatriazole, 4-hydroxy-2-*p*-bromo-, and oxide, 2-*p*-bromo- and 2-*p*-chloro- (CHARRIER, CRIPPA, TOIA, and BIANCHESSI), i, 591.
Phenyl*iso*naphthophenazonium salts, and amino-, constitution and absorption spectra of (KEHRMANN and SANDOZ), i, 983.
Phenyl-β-naphthylamine-*m*-sulphonic acid (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 591.
α-Phenyl-δ-naphthyl-*n*-butane, and its oxidation products (SCHROETER, VAN HULLE, GLUSCHKE, STIER, and MÜLLER), i, 125.
Phenylnaphthylenediamines (LEVI), i, 1186.
β-Phenyl-β-1-naphthylethylamine, and its salts (LUCE), i, 264.
Phenyl α-naphthylmethyl ketone (LUCE), i, 264.
Phenyl-1′-naphthylphthalide-4:5′-dicarboxylic acid, and its anhydride (LORRIMAN), i, 672.
Phenyl-1′-naphthylphthalide-4:4′:5′-tricarboxylic acid, and its anhydride (LORRIMAN), i, 673.
Phenyl-α-naphthylpropylene (LUCE), i, 263.
4-Phenyl-1:8-naphthyrid-2-one, supposed, constitution of (SEIDE), i, 437.
Phenyl-2(6?)-nitro-6(2?)-amino-*m*-tolylamine (BRADY, HEWETSON, and KLEIN), i, 16.
α-Phenyl-β-nitrocarbamide, α-2:4-*di*nitro- (GIUA and PETRONIO), i, 1396.
α-Phenyl-*p*-nitrocinnamic acid, ethyl ester (RANFALDI), i, 399.
Phenyl *o*-nitrocinnamylidenemethyl ketone (PFEIFFER), i, 409.
5-Phenyl-1-*p*-nitrophenyl-3-methylpyrazoline (v. AUWERS and KREUDER), i, 1455.
2-Phenyl-4-*o*-nitrophenyl-5-methyl-1:2:3-triazole (NEBER, HARTUNG, and RUOPP), i, 1073.
Phenyl-4-nitropiaselenazonium chloride, and *p*-hydroxy- (BATTEGAY and VÉCHOT), i, 1467.
2-Phenyl-5-oxazolidone, acetyl and benzoyl derivatives (BERGMANN, ENSSLIN, and ZERVAS), i, 891.
2-Phenyloxazoline-4-carboxylic acid, and its methyl ester and hydrochloride (BERGMANN and MIEKELEY), i, 235.
Phenylparaconic acid, *o*-bromo- (FUSON), i, 254.
m- and *p*-bromo- (FUSON), i, 540.
ϵ-Phenyl-$\Delta\beta\delta$-pentadien-α-al (VORLÄNDER, FISCHER, and KUNZE), i, 1068.
ϵ-Phenylpentadienylmalonic acid (VORLÄNDER, FISCHER, and KUNZE), i, 1068.
α-Phenyl-$\Delta^{\alpha\gamma}$-pentadi-inene, and its tetrabromides (PRÉVOST), i, 878.
γ-Phenylpenta-$\beta\delta$-dione, and its copper salt (MORGAN, DREW, and PORTER), i, 364.
α-Phenyl-γ-pentanol, resolution and rotation of, and its salts and esters (HEWITT and KENYON), i, 914.
α-Phenyl-$\Delta\gamma$-pentenonitrile (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.

3-Phenyl-3-phenacyl-4:5-benzocoumaran-2-one (Löwenbein, Simonis, Lang, and Jacobus), i, 147.
3-Phenyl-3-phenacyl-5-methylcoumaran-2-one (Löwenbein, Simonis, Lang, and Jacobus), i, 147.
9-Phenylphenanthraphenazonium chloride, 11:12-*di*amino-, and its salts (Kehrmann and Stanoyévitch), i, 1332.
N-Phenylphenanthraphenfluorindine (Kehrmann and Schedler), i, 442.
2-Phenylphenanthriminazole, and 2′-nitro- (Sircar and Ray), i, 980.
2-Phenylphenanthroxazole, 2′-hydroxy-, and 2′- and 3′-nitro- (Sircar and Ray), i, 980.
Phenyl β-phenyl-α-*p*-anisylethyl ketone (Tiffeneau and Orékhov), i, 680.
Phenyl δ-phenylbutyl ketone, and its oxime (Pfeiffer, Armbruster, Backes, and Oberlin), i, 270.
1-Phenyl-5-β-phenylethylbarbituric acid (Dox), i, 301.
1-Phenyl-5-β-phenylethyl-5-ethylbarbituric acid (Dox), i, 301.
Phenyl β-phenylethyl ketone dimethyl acetal (Straus and Ehrenstein), i, 535.
Phenyl-*N*-phenylnitron, *o*-hydroxy- (Bamberger), i, 142.
Phenyl γ-phenylpropyl ketone, and its semicarbazone (v. Auwers and Möller), i, 404.
4-Phenyl-1-*o*-phenylthiocarbamidophenylthiosemicarbazide (Guha and Rây), i, 1461.
3-Phenylphenylthiolmethyl-6-methylbenzthiopyrone (Krollpfeiffer, Schultze, Schlumbohm, and Sommermeyer), i, 1307.
2-Phenyl-4-phthalimidomethylquinoline (John), i, 1317.
Phenylpiaselenazonium chloride (Battegay and Véchot), i, 1467.
Phenylpiaselenazonium-4-sulphonic anhydride, and *p*-hydroxy- (Battegay and Véchot), i, 1468.
3-Phenyl*cyclo*propane-1:2-dicarboxylic acid, 1-bromo-, methyl esters (Haerdi and Thorpe), i, 924.
Phenylpropiolaldehyde, derivatives of (v. Auwers and Ottens), i, 1428.
β-Phenylpropionamide, β-amino- (Stosius and Philippi), i, 918.
2-Phenylpropionic acid, 1-α-amino-3:4-*di*hydroxy-, detection of, in presence of tyrosine (Schmalfuss and Werner), i, 1361.
3-Phenylpropionic acid, α-bromo-, amide and nitrile, and α-cyano-β-2:4-*di*hydroxy- (Baker and Lapworth), i, 30.
β-Phenylpropionic acid, β-bromo-, conversion of, into β-hydroxy-β-phenylpropionamide, and its ammonium and diethyl ammonium salts (Senter and Ward), i, 1128.
2:6-*di*hydroxy- (Chapman and Stephen), i, 669.
β-Phenylpropionic acids, β-hydroxy-, conversion of, into β-bromo-β-phenylpropionic acids (Senter and Ward), i, 31.
β-Phenylpropionic anhydride (Robinson and Shinoda), i, 1301.
β-Phenylpropionitrile, α-bromo- (Freudenberg, Fikentscher, and Harder), i, 420.
Phenylpropionylmandelic acids, ethyl and methyl esters (Freudenberg and Markert), i, 1275.
α-Phenylpropylamine, salts of (Mazourevitch), i, 1240.
N-γ-Phenylpropylaniline, and its hydrochloride (Bamberger), i, 142.
α-Phenyl-Δ^α^-propylene, β-chloro-α-2:4-*di*nitro- (Neber, Hartung, and Ruopp), i, 1073.
s-Phenyl*iso*propylhydrazine, and its salts and derivatives (Goodwin and Bailey), i, 843.
Phenyl *iso*propyl ketone, 2:4-*di*hydroxy- (Sharp & Dohme and Dohme), i, 541.
Phenyl*iso*propylsemicarbazides, and their derivatives (Goodwin and Bailey), i, 843.
α-Phenyl*iso*propylsuccinamic acid, ethyl ester (Farbwerke vorm. Meister, Lucius, & Brüning), i, 376.
α-Phenyl-α-*iso*propylsuccinimide (Farbwerke vorm. Meister, Lucius, & Brüning), i, 376.
1-Phenyl-4-*iso*propyl-1:2:3-triazole (Bertho), i, 840.
2-Phenyl-1-*iso*propylurazole (Goodwin and Bailey), i, 843.
3(5)-Phenylpyrazole, and its derivatives (v. Auwers and Schmidt), i, 585.
3(5)-Phenylpyrazole, 4-bromo-, hydrobromide (v. Auwers and Ottens), i, 1460.
Phenylpyrazoles, chloro-, acetyl, benzoyl, and nitrobenzoyl derivatives of (v. Auwers and Mauss), i, 1180.
3-Phenylpyrazole-1-carboxylamide, and 4-bromo- (v. Auwers and Ottens), i, 1460.
5-Phenylpyrazole-1-carboxylamide (v. Auwers and Ottens), i, 1460.
3-Phenylpyrazoline, derivatives of (Freudenberg and Stoll), i, 70.
1-Phenylpyridinium iodide, 3-bromo- and 3-iodo- (Baumgarten), i, 1381.

1-Phenylpyridinium salts, and 1-amino-, 4-chloro-, and 1-nitro- (VORLÄNDER), i, 1256.

1-Phenyl-4-pyridone, and 1-*p*-amino-, -*p*-chloro-, -*p*-hydroxy-, and -*p*-nitro- and their salts (VORLÄNDER), i, 1257.

1-Phenylpyrrole, compounds of, with mercuric chloride (PLANCHER and ROSSI), i, 601.

1-Phenylpyrrole, *di*bromo- (PLANCHER and ROSSI), i, 601.

1-Phenyl-5-pyrrolidone-4-carboxylic acid (KÜSTER and GRÄSSNER), i, 922.

4-Phenyl-2-pyrrolidone-5-carboxylic acid, and 4′-amino-, 3′:5′-*di*iodo-4′-amino-, 3′:4′:5′-*tri*iodo-, and 4′-nitro- (HARINGTON), i, 1094.

Phenylpyruvic acid, and its ethyl ester, *p*-tolylhydrazones (WALKER), i, 1193.

Phenylpyruvic acid, 2-nitro-4-cyano-, ethyl ester (KERMACK), i, 67.

2-Phenyl-4-quinazolone, 3-amino-, and its derivatives (HELLER, GÖRING, KLOSS, and KÖHLER), i, 1322.

2-Phenylquinoline-4-aldehyde, and its phenylhydrazone, preparation of (CHEM. FABRIK AUF AKTIEN, VORM. E. SCHERING), i, 1452.

2-Phenylquinoline-4-carboxylic acid, bismuth salts (RIEDEL), i, 1170.

Phenyl-8-quinolylamine-*p*-carboxylic acid, *o*-nitro- (SEKA), i, 587.

***s*-Phenyl-8-quinolylcarbamide** (SEKA), i, 587.

2-Phenyl-4-quinolyl δ-methylaminobutyl ketone, and its dihydrochloride (RUZICKA, SEIDEL, and LIEBL), i, 290.

2-Phenyl-4-quinolyl 3-*N*-methyl-2-piperidonyl ketone, and its picrate (RUZICKA, SEIDEL, and LIEBL), i, 290.

3-Phenylquinoxaline, 3-*o*-hydroxy- (FRIES and SAFTIEN), i, 570.

3-Phenylrhodanylidene-$\Delta^{5:3'}$-oxindoles (HANN), i, 987.

Phenylselenoglycollic acid, and *p*-bromo-, and their salts (MORGAN and PORRITT), i, 1196.

Phenylselenoxyglycollic acid, *p*-bromo-, and its salts (MORGAN and PORRITT), i, 1196.

Phenylsemicarbazide, action of, on acetylacetone (WHEELER and BROOKS), i, 1459.

2-Phenylsemicarbazide (GOODWIN and BAILEY), i, 318.

4-Phenylsemicarbazide, 2′:4′-*di*nitro-, and its semicarbazones (KNIPHORST), i, 907.

Phenylstibinic acid, *p*-amino-, sodium salt, glucoside of (WELLCOME FOUNDATION, LTD., and GRAY), i, 991.

Phenylstilbazonium salts, 3-chloro- (KEHRMANN and FALKE), i, 303.

2-Phenyl-4-styrylbenzopyrylium chloride, 4:5:7-*tri*hydroxy- (WALKER and HEILBRON), i, 693.

Phenyl styryl ketone (*benzylideneacetophenone*), 4-hydroxy-, glucoside (BARGELLINI and LEONE), i, 1283.

Phenyl styryl ketones, isomeric (DILTHEY and RADMACHER), i, 408.

Phenylsuccinic acid, *p*-hydroxy- (CHRZASZCZEWSKA), i, 956.

Phenylsulphur chloride, 2:5-*di*chloro- (MILLER and SMILES), i, 392.

9-Phenyltetrahydrocarbazole, and 5(?)-nitro- (LINNELL and PERKIN), i, 63.

9-Phenyl-1:2:3:4-tetrahydrocarbazole-8-carboxylic acid, 2′-amino- (LINNELL and PERKIN), i, 63.

4-Phenyltetrahydro-1:4-oxazine, and a green colouring matter therefrom (ADKINS and SIMINGTON), i, 986.

2-Phenyl-4:5:6:8-tetramethylquinoline, and its salts (JOHN and WEBER), i, 1452.

2-Phenyl-1:2:3:4-tetrazole, 5-amino-, and its derivatives (STOLTE and ORTH), i, 1464.

2-Phenyl-1:2:3:4-tetrazole-5-carboxylic hydrazide, and its derivatives (STOLTE and ORTH), i, 1464.

Phenylthiarsane, and its salts (JOB, REICH, and VERGNAUD), i, 173.

4-Phenylthiazole, 2-amino-, and its derivatives (BOGERT and CHERTCOFF), i, 315.

4-Phenyl-1-thiazole-5-carboxylic acid, 2-amino-, ethyl ester (HIRST, MACBETH, and TRAILL), i, 1251.

Phenyl-α-thienylmethylcarbamide (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.

Phenylthiocarbamide, condensation of diethylamine with (HUNTER), i, 805.

α-Phenylthiodi-*p*-anisylacetic acid, and its barium salt (BISTRZYCKI and RISI), i, 1426.

5-Phenyl-1:3:4-thiodiazine, 2-amino-, and its derivatives (BOSE), i, 167.

3-Phenyl-2-thiohydantoin-[$\Delta^{5:2'}$]-ψ-indoxyl (HILL and HENZE), i, 306.

3-Phenyl-2-thiohydantoin-[$\Delta^{5:3'}$]-oxindole (HILL and HENZE), i, 306.

β-Phenylthiol-*n*-butyric acid (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.

Phenylthiolcarbamic acid, benzyl and *p*-tolyl esters (GILMAN and KING), i, 811.

β′-Phenylthioldiethyl ether, β-chloro- (CRETCHER, KOCH, and PITTENGER), i, 628.

α-Phenylthioldiphenylacetic acid, and its salts and acid chloride (BISTRZYCKI and RISI), i, 1426.
3-Phenylthiolhydantoin, 3-*p*-nitro- (COGHILL and JOHNSON), i, 582.
β-Phenylthiolpropionic acid, β-*p*-bromo- (ARNDT), i, 1309.
β-*p*-chloro- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
Phenylthiophens, amino-, iodo-, and nitro- (CHRZASZCZEWSKA), i, 956.
Phenylthiophosphordihydrazide, dibenzylidene derivative (AUTENRIETH and MEYER), i, 990.
4-Phenylthiosemicarbazide, bromo- and chloro- (GUHA and RÂY), i, 703.
Phenylthiosemicarbazides, action of benzoyl chloride on (FROMM and TRUKA), i, 703.
Phenyl-*p*-tolyl-4-acenaphthylmethane (LORRIMAN), i, 673.
Phenyl-*p*-tolyl-4′-acenaphthylmethane-2-carboxylic acid, and its methyl ester (LORRIMAN), i, 673.
Phenyl-*p*-tolylacetic acid, benzyl ester (RAMART and AMAGAT), i, 659.
5-Phenyl-3-*o*-tolyl-1-*p*-anisyl-2-*p*-chlorophenyl-1:2:3:6-tetrahydro-1:3:4-triazine (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
5-Phenyl-3-*o*-tolyl-1-*p*-anisyl-2-*p*-dimethylaminophenyl-1:2:3:6-tetrahydro-1:3:4-triazine (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
5-Phenyl-3-*o*-tolyl-1-*p*-anisyl-2-methyl-1:2:3:6-tetrahydro-1:3:4-triazine (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
5-Phenyl-3-*o*-tolyl-1-*p*-anisyl-1:2:3:6-tetrahydro-1:3:4-triazine (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
Phenyl-*p*-tolylbenzylacetic acid, and its benzyl ester (RAMART and AMAGAT), i, 659.
5-Phenyl-1-tolyl-3-*tert.*-butylpyrazolines (v. AUWERS and KREUDER), i, 1455.
Phenyltolylcarbamides, *di*nitro- (KNIPHORST), i, 907.
5-Phenyl-3-*o*-tolyl-1:2-di-*p*-anisyl-1:2:3:6-tetrahydro-1:3:4-triazine (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.
β-Phenyl-β-*p*-tolylethyl alcohol (RAMART and AMAGAT), i, 659.
Phenyl-*p*-tolylformamidines, *N*-hydroxy-, and their derivatives (FARROW and INGOLD), i, 155.
3-Phenyl-1-*o*-tolyl-3-methylpyrazole, 4-chloro- (v. AUWERS and KREUDER), i, 1455.
1-Phenyl-3-*p*-tolyl-5-methylpyrazole-4-carboxylic acid, and its ethyl ester (MINUNNI, LAZZARINI, and D'URSO), i, 1176.
5-Phenyltolylmethylpyrazolines, and *o*-chloro- (v. AUWERS and KREUDER), i, 1455.
Phenyl-*p*-tolyl-α-naphthylmethane (DILTHEY), i, 652.
Phenyl-*p*-tolyl-α-naphthylmethyl bromide, chloride, and methyl ether (DILTHEY), i, 652.
Phenyl-*N*-*p*-tolylnitron, *o*-hydroxy- (BAMBERGER), i, 142.
2-Phenyl-3-*p*-tolyloxazolidine, 2-*p*-bromo- (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1064.
αα-Phenyl-*p*-tolylpropionic acid, and its benzyl ester (RAMART and AMAGAT), i, 659.
4-Phenyl-1-*p*-tolyl-1:2:3-triazole, 5-chloro- and 5-hydroxy- (CARNELLEY and DUTT), i, 166.
Phenyltriazoles (ELBS), i, 163.
vic.-2-Phenyltriazolephthalonic acid, and its derivatives, true nature of supposed (CHARRIER), i, 76.
1-Phenyl-3:4:5-trimethylpyrazole, *p*-nitro- (v. AUWERS and KREUDER), i, 1454.
1-Phenyl-3:5:5-trimethylpyrazoline, *p*-nitro- (v. AUWERS and KREUDER), i, 1454.
2-Phenyl-4:5:8-trimethylquinoline, and its salts (JOHN and WEBER), i, 1452.
9-Phenyl-1:3:7-trimethyluric acid, action of alkalis on (GATEWOOD), i, 1188.
Phenyltriphenazineoxazine, and its derivatives (KEHRMANN and SCHEDLER), i, 444.
N-Phenyltriphenazineoxazine, and its derivatives (KEHRMANN and SCHEDLER), i, 444.
β-Phenyl-Δβ-undecene (THOMS and AMBRUS), i, 790.
3-ω-Phenylvinyl-2-methylindole, ω-cyano- (SEKA), i, 67.
Phenylxanthene, *p*-hydroxy- (GOMBERG and SNOW), i, 660.
Phenylxylylformazylcarboxylic acid, and *p*-bromo-, and *p*-nitro-, methyl esters (BUSCH and v. BEUST), i, 400.
Phenylxylyl-α-naphthylmethyl chlorides and methyl ether (DILTHEY), i, 652.
Phloridzin, clinical experiments with (DÜNNER and MECKLENBURG), i, 1500.
action of, on blood (ETS), i, 734.

Phloroacetophenone, derivatives of (SONN and BÜLOW), i, 1268.
Phloroacetophenone-*o*-carboxylic acid, methyl ester (SONN and BÜLOW), i, 1268.
Phloroacetophenone-*o*-dicarboxylic acid, dimethyl ester (SONN and BÜLOW), i, 1268.
Phloroacetophenonetricarboxylic acid, trimethyl ester (SONN and BÜLOW), i, 1268.
Phloroglucinol, tautomerism of derivatives of (SONN and BÜLOW), i, 1267.
***iso*Phonopyrrolecarboxylic acid**, synthesis of (FISCHER and NENITZESCU), i, 835.
Phormidium laminosum, enzymes of (HARVEY), i, 746.
Phosgene. See Carbonyl chloride.
Phosphatase in the liver (BRUGSCH and HORSTERS), i, 483.
Phosphates. See under Phosphorus.
Phosphatese in the liver (BRUGSCH and HORSTERS), i, 483.
Phosphatides, formation of choline from (ABDERHALDEN and PAFFRATH), i, 1016.
of brain, preparation of (THIERFELDER and KLENK), i, 997.
of plants (GRAFE; GRAFE and HORVAT), i, 1522.
Phosphine. See Phosphorus *tri*hydride.
Phosphinic acids, hydroxy-, aliphatic (BERNTON), i, 646.
Phosphinoacetic acid, and its salts and derivatives (NYLÉN), i, 1135.
Phosphinoformic acid, salts and derivatives of (NYLÉN), i, 1135.
α-Phosphinopropionic acid, and its salts (NYLÉN), i, 1136.
Phosphonium compounds, effect of, on the nervous system (HUNT and RENSHAW), i, 861.
Phosphors, luminescence of, under magnetic and electric fields (RUPP), ii, 13.
alkaline earth, rare earths in (TOMASCHEK), ii, 354.
of boric acid (MICKWITZ), ii, 476.
Phosphorescence, excitation of (RUPP), ii, 262.
Phosphorescent compounds, economy coefficients of (SCHMIEDER), ii, 931.
Phosphoric acid. See under Phosphorus.
Phosphorus, spectra of (SALTMARSH), ii, 724.
spectral frequencies of (HOLWECK), ii, 336.
arc spectrum of (DUFFENBACK and HUTHSTEINER), ii, 452; (SUR), ii 1014.
Phosphorus, spectrum of electrodeless discharge in vapour of (SHAVER), ii, 471.
Röntgen ray spectrum of (LUNDQUIST), ii, 1014.
series spectra of (BOWEN and MILLIKAN), ii, 342, 610.
luminescence of (EMELÉUS and DOWNEY), ii, 89; (EMELÉUS), ii, 354.
critical potential of (HOLWECK), ii, 729.
action of, on nickel nitrate (SCHMOSS), ii, 889.
effect of, on lipins and fats in the liver (SACCHETTO), i, 1357.
in blood of children (ANDERSON), i, 188.
metabolism. See Metabolism.
black, Röntgen ray structure of (LINCK and JUNG), ii, 1035.
red, action of, on carbon disulphide solutions of (TRAXLER and GERMANN), ii, 1087.
white, doubly-refractive (VORLÄNDER, SELKE, and KREISS), ii, 1086.
yellow, effect of, on bone formation (BERNHARDT and RABL), i, 1357.
Phosphorus compounds, *K* absorption spectra of (STELLING), ii, 935.
in milk (KAY), i, 998.
effect of heat on solubility of, in milk (BELL), i, 998.
fixation of, in bones (TELFER), i, 859.
determination of, in blood, and their distribution (STANFORD and WHEATLEY), i, 1200.
Phosphorus *tri*bromide and *tri*iodide, preparation of (REKSCHINSKI), ii, 994.
*tri*chloride, hydrolysis of (MITCHELL), ii, 316.
chlorides, action of ammonia on (PERPÉROT), ii, 1186.
oxychloride, electrolysis in, and its physical constants (CADY and TAFT), ii, 1073.
influence of, on the catalytic reduction of acid chlorides (ZETZSCHE and ARND), i, 1415.
*tri*hydride (*phosphine*), spectrum of the combustion of (EMELÉUS), ii, 740.
*tri*iodide, preparation of sulphide compounds of (KARANTASSIS), ii, 998.
nitride, nitrification of (ALLISON), i, 218.
*tri*oxide, preparation of, and spectrum of its combustion (EMELÉUS), ii, 740.

Phosphorus *pento*xide, vapour pressure of (SMITS and RUTGERS), ii, 268.
purification of (WHITAKER), ii, 1195.
drying tube for (DENNIS), ii, 428.
Phosphorous acid and its derivatives, constitution and *K* absorption spectra of (STELLING), ii, 936.
Phosphoric acid, constitution of (FRÖSCHL), ii, 19.
esterification of, by yeast (GOTTSCHALK and NEUBERG), i, 337.
formation of, in muscle (LANGE and MAYER), i, 729.
esters, synthesis of (KOMATSU and NODZU), i, 515.
detection of (FEIGL), ii, 435.
determination of (MCCANDLESS and BURTON), ii, 157; (JÖRGENSEN), ii, 824.
determination of, electrometrically, with alkalis (HOFFMAN and GORTNER), ii, 1011.
determination of, by the magnesium ammonium phosphate method (L. and J. DESHUSSES), ii, 67.
use of phenolphthalein as indicator for determination of (NYSSENS), ii, 1201.
determination of, in vegetable ash (L. and J. DESHUSSES), ii, 67.
separation of, in analysis, by means of bismuth nitrate (KESCHAN), ii, 328.
separation of, from metals of the group (JÄRVINEN), ii, 602.
Phosphoric acids, absorption of ethylene by (MÜLLER), i, 1373.
Phosphates, absorption spectra of beads of (SCHAUM and FUNCK), ii, 178.
absorption of, by Pasteur–Chamberlain filters (PARKER), i, 1372.
action of sodium carbonate on (COLANI), ii, 1001.
effect of adrenaline and phloridzin on excretion of (ALLAN, DICKSON, and MARKOWITZ), i, 726.
removal of, in qualitative analysis (CURTMAN, MARGULIES, and PLECHNER), ii, 68.
determination of (LE GUYON and MAY), ii, 1202.
determination of, in blood (MCCLUSKEY), i, 605.
determination of calcium and, in bone (v. EULER and JOHANSSON), i, 1489.
determination of, in presence of organic matter (SCHMITT-KRAHMER), i, 613.
Phosphorus:—
Phosphates, determination of, in serum (ESSINGER and GYÖRGY), i, 178.
Orthophosphoric acid, solubility and freezing point curves of (ROSS and JONES), ii, 971.
Orthophosphates, detection of metaphosphates, pyrophosphates, and (DE BOER), ii, 67.
Hexametaphosphates, preparation of (PASCAL), ii, 420.
Phosphorus organic compounds (NYLÉN), i, 1134.
Phosphites, neutral, preparation of (JANCZAK), i, 1051.
Thiophosphorous acid, aryl derivatives of (AUTENRIETH and MEYER), i, 807.
Thiophosphoryl chloride, aryl derivatives of (AUTENRIETH and MEYER), i, 807.
Phosphorus determination:—
determination of (RICHARDS and GODDEN), ii, 66; (STEWART and ARCHIBALD), ii, 824.
effect of ammonium sulphate on the determination of, colorimetrically (RIMINGTON), i, 183.
determination of, by means of lead amalgam (SOMEYA), ii, 1201.
determination of, in blood (MYRBÄCK), i, 1485.
lipoid, determination of, in blood and plasma (WHITEHORN), i, 95.
determination of, in proteins (SØRENSEN), ii, 900.
determination of, in presence of vanadium (GRAY and GARBUTT), ii, 600.
Photocatalysis with neutral salts (BERGER), ii, 313.
Photochemical equivalence, law of (BERTHELOT), ii, 1022; (ALLMAND), ii, 1074; (DHAR and MUKERJI; WEIGERT and BRODMANN), ii, 1075.
reactions (DHAR and MUKERJI), ii, 1079.
Becquerel effect in (SCHAUM and SCHLEUSSNER), ii, 985.
importance of water and of intensity of light in (CHAPMAN), ii, 1078.
temperature-coefficients of (DHAR), ii, 135; (PADOA), ii, 415.
and thermal reactions (DHAR and MUKERJI), ii, 809.
mechanism of (BODENSTEIN), ii, 1075.
elementary processes of (FRANCK), ii, 1077.
quantum sensitivity in (WINTHER), ii, 1074.

Photochemical reactions, relation between velocity of, and dielectric constants (WINTHER), ii, 1082.
formation of polar compounds in (NOYES), ii, 1081.
sensitisation (BERTHOUD), ii, 1083.
studies (REYCHLER), ii, 219, 1180; (NOYES), ii, 573.
thresholds and the dissociation theory (BOWEN), ii, 1074.
Photochemistry, technique of (REEVE), ii, 234; (FRANKLIN, MADDISON, and REEVE), ii, 809.
quantum laws in (WARBURG), ii, 984.
periodic reactions in (PLOTNIKOV), ii, 883.
of complex compounds (SCHWARZ and WEISS), ii, 576.
Photo-electric absorption coefficient (MILNE), ii, 920.
activity of elements (HAMER), ii, 7.
effect (AUDUBERT), ii, 43.
influence of temperature on (NIELSEN), ii, 172.
on metallic films (GROSS), ii, 344.
Photo-electrons, direction of emission of (AUGER), ii, 730.
Photographic blackening with Röntgen rays (BUSSE), ii, 1080.
developers (HORII and KOMORI), i, 1410.
fluorescence of (A. and L. LUMIÈRE and SEYEWETZ), i, 1060.
blackening curve for (MEIDINGER), ii, 143.
emulsions, ripening of (SCHMIDT), ii, 810; (LÜPPO-CRAMER), ii, 810, 986.
films, Röntgen ray measurements of (BLUNCK and KOCH), ii, 940; (KOCH and VOGLER), ii, 941.
image, latent (AUDUBERT), ii, 56; (TOY), ii, 143.
history and theory of (LÜPPO-CRAMER), ii, 575, 811.
plates, blackening of (ROBERTSON and THWAITES), ii, 575.
effect of coating, with fluorescent oils (HARRISON), ii, 930.
solarisation of (EDER), ii, 986.
for detection of mass rays (ASTON), ii, 706.
reversal (ARENS), ii, 313.
Photography, gelatin in (SHEPPARD), ii, 966.
silver in (LÜPPO-CRAMER), ii, 935.
silver bromide grain in (BAKER; LÜPPO-CRAMER), ii, 574.
Photolysis, mechanism of (BAUR), ii, 1082.
Photometer, rotatory dispersion (GIBSON), ii, 934.
Photometric studies (SCHAUM and FUNCK), ii, 178.
Photosensitisation (TAYLOR), ii, 1078.
Photosynthesis (MAZÉ), i, 485.
in tropical sunlight (DHAR and SANYAL), ii, 884.
activity of various radiations in (WURMSER), ii, 1082.
Phototropism in solution (SINGH), ii, 195.
Phtanites, hydrocarbons and carbonates in (DE LAPPARENT), ii, 821.
Phthalaldehyde 1-oxime, derivatives of (GRIFFITHS and INGOLD), i, 1190.
o-**Phthalaldehydic acid**, refractivity of (SEEKLES), i, 31.
Phthalamic acids, preparation of, and their conversion into anthranilic acids (CHAPMAN and STEPHEN), i, 1151.
Phthalazine, 4-chloro-1-hydroxy-, and 1:4-*di*thio- (RADULESCU and GEORGESCU), i, 1186.
Phthaleins, excretion of, in bile (ROSENTHAL and WHITE), i, 101.
Phthalhydrazide, and its acetyl derivatives (RADULESCU and GEORGESCU), i, 1185.
derivatives of (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1324.
Phthalic acid, salts, instability of, with hydrogen electrodes (DRAVES and TARTAR), ii, 695.
camphoryl hydrogen esters (FORSTER and SHUKLA), i, 1161.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
ethyl ester, detection of (LEFFMANN and TRUMPER; LEVINSON; THOMS), ii, 1008.
detection of, in ethyl alcohol (RALEIGH and MARIE), ii, 605.
determination of (HANDY and HOYT), ii, 1210.
determination of, oxidimetrically (TÄUFEL and WAGNER), ii, 1008.
Phthalic acid, 3-nitro-, preparation of (LITTMANN), i, 1066.
esters of, and their solubilities (NICOLET and SACKS), i, 1277.
Phthalic anhydride, 3-nitro-, as a reagent for identification of (NICOLET and SACKS), i, 1277.
Phthalidylidenedi-4-[salicylic phthalidylidene ether ester] *di*thioether (KAUFMANN and ROSSBACH), i, 1273.
Phthalimide, mercury derivatives of (LYONS), i, 645.
β'-**Phthalimidodiethyl** ether, *β*-chloro- (CRETCHER, KOCH, and PITTENGER), i, 628.
Phthalobenzylamic acid (HOLMES and INGOLD), i, 1142

Phthalonitrile, action of magnesium organic compounds on (WEISS and FREUND), i, 139.
Phthalophenone derivatives, structure of (DOMINIKIEWICZ), i, 53.
Phthalylglycylglycine, ethyl ester (GRANÄCHER), i, 594.
Phthalyl-*p*-tolil, nitration of (BRADY, QUICK, and WELLING), i, 1400.
Phycocyanine (KITASATO), i, 1111.
Phycoerythrin (KITASATO), i, 1111.
Phylloerythrin (FISCHER and HILMER), i, 855.
Physics, molecular (LASAREV), ii, 1134.
Physical chemistry, apparatus for (SCARPA), ii, 150.
influence of Willard Gibbs on (CONNAN), ii, 395.
constants in relation to metastability of matter (COHEN), ii, 1138.
Physiological action and chemical constitution (GILMAN and PICKENS), i, 333; (DUBIN, CORBITT, and FREEDMAN), i, 1502.
fluids, dextrose in (LUNDSGAARD and HOLBØLL), i, 1207.
electrometric analysis of (MISLOWITZER and VOGT), i, 1485.
Physostigmine. See Eserine.
Phytic acid, and its barium salt (CONTARDI), i, 277.
Phytosterols (VESTERBERG and BORGE), i, 252.
Phytosterols, irradiated, antirachitic value of (HESS, WEINSTOCK, and HELMAN), i, 750; (HESS and WEINSTOCK), i, 1020.
Piaselenazonium salts (BATTEGAY and VÉCHOT), i, 1466.
α-Picoline, 6-amino-, derivatives of (MEYER), i, 836.
γ-Picoline chlorostannate (DRUCE), i, 1096.
Picolinic acid, derivatives of (MEYER), i, 836.
Picric acid, conductivity of, in methyl alcohol (GOLDSCHMIDT and AARFLOT), ii, 976.
heat of fusion of (RINKENBACH and HALL), ii, 207.
reduction of, in organs of the body (GIORGI), i, 733.
detection of, colorimetrically (TORTI), ii, 905.
determination of, in presence of nitrocompounds (DESVERGNES), ii, 607.
Picrolonic acid, preparation and properties of (HUGOUNENQ, FLORENCE, and COUTURE), i, 435.
Picrotoxin, constitution of (BAKUNIN and GIORDANI), i, 691.
Picrylbenz*syn*aldoxime (BRADY and KLEIN), i, 674.
Picrylcinnam*syn*aldoxime (BRADY and KLEIN), i, 674.
Picryl-*p*-dimethylaminobenz*syn*aldoxime (BRADY and KLEIN), i, 674.
Picryl-2:3-dimethylindole (KORCZYŃSKI and KIERZEK), i, 1097.
***N*-Picryldi-*n*-propylcarbamide** (LECHER), i, 1391.
Picrylmethoxybenz*syn*aldoximes (BRADY and KLEIN), i, 674.
Picryl-3:4-methylenedioxybenz*syn*aldoxime (BRADY and KLEIN), i, 674.
Picryl-2-methylindole (KORCZYŃSKI and KIERZEK), i, 1097.
Picrylnitrobenz*syn*aldoximes (BRADY and KLEIN), i, 674.
Picryl-4-picryloxy-3-methoxybenz*syn*aldoxime (BRADY and KLEIN), i, 674.
Picrylsemicarbazide (GIUA and PETRONIO), i, 1397.
Picrylsemioxamazide (GIUA and PETRONIO), i, 1397.
Piezochemical studies (COHEN, DE MEESTER, and MOESVELD), ii, 190; (COHEN and BRUINS), ii, 280; (COHEN and VAN DER BOSCH), ii, 283.
Pigs, effect of iodine on assimilation of nitrogen, phosphorus, and calcium in (KELLY), i, 1210.
Pigeons, digestion in (MANGOLD), i, 615.
Pigments, formation of (SCHMALFUSS and WERNER), i, 1361.
by fungi (DANILOV), i, 1013.
metabolism of. See Metabolism.
Pilocarpidine, constitution of (BURTLES, PYMAN, and ROYLANCE), i, 696.
constitution and derivatives of (SPÄTH and KUNZ), i, 575.
***iso*Pilocarpidine** nitrate (SPÄTH and KUNZ), i, 576.
Pilocarpine 2:4:6-*tri*nitro-*m*-tolyloxide (SPÄTH and KUNZ), i, 576.
***iso*Pilocarpine** methopicrate (SPÄTH and KUNZ), i, 576.
***n*- and *iso*-Pilocarpines**, and their derivatives (LANGENBECK), i, 151.
***n*- and *iso-neo*Pilocarpines**, and their salts (BURTLES, PYMAN, and ROYLANCE), i, 696.
Pimenta officinalis, oil from leaves of (KEMP), i, 565.
Pinacolin, decomposition of (HURD and TALLYN), i, 885.
Pinacolin, chloro-oximino-, and its benzoyl derivative (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.
Pinacone, compound of boric acid and (HERMANS), i, 501.
Pinane (LIPP), i, 1080.
Pine lignin. See Lignin.

Pineapples, non-volatile acids of (NELSON), i, 762.
nitrogen assimilation of (STEWART, THOMAS, and HORNER), i, 1366.
Pinene (KONDAKOV and SAPRIKIN), i, 1080.
oxide, hydration of (NAMETKIN and JARCEVA), i, 1081.
α-Pinene, catalytic hydrogenation of (ZELINSKI), i, 821.
action of chlorine on (BRUS), i, 821.
Pinenes, relation between terpineols and (DÉLÉPINE), i, 564.
Pinus longifolia, abietic acid from rosin of (RAO and SIMONSEN), i, 687.
Piperazine, compounds of, with amino-acids (ABDERHALDEN and ROSSNER), i, 975.
1:4-dichloroacetyl derivative (ABDERHALDEN and ROSSNER), i, 976.
hydroferricyanide (CUMMING), i, 122.
Piperidine, preparation of (MARIE and LEJEUNE), i, 577.
influence of, in rickets (ÉDERER), i, 869.
chlorostannate (DRUCE), i, 1096.
hydroferricyanide (CUMMING), i, 122.
Piperidinoacetic acid, phenyl ethyl ester, and its hydrochloride (WEIL), i, 157.
9-Piperidinoanthracene (BARNETT, COOK, and MATTHEWS), i, 648.
9-Piperidinoanthrone, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1399.
α-Piperidino-β-benzylbutan-γ-one, and its hydrochloride (MANNICH), i, 375.
Piperidinodiphenylmethane, and its hydrochloride (CHRISTIAENN), i, 23.
β-*N*-Piperidinoethyl phenyl ether, and its hydrobromide and hydrochloride (BRILL), i, 833.
α-Piperidino-β-ethylbutan-γ-one, and its hydrochloride (MANNICH), i, 375.
***N*-Piperidinoethyloleamide** (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
2-Piperidinohydroindene, 1-oximino- (STRAUS and EKHARD), i, 1139.
Piperidino-1-ketotetrahydronaphthalene (STRAUS, BERNOULLY, and (MAUTNER), i, 1155.
Piperidinomethylallylmalonic acid (MANNICH and SUTTER), i, 1037.
α-Piperidinomethyl-γ-valerolactone, and δ-bromo-, and their derivatives (MANNICH and SUTTER), i, 1038.
Piperidinophenylbenzylmethane, and its hydrochloride (CHRISTIAENN), i, 23.
α-Piperidino-α-phenyl-*n*-propane, and its hydrochloride (CHRISTIAENN), 23.
γ-*N*-Piperidinopropyl benzoate, and phenyl ether and their salts (BRILL), i, 833.
2-Piperidinotetrahydronaphthalene, 1-oximino- (STRAUS and EKHARD), i, 1139.
***d*-Piperitol** (SIMONSEN), i, 1165.
Piperonal, preparation of (BRINER, v. TSCHARNER, and PAILLARD), i, 1069.
determination of (RADCLIFFE and SHARPLES), ii, 1210.
Piperonaldoxime *N*-phenyl ether (BAMBERGER), i, 142.
Piperonyl bromide, preparation of (CHEMISCHE FABRIK FLORA), i, 1413.
Piperonyl compounds, carbon-like residue from heating (PASCAL), i, 1278.
α-Piperonylideneacetohexoic acid (RYAN and SHANNON), i, 558.
Piperonylidenemethyl amyl ketone, and its derivatives (RYAN and SHANNON), i, 558.
Piperonylidenemethyl ethyl ketone (RYAN and CAHILL), i, 558.
Piperonylideneoxindole, 6′-amino-, and its methosulphate (ARMIT and ROBINSON), i, 1172.
2-Piperonylidene-4-phenyl-3-anisyl-5-methyl-Δ^3-*cyclo*penten-1-one (RYAN and LENNON), i, 1282.
Piperonylidene-γ-piperonylpropylamine (BAKER and ROBINSON), i, 925.
3 Piperonyl-4-phenyl-5-methyl-Δ^2-*cyclo*penten-1-one (RYAN and LENNON), i, 1282.
β-Piperonylpropionic acid, 6-nitro- (BAKER and ROBINSON), i, 925.
β-Piperonylpropionitrile, and 6-nitro- (BAKER and ROBINSON), i, 925.
γ-Piperonylpropylamine, and its derivatives (BAKER and ROBINSON), i, 925.
γ-Piperonylpropyltrimethylammonium iodide (BAKER and ROBINSON), i, 925.
Piperonylsuccinic anhydride (BAKER and LAPWORTH), i, 671.
Pipette, Cornec–Cottet, for measurement of small volumes (NICLOUX), ii, 898.
Pistacia terebintus, oil from (TIMOSUFF), i, 1124.
Pituitary extracts, dialysis of, and their quantitative effect on secretion of urine (SMITH and MCCLOSKY), i, 207.
Placenta, transmission of blood constituents through the (PLASS and MATTHEW), i, 1489.
Planck's law, deduction of (EDDINGTON), ii, 1022.

Plants, photosynthesis by (MAZÉ), i, 485.
absorption of ultra-violet light by (PALLADIN and HÜBBENET), i, 1223.
absorption of salts by (LUNDEGÅRDH and MORÁVEK), i, 214.
absorption of mineral salts by (DUSTMAN), i, 1123.
absorption of potassium by (ANDRÉ and DEMOUSSY), i, 758.
anaërobic respiration in (NEUBERG and GOTTSCHALK), i, 213.
effect of wounding on respiration of (PALLADIN), i, 1221.
apparatus for study of the respiration of (GINSBURG), i, 1120.
influence of end-products of metabolism on (SIGMUND), i, 344.
occurrence of aromatic compounds in (RETI), i, 418.
influence of external factors on the ash-content of (SEIDEN), i, 1518.
relation between yield of, and the intensity of external factors (BRIGGS), i, 1222.
suitable depth in soil for (LEMMERMANN, WIESSMANN, and ECKL), i, 1029.
equilibria of nutrition in (RIPPEL and LUDWIG), i, 485.
effect of bases on growth of seedling (BOKORNY), i, 489.
effect of, on reaction of culture solutions (HOAGLAND), i, 1368.
acidity of the sap of (ARLAND), i, 213.
cuticle of (LEGG and WHEELER), i, 1025.
formation of asparagine in (PRIANISCHNIKOV), i, 213.
formation of carbohydrates in, from proteins and fats (TERROINE, TRAUTMANN, and BONNET), i, 755.
carbon dioxide as a climatic factor in growth of (REINAU), i, 213.
effect of carbon dioxide in soil air on growth of (PARKER), i, 1223.
effect of dicyanodiamide on (ALLISON, SKINNER, and REID), i, 1030.
oxidation by enzymes of (ONSLOW and ROBINSON), i, 1010.
specificity of enzymes of (BLAGOVESCHENSKI and SOSSIEDOV), i, 1007; (BLAGOVESCHENSKI and BIELOZERSKI), i, 1009.
glycuronic acid in (PALLADIN and LEVTSCHENKO), i, 1369.
stimulation of, by hydrogen cyanide (GASSNER), i, 1029.
incrustive substances of (SCHMIDT and MAHLER), i, 213; (SCHMIDT, HAAG, and SPERLING), i, 1370.
Plants, lævulosans in (COLIN), i, 618.
occurrence of metals in (MCHARGUE), i, 1023.
mineral constituents in (SMIRNOV), i, 486.
nitrates in, in relation to nitrogen nutrition (NIKLAS and VOGEL), i, 213.
utilisation of ammonium nitrate by (PRIANISCHNIKOV), i, 757.
action of nitrites on growth of (FEHÉR and VÁGI), i, 488.
decomposition of oxalic acid by (PALLADIN and LOVTSCHINOVSKAJA), i, 1222.
pectic substances in (NORRIS and SCHRYVER), i, 1226.
pentoses in (ENGLIS and HALE), i, 618.
effect of phosphate manuring on vitamin-*B* in (HORNEMANN), i, 623.
phosphatides of (LEVENE and ROLF), i, 487; (GRAFE; GRAFE and HORVAT), i, 1522.
availability of potassium silicates to (DOBRESCU-CLUY), i, 1223.
silica in growth of, and its relation to phosphoric acid (NANJI and SHAW), i, 214.
influence of silica and silicates on growth of (LEMMERMANN, WIESSMANN, and SAMMET), i, 766; (DUCHON; LEMMERMANN; DENSCH), i, 767.
action of sodium carbonate on germination and growth of (FEHÉR and VÁGI), i, 1023.
action of soil solutions on development of roots of (TERLIKOWSKI), i, 1029.
formation of starch from arabinose by (POLONOVSKI and MORVILLEZ), i, 1222.
effect of desiccation on sugar content of (LINK), i, 618.
tyrosinase in (BOAS and MERKENSCHLAGER), i, 474.
formation of vegetable oils in (FRANCESCONI, MANFREDI, and ASTENGO), i, 759.
zymase in (PALLADIN and ILLJUVIEV), i, 1519.
diseases of (ANDERSON), i, 1522.
green, poisonous action of carbon monoxide on (WEHMER), i, 1029.
higher, sources of available nitrogen for (BIALOSUKNIA), i, 1366.
effect of urea, thiourea, and allylthiourea on (E. and G. NICOLAS), i, 757.
chemistry of (KOMATSU and UEDA), i, 762; (KOMATSU and YAMADA), i, 881; (KOMATSU and NODZU), i, 1025; (KOMATSU and TANAKA), i, 1369.

Plants, lower, effect of oxygen on energy balance of (TERROINE, BONNET, and HEE), i, 1517.
medicinal, constituents of (ZELLNER), i, 763.
South African, active principles of (JURITZ), i, 761.
young, influence of light on absorption of nutrients by (WIESSMANN), i, 757.
detection of phenols in (WARE), i, 1122.
determination of camphor in (GORI), ii, 1009.
determination of chlorides and sulphates in sap of (GORTNER and HOFFMAN), i, 485.
determination of nitrate nitrogen in (BURRELL and PHILLIPS), i, 1367.
Plant ash, physico-chemical analysis of (L. and J. DESHUSSES), ii, 67.
Plant cells, equilibrium and oxidation in (MAYER and PLANTEFOL), i, 1120.
staining of, with colouring matters (SCHWARZ), i, 755.
effect of poisons on (ARZICHOVSKI and SCHELJAKIN), i, 1227.
Plant extracts, blood-sugar depressant action of (GLASER and WITTNER), i, 209.
Plant fibres, Röntgen ray patterns from (SPONSLER), ii, 844.
Plant juices, hydrogen-ion concentration of (GUSTAFSON), i, 1023.
Plant plasma, influence of alkaline earth salts on the heat coagulation of (KAHO), i, 217.
Plant roots, exposed to light, development and distribution of chlorophyll in (POWELL), i, 1221.
Plant tissues, distribution of potassium in (DOWDING), i, 871.
laboratory apparatus for wet grinding of (ROACH), i, 1517.
Plaster, hard, preparation of (CHASSEVENT), ii, 559.
Plasticity (SHEPPARD; BOGUE; SHEPPARD and CARVER; VENABLE), ii, 1058.
Plastids, amylogenic activity of (MAIGE), i, 486.
Platinum, spark spectrum of (L. and E. BLOCH), ii, 829.
photo-electric effect and conductivity of (HERRMANN), ii, 947.
photo-electric sensitivity of (SUHRMANN), ii, 831.
valency of, in respect to mercaptans (P. C. and K. C. B. RÂY), ii, 1121.
melting point of (HOFMANN), ii, 99.
Platinum, adsorption of metals by (MAXTED), ii, 384.
adsorption of water on (MCHAFFIE and LENHER), ii, 854.
effect of Röntgen rays on the catalytic activity of (CLARK, MCGRATH, and JOHNSON), ii, 1176.
physical state and catalytic action of (SMITH; GAUGER), ii, 1072.
catalytic hydrogenation with (BODENSTEIN), ii, 216; (WALDSCHMIDT-LEITZ and SEITZ), ii, 411.
behaviour of, with fused silicates (JANDER), ii, 416.
colloidal, nuclear hydrogenation with (SKITA), i, 140.
oxide-coated, emission of negative ions from (BARTON), ii, 1020.
thermionic work function of (DAVISSON and GERMER), ii, 81.
sols, cataphoresis of, in presence of caoutchouc (EVERS), ii, 668.
Platinum alloys, reaction limits of (TAMMANN), ii, 378.
Platinum salts, trypanocidal action of (LEVADITI, GIRARD, and NICOLAU), i, 1117.
Platinum oxide, catalytic reduction with (KERN, SHRINER, and ADAMS), i, 625; (PIERCE and ADAMS), i, 824; (HECKEL and ADAMS), i, 909; (CAROTHERS and ADAMS), ii, 693.
Platinic chloride, compounds of ethyl sulphide and (P. C. and K. C. B. RÂY), ii, 1121.
selenide (MOSER and ATYNSKI), ii, 584.
telluride (BRUKL), ii, 895.
Chloroplatinic acid, compounds of acid amides with (FRICKE and RUSCHHAUPT), ii, 894.
Platinum organic compounds:—
Platinum, hydrazine carbylamine compounds of (TSCHUGAEV, SKANAVY-GRIGORJEVA and POSNJAK), i, 1395.
dimethylglyoxime (COOPER), ii, 827.
Platinicyanides, optical properties of crystals of (POCHETTINO), ii, 21.
Platinum separation:—
separation of palladium from (KRAUSS and DENEKE), ii, 1005.
separation of ruthenium and (RUFF and VIDIC), ii, 443.
Platinum black, structure of (OSAWA), ii, 747.
preparation and activation of (KÄB), ii, 564.
catalytic hydrogenation with (WASER), i, 584.
effect of chlorine on catalysis by (BOSWELL and BAYLEY), ii, 215.

Platinum electrodes. See Electrodes.
Platinum films, velocity of photo-electrons emitted from (CHA), ii, 476.
electrical resistance of, in presence of hydrogen (GAUGER), ii, 1040.
sputtered, effect of gas on the resistance of (REYNOLDS), ii, 108.
Platinum wedges for spectrophotometry (MERTON), ii, 78.
Platinum wire, effect of absorption of gas on resistance of (KLEINE), ii, 947.
Plum, wild. See *Ximenia americana.*
Pneumococcus, oxidation and reduction by (NEILL and AVERY), i, 340, 867; (NEILL), i, 868.
Pneumonia, excretion of organic acids after (CLAUSEN), i, 1491.
Poison, rattlesnake, fractionation of the proteins of (WELKER), i, 998.
Poisons, adsorption of, by charcoal (DINGEMANSE and LAQUEUR), i, 1500.
adsorption of, by a new plant charcoal (LAQUEUR and SLUYTERS), i, 736.
effect of, on plant cells (ARZICHOVSKI and SCHELJAKIN), i, 1227.
convulsive, influence of acids and alkalis on the action of (FRÖHLICH and SOLÉ), i, 334.
use of hydrogen peroxide in analysis of (MAGNIN), ii, 594.
Poisoning, carbon monoxide, spectrochemistry of (BALTHAZARD), i, 196.
Polar compounds, formation of, in photochemical reactions (NOYER), ii, 1081.
Polarisation (GLASSTONE), ii, 43, 133; (HOLLER), ii, 793.
and electrical double layers (CLARK), ii, 673.
effect of alternating currents on (GLASSTONE; ISGARISCHEV and BERKMANN), ii, 548.
of metallic electrodes (DRESBACH and HOSMER), ii, 1068.
anodic, oxygen evolution theory of (JIRSA and LORIS; JIRSA), ii, 45.
dielectric (EBERT), ii, 14.
rotatory, theory of (DE MALLEMANN), ii, 1029.
Polarity and optical activity of substituent groups (RULE and SMITH), ii, 1120.
induced alternate (LAPWORTH), ii, 636.
Polarograph (HEYROVSKÝ and SHIKATA), ii, 674.
Polonium, α-particles from (CURIE), ii, 343, 834.
ionisation due to α-particles from (EVANS), ii, 343.
Polonium, distribution of length of α-particles of, in oxygen and nitrogen (CURIE and YAMADA), ii, 175.
long-range particles from (YAMADA), ii, 255; (CURIE and YAMADA), ii, 621.
adsorption of, by various substances (BRENNEN), ii, 770.
growth of, in radium preparations (CURIE and YOVANOVITCH), ii, 464.
Polydihydrodi*cyclo*pentadiene ozonide (STAUDINGER), i, 898.
Polydi*cyclo*pentadiene diozonide (STAUDINGER), i, 898.
Polymerides, magnetochemistry of (PASCAL), ii, 371.
Polymerisation (LEBEDEV and FILONENKO), i, 225; (STAUDINGER and LÜTHY), i, 360, 361; (STAUDINGER), i, 362.
by means of aluminium oxide and iron (IPATIEV and KIJUKVIN), i, 226.
Polymethine colouring matters, preparation of (FARBENFABRIKEN VORM F. BAYER & Co.), i, 839.
Polymorphism, aggregation and (SCHAUM, NAUMANN, UNGER, and HOFFARTH), ii, 1132.
and isomerism (PFEIFFER, KALCKBRENNER, and BEHR), i, 547.
Polyoxymethylenes, constitution of (STAUDINGER and LÜTHY), i, 360; (STAUDINGER), i, 362.
Polypeptides, oxidation of (ABDERHALDEN and KOMM), i, 848.
cleavage of, by yeast enzymes (FODOR and EPSTEIN), i, 1214; (FODOR, BERNFELD, and SCHÖNFELD), i, 1215.
Polysaccharides (KARRER, SCHNIDER, and SMIRNOV), i, 418; (KARRER and ILLING), i, 741, 1029; (KOMATSU and UEDA), i, 762; (KARRER and LIER), i, 793; (KARRER and JOOS), i, 1028.
synthesis of (SCHLUBACH and MAURER; SCHLUBACH and RAUCHENBERGER), i, 888.
methylation of (SCHMID), i, 1386.
ethers of (WELTZIEN), i, 12; (HERZOG), i, 371.
Polystictus versicolor, attack of apples by (SMITH), i, 1226.
Polysulphides. See under Sulphur.
Polythionates. See under Sulphur.
Porcelain, action of metals and gases on vessels of (v. WARTENBERG), ii, 699.
Porphyrin, formation of, from hæmoglobin (SCHUMM), i, 88.
of fæces (PAPENDIECK), i, 98; (KÉMERI), i, 188.

Porphyrins, natural (FISCHER and HILGER), i, 307; (KÜSTER and HUTTENLOCHER), i, 845; (FISCHER and MÜLLER), i, 845, 846; (SCHUMM), i, 846; (FISCHER and LINDNER), i, 992, 997.
in blood serum (PAPENDIECK), i, 96.
in yeast (FISCHER and FINK), i, 866.
Potamogeton, leaf pigments of (PRÁT), i, 487.
Potash-oligoclase from Mt. Erebus (MOUNTAIN), ii, 819.
Potassamide, reactions of, with cobalt and iron salts in liquid ammonia (BERGSTROM), ii, 231.
Potassium, molecular weight of (JOUNIAUX), ii, 187.
Potassium, spectrum of, at low voltage (NEWMAN), ii, 1014.
spectrum of, burning in chlorine (RAMDAS), ii, 334.
absorption spectrum of (SUR and GHOSH), ii, 453.
absorption and emission spectra of (NARAYAN and GUNNAIYA; NARAYAN and SUBRAHMANYAM), ii, 737.
band spectrum of, and of mixtures of the vapours with sodium vapour (SMITH), ii, 86.
Röntgen ray spectrum of (LUNDQUIST), ii, 1014.
spark spectrum of (DAHMEN; DE BRUIN and ZEEMAN), ii, 167.
photo-electric effect of (HORNBECK), ii, 81; (LAWRENCE), ii, 831.
ionisation of the vapour of, by light (SAMUEL), ii, 459; (ARNULF), ii, 460.
vapour, low voltage arcs in (NEWMAN), ii, 450.
radioactivity of (HARKINS and GUY), ii, 1109.
as a trap for mercury vapour (HUGHES and POINDEXTER), ii, 895.
Potassium alloys with mercury, electrolysis of (KREMANN, MÜLLER, and ORTNER), ii, 132.
effect of light on the action of water with (BHATNAGAR, PRASAD, and MUKERJI), ii, 811.
interfacial tension between benzene and (BHATNAGAR, PRASAD, and MUKERJI), ii, 194.
with sodium, electrolysis of (KREMANN and v. REHENBURG), ii, 132.
Potassium salts, distribution of, in plant tissues (DOWDING), i, 871.
adsorption of, by plants (ANDRÉ and DEMOUSSY), i, 758.
in soils, effect of fertilisers and cropping on (AMES and SIMON; FRAPS), i, 1523.
Potassium bromate, electrolytic preparation of (EWING and SCHMIDT), ii, 551.
bromide, reflection of Röntgen rays by crystals of (KULENKAMPFF), ii, 1033.
bromide and chloride, mixed crystals of (BROOMÉ), ii, 366.
Röntgen ray analysis of solid solutions of (SASAHARA), ii, 745.
bromide or iodide, action of chlorine on, in presence of water (PARSONS), ii, 880.
sodium carbonates (BAIN), ii, 577.
chlorate, effect of, on blood, and its excretion (ROSS), i, 732.
chloride, dispersion of (HERZFELD and WOLF), ii, 1119.
electrical conductivity of solutions of (LORENZ and VOIGT), ii, 871.
activity coefficient of (SCATCHARD), ii, 397.
liquid junction potential between hydrochloric acid and (SCATCHARD), ii, 398.
transference numbers of, and its mixtures with sodium chloride (MACINNES), ii, 872; (DEWEY), ii, 873.
density of aqueous solutions of (H. C. and E. W. PARKER), ii, 288.
equilibrium of ammonium and mercuric chlorides, water, and (OSAKA and ANDO), ii, 123.
reaction between sodium dichromate and (ROBERTSON), ii, 121.
chromate, equilibrium of ammonium chromate, water, and (ARAKI), ii, 786.
*di*chromate, melting and transition points of (ROBINSON, STEPHENSON, and BRISCOE), ii, 374.
depolarising action of (VINCENT), ii, 882.
lanthanum chromates (CAROBBI), ii, 315.
hydroxide, activity coefficient of (SCATCHARD), ii, 397; (HARNED), ii, 398.
iodide, action of light on, in presence of potassium dichromate and eosin (REYCHLER), ii, 1180.
electrical conductivity of bromine–iodine solutions of (PLOTNIKOV), ii, 791.
absorption of, by the skin (CANALS and GIDON), i, 1116.
iodide and *per*sulphate, reaction between, in gelatin sols (RAWLING and GLASSETT), ii, 561.
*per*manganate, ultra-violet absorption spectrum of (VITERBI), ii, 352.

Potassium *per*manganate, oxidation of hydrogen by (WILKE and KUHN), ii, 51.
decomposition of solutions of (HOLLUTA), ii, 422.
titration of, with hydrogen peroxide in presence of ammonium sulphate (TANANAEV), ii, 430.
standardisation of, with sodium oxalate (DEL FRESNO), ii, 602, 904.
ammonomolybdite and ammonotungstite (BERGSTROM), ii, 1084.
dihydrogen phosphate, crystal structure of (HASSEL), ii, 1130.
chlororuthenates (BRIGGS), ii, 703.
chlororuthenites (CHARONNAT), ii, 586.
pentachlororuthenite and hexachlororuthenate (AOYAMA), ii, 816.
pentachlororuthenites (GUTBIER and NIEMANN), ii, 231.
silicates, assimilation of, by plants (DOBRESCU-CLUY), i, 1223.
chromosilicate, synthesis of (KARFIOL), ii, 1087.
lanthanum sulphates (ZAMBONINI and CAROBBI), ii, 222.
lithium sulphate, crystal structure of (BRADLEY), ii, 638.
neodymium sulphates (ZAMBONINI and CAGLIOTI), ii, 222, 315.
*penta*sulphide, action of allyl iodide on (THOMAS and RIDING), i, 4.
sulphite (FOERSTER, BROSCHE, and NORBERG-SCHULZ), ii, 120.
pyrosulphite, absorption spectrum of (DIETZEL and GALANOS), ii, 1115.
dinitrososulphonate (*nitrososulphite*) (RASCHIG), ii, 226.
chloroiminodisulphonate (RASCHIG), ii, 986.
tantalate, diffusion and molecular weight of (JANDER and SCHULZ), ii, 528.
tungstate, equilibria of, with lithium tungstate and tungsten trioxide (VAN LIEMPT), ii, 421.

Potassium organic compounds:—
Potassium ferritripyrocatecholoxide, use of, as an indicator (BINDER), ii, 596.

Potassium detection, determination, and separation:—
substitute for blue glass in detection of (MEYER), ii, 601.
distinction between sodium and, by means of ammonium oxalate (MEYER-WELO), ii, 1202.
determination of (VÜRTHEIM), ii, 487; (MENDRICK), ii, 825; (YOE), ii, 902.

Potassium detection, determination, and separation:—
determination of, polarimetrically (WRÓBEL), ii, 240.
determination of, in blood serum (LEBERMANN), i, 96, 714.
determination of, in urine (v. DEHN), i, 855.
determination and separation of (SMITH and ROSS), ii, 601.

Potatoes, composition of (WILLAMAN and WEST), i, 1522.
respiration and carbohydrate changes in, at low temperatures (HOPKINS), i, 344.
cork layer of the skin of (RHODES), i, 1026.

Potato plants, growth of, in nutrient solutions (JOHNSON), i, 1367.

Potential, effect of presence of porous materials on measurements of (FRICKE), ii, 544.
relation between energy of escape of electrons and (GÜNTHER-SCHULZE), ii, 477.
effect of filtration on (RIETY), ii, 796.
at surfaces of inorganic liquids (WESSEL), ii, 795.
fall of, in liquids, produced by air bubbles (KLEEMAN and PITTS), ii, 659.
differences of, between liquids and air (FRUMKIN), ii, 544.
differences of, at the junction of two liquids (VOSNESSENSKI), ii, 673.
differences of, at the boundary of two phases (REICHINSTEIN), ii, 545.
electronegative series of, in liquid ammonia (BERGSTROM), ii, 794.
contact, of metals (DOWLING), ii, 796.
decomposition, of non-aqueous solutions (FINKELSTEIN), ii, 546.
of electrodes (HOLLER), ii, 793.
of metals against pure water (SMITS, GERDING, and KROON), ii, 795.
single-phase boundary, measurement of (BAUR), ii, 1164.
spark, Townsend theory of (DÄLLENBACH), ii, 740.

Potential scales, comparison of electrode potentials and (BIRCHER), ii, 711.

Potentiometer, new (MISLOWITZER), i, 1485.

Praseodymium, preparation and properties of (WIERDA and KREMERS), ii, 993.
Röntgen ray spectrum of (GLEDITSCH and BOTOLFSEN), ii, 612.

Praseodymium chlorovanadinite (CAROBBI), ii, 582.

Precipitates, stratified structure of (v. WEIMARN), ii, 959.

Precipitates, adsorption by (WEISER), ii, 108.
emanating capacity of, and surface variation (HAHN), ii, 177.
ignition of (BRINTON and STOPPEL), ii, 72.
Precipitation, laws of (v. WEIMARN), ii, 1064.
of coloured salts in gels (RIEGEL and WIDGOFF), ii, 863.
fractional (RUFF and HIRSCH), ii, 992.
rhythmic, in gels (FISCHER), ii, 853.
in gelatin gels (SCOTT-BLAIR), ii, 519.
Precipitin, behaviour of, when adsorbed, to its antigen (EISLER), i, 96.
Pregnancy, toxæmia of (STANDER, DUNCAN, and SISSON), i, 1492.
storage of vitamin-*A* in white rats during (SCHEUNERT and CANDELIN), i, 1515.
Pressure, internal, in terms of critical pressure and temperature (SCHUSTER), ii, 951.
and molecular volume (SCHUSTER), ii, 1142.
Pressure equaliser (PATTERSON), ii, 151.
Primeverase, from almond emulsin (BRIDEL), i, 1438.
Primeverose (BRIDEL), i, 336, 615, 760.
Primeverosidase (BRIDEL), i, 760, 1438.
Primula, unpleasant taste of roots of (KOFLER and BRAUNER), i, 1224.
Privet berries, colouring matter of (PFAU), i, 572.
Proflavine, effect of, on infusoria (ROBERTSON), i, 1012.
Prolamines (HOFFMAN and GORTNER), i, 1479.
Propane, *αβγ-tri*amino-, and its derivatives and complex metallic compounds (MANN and POPE), i, 373.
l-**Propane**, *α*-amino-*β*-hydroxy-, and its salts (KARRER and KLARER), i, 1036.
*αβ-di*hydroxy-, preparation of (LEVENE and HALLER), i, 1375.
*cyclo***Propane compounds**, influence of phenyl groups on the formation of (HAERDI and THORPE), i, 923.
*cyclo***Propane series**, three-carbon tautomerism in (GOSS, INGOLD, and THORPE), i, 549.
*cyclo***Propanebis-2:6-diketophenyl*cyclo*hexanedispiran** (RADULESCU and GEORGESCU), i, 820.
*cyclo***Propanedicarboxylic acid**, derivatives of (KÜSTER and GRÄSSNER), i, 922.
2-Propenyl-3-*o*-anisolesulphonyl-2-methylquinoline (TRÖGER and BROHM), i, 1453.
Propepsin in blood and urine (GOTTLIEB), i, 742.
Propinene, synthesis from (YVON), i, 514.
Propiolic acid, methyl ester (INGOLD), i, 779.
l-**Propionamide**, *α*-amino-, *p*-toluenesulphonate (FREUDENBERG and HUBER), i, 229.
Propionic acid, partition of, between water and ethyl ether (DE KOLOSOVSKI), ii, 506.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
alkoxymethyl esters (FARREN, FIFE, CLARK, and GARLAND), i, 1230.
furfuryl ester (ZANETTI), i, 567.
Propionic acid, *α*-bromonitro-, *α*-chloronitro-, and *α*-nitro-, ethyl esters, and hydrazine derivative of the latter (MACBETH and TRAILL), i, 629.
β-chloro-, preparation of (POWELL), i, 228.
d-**Prepionic acid**, *α*-thiol-, sodium salts (LEVENE and MIKESKA), i, 512.
Propionitrile, *β*-chloro-, reaction of resorcinol with (CHAPMAN and STEPHEN), i, 669.
β-nitro-*α*-oximino-, and its derivatives (WIELAND), i, 1049.
3-Propionylbornylene. See *α*-Bornylene ethyl ketone.
3-Propionylcamphane. See *α*-Camphanyl ethyl ketone.
Propionylcarbazole, and its picrate, and nitro- (ODDO), i, 296.
5-Propionyl-5:10-dihydrophenarsazine, 10-chloro- (BURTON and GIBSON), i, 85.
3-Propionylphenylarsinic acid, 4-hydroxy-, *p*-nitrophenylhydrazone (MARGULIES), i, 447.
2-Propionylpyrrole, 3:4-*di*- and 3:4:5-*tri*-iodo- (TERENTIEV and TSCHELINCEV), i, 295.
Propionylveratrole, *β*-chloro- (FREUDENBERG and FIKENTSCHER), i, 69.
***β*-Propoxybenzoic acids**, *p*-bromo-, *p*-chloro-, *p*-iodo-, and *p*-hydroxy-, and their derivatives (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 1424.
2-Propoxy-Δ^1-*cyclo*hexene, 1-cyano- (v. AUWERS, BAHR, and FRESE), i, 312.
*iso***Propoxy-5-methylacetophenone**, and its derivatives (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.

Propyl alcohol, β-chloro-, conversion of, into β-hydroxybutyronitrile (DEWAEL), i, 14.

*iso***Propyl alcohol**, latent and specific heats of (PARKS and KELLEY), ii, 949.

properties of mixtures of ethyl alcohol and (PARKS and KELLEY), ii, 764.

*l-iso***Propyl alcohol**, αα-*di*chloro-, urethane of (SEN), i, 337.

n- and *iso*-**Propyl alcohols**, refractive indices of (BENNETT and GARRATT), i, 498.

l-**Propylallylbarbituric acid** (VOLWILER), i, 1174.

l-**Propylamine**, β-hydroxy-, hydrochloride (LEVENE and HALLER), i, 1375.

Propylammonium chloroferrates (REMY and ROTHE), ii, 1089.

n-**Propylaniline** *m*-nitrobenzenesulphonamide (MARVEL, KINGSBURY, and SMITH), i, 245.

n-**Propylbenzene**, 3:5-*di*hydroxy- (MAUTHNER), i, 25.

γ-**Propylbenzoic acid**, *o*-amino-, and the corresponding lactam (v. BRAUN and REICH), i, 1407.

n-**Propylbenzoyloximidocarbonic acid**, ethyl ester (OESPER and COOK), i, 523.

γ-**Propylbenzyl bromide**, *o*-bromo- (v. BRAUN and KAISER), i, 1414.

*iso***Propyl-β-bromoallylbarbituric acid** (RIEDEL), i, 1453.

Propylbutylals (ADAMS and ADKINS), i, 785.

s-**Propylcarbamide**, *di*-β-hydroxy- (LEVENE and HALLER), i, 1375.

*p-iso***Propyl-γ-chloroallylbenzene**, and its dibromide (BERT), i, 804.

*p-iso***Propyl-ω-chlorobutenylbenzene** (BERT), i, 804.

Propylene, equilibrium of hydrogen bromide with (MAASS and WRIGHT), ii, 214.

catalytic addition of halogen acids to (WIBAUT, DIEKMANN, and RUTGERS), i, 494.

inhalation of (DAVIDSON), i, 1503.

Propylene, αβγ-*tri*bromo-αγ-*di*nitro- (WIELAND and JUNG), i, 1374.

α-**Propylene oxide**, heat of combustion of (ZUBOV and SWIENTOSLAWSKI), ii, 364.

*iso***Propylfurfurylal** (ADAMS and ADKINS), i, 785.

*iso***Propylheptylal** (ADAMS and ADKINS), i, 785.

1-*iso*Propylcyclohexan-3-one, and its semicarbazone (SEIFERT), i, 407.

2-Propylcyclohexanone, 2-cyano-, and its semicarbazone (v. AUWERS, BAHR, and FRESE), i, 312.

o-**Propylcyclohexylamines**, and their salts (v. BRAUN and BAYER), i, 428.

*iso***Propylidene compounds** of sugars (FREUDENBERG and DOSER), i, 366; (FREUDENBERG and WOLFF), i, 367.

Propylidenedi-indone (RADULESCU and GEORGESCU), i, 1287.

*iso***Propylidenequinamide** (KARRER, WIDMER, and RISO), i, 673.

α-**Propylindole** (VERLEY and BEDUWÉ), i, 578.

3-**Propylindole**, 3-γ-amino-, and its salts (MAJIMA and HOSHINO), i, 1451.

*cyclo***Propylmethylthiocyanate** (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.

*cyclo***Propylmethylamine**, and its benzoyl derivative (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.

*cyclo***Propylmethylbenzylmethylamine**, and its hydrochloride (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.

*cyclo***Propylmethylmethylaniline**, and its salts (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.

*cyclo***Propylmethylmethylcyanamide** (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1402.

2-**Propyl-3-phenyl*iso*indolinone**, 3-hydroxy-2-γ-bromo-, and its derivatives (KOHN and LAKNER), i, 1276.

γ-4-*iso***Propylphenylpropinene** (BERT, DORIER, and LAMY), i, 1373.

Propylphthalimide, γ-bromo-, action of magnesium phenyl bromide on (KOHN and LAKNER), i, 1276.

n-**Propyl-*m*-toluidine**, 2:4- and 4:6-*di*nitro- (GIUA and PETRONIO), i, 1397.

1-*iso***Propylurazole** (GOODWIN and BAILEY), i, 843.

*iso***Propylurethane**, αα-*di*chloro-, and αα'-*di*iodo- (CHINOIN FABRIK CHEMISCH-PHARMAZEUTISCHER PRODUKTE), 1, 13.

n-**Propylvinylcarbinol**, resolution and rotation of, and its salts and esters (KENYON and SNELLGROVE), i, 771.

4-*iso***Propyl-*o*-xylene**, *tri*nitro- (KRUBER), i, 1138.

4-*iso***Propyl-*o*-xylenesulphonic acid**, and its sodium salt and amide (KRUBER), i, 1138.

Prosopanche Burmeisteri, constituents of (ZELLNER), i, 1025.

Prostate, tuberculosis and calcification of (MCKENZIE, SENG, and MACALLUM), i, 330.

effect of injections of emulsions of, on metabolism (KORENCHEVSKY and CARR), i, 1513.

Prostate, nitrogen excretion in hypertrophy of (NICOLAYSEN), i, 857.
Proteases, animal, specificity of (WALDSCHMIDT-LEITZ and SCHÄFFNER), i, 1110.
α-Proteases, effect of quinine compounds and urea on (SMORODINCEV and ADOVA), i, 335.
Proteic acid, hydroxy-, in urine (FREUND and SITTENBERGER-KRAFT), i, 723.
Proteins (JOHNSON and DASCHAVSKY), i, 176; (LÜDTKE), i, 450; (SHELTON and JOHNSON), i, 602; (SÖRENSEN), i, 1110; (HOFFMAN and GORTNER), i, 1479.
structure of (ABDERHALDEN, KLARMANN, and KOMM), i, 174; (ABDERHALDEN and KOMM), i, 175, 320, 848, 1475; (HERZOG), i, 450; (BLANCHETIÈRE), i, 602; (TROENSEGAARD and FISCHER; BERGMANN), i, 848; (ABDERHALDEN), i, 848, 1341; (ABDERHALDEN and SCHWAB), i, 991.
structure and synthesis of (WALDSCHMIDT-LEITZ and SCHÄFFNER), i, 1110.
synthesis of, by enzymes (WASTENEYS and BORSOOK), i, 102; (BORSOOK and WASTENEYS), i, 472, 864, 865; (RONA and KLEINMANN), i, 473.
molecular weights of (COHN, HENDRY, and PRENTISS), ii, 641.
ionisation of (LINDERSTRØM-LANG), ii, 203.
heat denaturation of (H. and D. Y. WU), i, 1110.
adsorption of, by collodion membranes (HITCHCOCK), ii, 1054.
adsorption of phenolsulphonephthalein by (GROLLMAN), i, 1000.
liberation of adsorbed substances from (ROSENTHAL), i, 1203.
solubility of (SÖRENSEN), i, 602.
solubility of, in organic solvents (COOPER and NICHOLAS), i, 955.
depolymerisation of (SHIBATA), i, 1109.
coagulation of, in drops (MORAŠKO), i, 1487.
by heat (M. and P. L. SÖRENSEN), ii, 518.
hydrolysis of (SCHRYVER, BUSTON, and MUKHERJEE), i, 794.
by enzymes (RONA and KLEINMANN), i, 103.
with hydrochloric acid (YAITSCHNIKOV), i, 320.
decomposition of, by microbes (WAKSMAN and LOMANITZ), i, 867.
Proteins, decomposition of, by pepsin (UHLENBRUCK), i, 742.
effect of amino-acids on (SEUFFERT and MARKS), i, 730.
decomposition products of (IVANOV), i, 1480.
influence of glutathione on oxidation of (HOPKINS), i, 1499.
compounds of acids with (MODERN and PAULI), ii, 518.
combination of, with acids and alkalis (HARRIS), i, 450.
cystine and tryptophan in (JONES, GERSDORFF, and MOELLER), i, 98.
action of, on gold sols (ZSIGMONDY and JOËL), ii, 35; (REINDERS), ii, 1059; (KREBS), ii, 1155.
action of hypobromites on (GOLDSCHMIDT and STEIGERWALD), i, 1109; (ABDERHALDEN), i, 1475.
action of paraldehyde on (COOPER), i, 91.
action of pepsin and hydrochloric acid on (VAN URK), i, 1507.
sulphur in (HOFFMAN), i, 1480.
compounds of zinc chloride with (PAULI and SCHÖN), ii, 198.
new amino-acid from (GORTNER and HOFFMAN), i, 602.
metabolism of. See Metabolism.
action of bile on pancreatic digestion of (ROSENOV), i, 1507.
precipitation of, from body fluids (WUNSCHENDORFF), i, 1346.
substitutes for, in diet of goats (PAASCH), i, 1498.
replacement of, by urea in diet of milch animals (MORGAN, WINDHEUSER, and OHLMER), i, 217.
Bence-Jones, precipitin reaction of (HEKTOEN and WELKER), i, 328.
in blood, and their determination (HUECK), i, 1484; (HOLM and TÓMASSON), i, 1485.
gluten, from wheat flour (BLISH and PINCKNEY), i, 176.
halogenated (VANDEVELDE), i, 91, 707, 1477.
hydrolysed, dynamic action of, as foodstuffs (MELLY and v. RÖTTH), i, 193.
of muscle, isoelectric points of (WÖHLISCH and SCHRIEVER), i, 1488.
colloid characteristics of (WEBER), i, 995.
in germinating seeds (FODOR and REIFENBERG), i, 756.
of serum (LEENDERTZ), i, 96.
calcium content of (CSAPÓ and FAUBL), i, 96.
precipitation of (RUSZCZYNSKI), i, 322.

Proteins, of serum, precipitation of, by salts (CSAPÓ and v. KLOBUSITZKY), i, 178.
precipitin reactions of (HEKTOEN and WELKER), i, 823.
of skin, extraction of (PINESS, MILLER, and ALLES), i, 331.
water-soluble, electrolyte-free (ADOLF and PAULI), ii, 289; (PAULI), ii, 319.
effect of glycerol on the biuret reaction for (SEIBERT and LONG), i, 1110.
reaction of, with phosphoric acid (ROMIEU), i, 607.
analysis of the hydrolysis products of (WASTENEYS and BORSOOK), i, 97.
detection of (NOUY), ii, 1212.
determination of, electrometrically, with alkalis (HOFFMAN and GORTNER), ii, 1011.
determination of amino acids from hydrolysis of (CHERBULIEZ and WAHL), ii, 1211.
determination of nitrogen in (MAIN and LOCKE), i, 997; (TER MEULEN), ii, 599.
determination of nitrogen distribution in (GORTNER and SANDSTROM), ii, 908.
determination of phosphorus in (SØRENSEN), ii, 900.
determination of tyrosine in (FÜRTH and FISCHER), ii, 448.
Proteoses, solubility of, in organic solvents (COOPER and NICHOLAS), ii, 955.
of egg-albumin (RUDD), i, 320, 321.
Proteus, formation of gelatinase by (CLARK and MERRILL), i, 1511.
Protoparaffin. See Ceresin.
Protoplasm, toxic action of copper and gold salts on (VOEGTLIN, JOHNSON, and DYER), i, 1116.
living, permeability of (OSTERHOUT), i, 1355.
Prowazekia edax, influence of hydrogen-ion concentration on the growth of (RAABE), i, 868.
Prunus pissardi, flavone from the leaves of, and its reactions (JONESCO), i, 824, 825.
Prussian blue, formation of, in cyanide test (SCHÜLEK), ii, 71.
sols, coagulation of (GHOSH and DHAR), ii, 778; (WEIR), ii, 1155.
Prussic acid, labile. See *iso*Hydrocyanic acid.
Pseudo-acids (KARVE), ii, 1188.
Psicaine, synthesis of (WILLSTÄTTER), i, 424.
experiments with (WAGNER), i, 1503.
Ptychotis verticillata, essential oil of (MORANI), i, 146.
Pulmonaria officinalis, constituents of (ZELLNER), i, 763.
Pump for circulation of gases (MENZIES, COLLINS, and TYSON), ii, 818.
automatic mercury (MCLAUGHLIN and BROWN), ii, 428.
laboratory (CAMERON), ii, 707.
circulating, for corrosive gases (KREMERS), ii, 427.
Pungency in relation to chemical constitution (NOMURA and HOTTA), i, 1156.
Purine derivatives, excretion of, in dogs (LANGFELDT and HOLMSEN), i, 1205.
Putrescine, behaviour of, in the liver (FELIX and ROTHLER), i, 859.
Pycnometer, new (H. C. and E. W. PARKER), ii, 288.
Pylorus, dehydration after obstruction of the (GAMBLE and ROSS), i, 1852.
Pyocyanine (WREDE and STRACK), i, 174.
and its derivatives (WREDE and STRACK), i, 844.
Pyramidone, compound of veronal with (PFEIFFER), i, 1318.
Pyranones, 1-thio- (ARNDT, NACHTWEY, and PUSCH), i, 1307.
Pyrazoles, synthesis of (BÜLOW and BAUR), i, 1827.
Pyrazole series, isomerism in (v. AUWERS and NIEMEYER), i, 1176; (v. AUWERS and MAUSS), i, 1178; (v. AUWERS and DANIEL), i, 1180.
Pyrazole-blue, *m*- and *p*-chloro- (CHATTAWAY and STROUTS), i, 71.
Pyrazolecarboxylamides, formation and transformation of (v. AUWERS and OTTENS), i, 1459.
Pyrazolecarboxylic acids, synthesis of (MINUNNI), i, 1175.
Pyrazolines, influence of constitution on formation of, from phenylhydrazones (v. AUWERS and KREUDER), i, 1454.
spontaneous oxidation of (LOCQUIN and HEILMANN), i, 1185.
substituted isomeric (FREUDENBERG and STOLL), i, 70.
Pyrazolone derivatives, preparation of (FARBENFABRIKEN VORM. F. BAYER & Co.), i, 301.
Pyrid-2-imine, 1-chloroacetyl derivative, and its salts (FINGER and KRAFT), i, 73.
Pyridine, electrolytic reduction of (MARIE and LEJEUNE), i, 577.
nucleus, fission of, during reduction (SHAW), i, 299.

Pyridine, equilibria of, with cadmium chloride and with zinc chloride (MASON and MATHEWS), ii, 1063.
arsenyl tartrate (DEBUCQUET), i, 973.
compounds formed by action of, on βγ-dibromoallyl bromide (v. BRAUN and KÜHN), i, 1375.
compound of hexanitrodiphenylamine and (DESVERGNES), i, 1056.
hydroferricyanide (CUMMING), i, 122.
compounds of silver perchlorate, water, and (MACY), ii, 536.
derivatives, formation of, from acyclic δ-diketones (BLAISE and MONTAGNE), i, 835.
preparation of alkyl derivatives of (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 431.
Pyridine, 2-amino-, tautomerism of, and its derivatives (TSCHITSCHIBABIN), i, 158.
condensation of, with fatty-aromatic ketones (SCHMID and BANGLER), i, 1459.
2:6-*di*amino-, preparation of (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 589.
2:3-*di*amino-, and 3-nitro-2-amino-, acetyl derivatives, and 2-chloro-, 2-chloro-5-bromo-3-nitro-, 2-chloro-5-iodoxy-, and their derivatives (PIERONI and HAUPT), i, 1316.
3-bromo-, and 3-iodo-, and their salts (BAUMGARTEN), i, 1381.
2-chloro-5-iodo-, 5-iodo-2-amino-, and 5-iodo-2-nitroamino-, and their derivatives (MAGIDSON and MENSCHIKOFF), i, 301.
hydroxy-derivatives (TSCHITSCHIBABIN), i, 299.
3-nitro-, and 3-nitroso- (KIRPAL and REITER), i, 697.
*di*nitro-2-amino- (TSCHITSCHIBABIN), i, 1328.
3-nitro-2-nitroamino- (TSCHITSCHIBABIN and KONOVALOVA), i, 1329.
5-nitro-2-nitroamino-, reactions of, and 5-nitro-2-nitroso- (RÄTH and PRANGE), i, 978.
Pyridines, arylated (DILTHEY and SCHAEFER), i, 153; (DILTHEY and RADMACHER), i, 1441.
Pyridines, amino-, tautomerism of (TSCHITSCHIBABIN and OSSETROVA; TSCHITSCHIBABIN), i, 1328.
Pyridine-1-acetic acid, 1-chloro-2-hydroxy- (KIRPAL), i, 66.
Pyridine-2-carboxylic acid, 4:6-*di*chloro-5-cyano- (SPÄTH and KOLLER), i, 1446.
2-Pyridine-3-carboxylic acid, 2-amino-, anhydride and acetyl derivative, methyl ester (SEIDE), i, 72.
Pyridine-3-sulphonic acid, 4-amino-, and 4-hydroxy-, and their barium salts (KOENIGS and JUNGFER), i, 154.
Pyridinium methiodide, compound of benzidine with (EMMERT, ROH, and KOBERNE), i, 588.
Pyridofluorene, and its derivatives (MILLS, PALMER, and TOMKINSON), i, 69.
Pyridofluorenone-1:3:4-tricarboxylic acid (MILLS, PALMER, and TOMKINSON), i, 69.
2-Pyridone, 5-iodo- (MAGIDSON and MENSCHIKOFF), i, 302.
4-Pyridone, 3-amino-, and 3-nitro-5-amino-, salts of (CROWE), i, 1319.
2-Pyridone-1-acetic acid, and its silver salt and derivatives (KIRPAL), i, 66.
2-Pyridoneimine-1-acetic acid, and its chloroplatinate (TSCHITSCHIBABIN), i, 158.
Pyridonemethides. See Methylenedihydropyridines.
4:5-Pyridothiophen, 3-hydroxy- (KOENIGS and GEISSLER), i, 166.
Pyridotripyrocatechylantimonic acid, potassium and sodium salts (REIHLEN, SAPPER, and KALL), i, 912.
Pyridotripyrocatechylarsenic acid, sodium salt (REIHLEN, SAPPER, and KALL), i, 912.
α-Pyridylanthranilic acid, sodium salt (SEIDE), i, 160.
5-Pyridylazo-β-naphthol, 2-chloro- (PIERONI and HAUPT), i, 1316.
Pyridylglycine, and its derivatives (REINDEL and RAUCH), i, 438.
monohydrate (FINGER and KRAFT), i, 73.
3-Pyridylglycine-2-carboxylic acid, (SUCHARDA), i, 1331.
5-Pyridylhydrazine, 2-chloro- (PIERONI and HAUPT), i, 1316.
β-3-Pyridylhydroxylamine (KIRPAL and REITER), i, 698.
3-Pyridyl δ-methylaminobutyl ketone, and its salts (RUZICKA, SEIDEL, and LIEBL), i, 290.
3-Pyridyl 3-*N*-methyl-2-piperidonyl ketone, and its picronolate (RUZICKA, SEIDEL, and LIEBL), i, 290.
***C*-(2′-Pyridyl)-1-methylpyrrole**, and its methiodide (WIBAUT and COPPENS), i, 75.
Pyridyl-2-nitroamine, alkylation of (TSCHITSCHIBABIN and MENSCHIKOV), i, 487.
***N*-2-Pyridylpyrrole** (CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING), i, 1329.
2-Pyridylpyrroles, and their picrates (TSCHITSCHIBABIN and BYLINKIN), i, 1174.

Pyrimidines, phenylhydrazine derivatives of (LEVENE), i, 979.
Pyriminazole, and its chloroplatinate (TSCHITSCHIBABIN), i, 1328.
δ-Pyrindigotin, and its derivatives (SUCHARDA), i, 1331.
Pyrindoxyl, constitution of (FINGER and KRAFT), i, 73.
Pyrites from Serbia (BARTHOUX), ii, 429.
Pyrocatechol, antimony, arsenic, and bismuth compounds with (ROSENHEIM and BARUTTSCHISKY), i, 808.
compounds of boric acid and (WEIL and ADLER), i, 136.
compounds of molybdic, tungstic, and uranic acids with, and their salts (FERNANDES), i, 912, 1061.
complex vanadyl salts (ROSENHEIM and MONG), i, 1412.
determination of derivatives of, colorimetrically (GLASSTONE), ii, 331.
Pyrocatechol, 4-amino-, acetyl and benzoyl derivatives (KEHRMANN and HOEHN), i, 560.
4:5-*di*amino-, and its derivatives, and 5-nitroso-4-amino-, 4-acetyl derivative (HOEHN), i, 938.
Pyrocatecholboric acid, 3-nitro-, salts of (BÖESEKEN and MIJS), i, 912.
Pyrocatechol tannins, detection of (VOGEL), ii, 827.
Pyrocholoidanic acid, oxidation of (WIELAND), i, 1066.
Pyrodeoxybilianic acid, derivatives of (WIELAND), i, 1066.
Pyrogallol, compounds of molybdic, tungstic, and uranic acids with, and their salts (FERNANDES), i, 912, 1061.
determination of derivatives of, colorimetrically (GLASSTONE), ii, 331.
Pyrogallolacrolein (SEN and SARKAR), i, 812.
Pyrogallolbenzein, and its hydrochloride (ORNDORFF and WANG), i, 277.
and its *o*-hydroxy derivative (SEN and SARKAR), i, 812.
Pyrogallolcoumarein (SEN and SIRCAR), i, 554.
Pyrogallolglycerein (SEN and SARKAR), i, 812.
Pyrogallol-*omp-trihydroxybenzein* (SEN, SINHA, and SARKAR), i, 916.
Pyrogallolisatein (SEN and SIRCAR), i, 555.
Pyrogallolsalicylein (SEN and SIRCAR), i, 554.
Pyrolithobilianic acid, methyl ester (WINDAUS, BOHNE, and SCHWARZKOPF), i, 406.
Pyromellitic acid, condensation of, with decalin and tetralin (PHILIPPI, SEKA, and FUNKE), i, 556.
derivatives of (DE DIESBACH and ZURBRIGGEN), i, 1427.
Pyromellitic acid, bromo-, and its anhydride (PHILIPPI, SEKA, and BAUER), i, 555.
Pyromelliticdi-imidines. See Bis(aminomethyl)-benzenedicarboxylic acid, dilactams.
Pyromellitide. See Bis(hydroxymethyl)-benzenedicarboxylic acid dilactone.
Pyrometers, black body for calibration of (ROBERTS), ii, 756.
micro- (HENNING and HAUSE), ii, 427.
Pyromucic acid, *iso*amyl ester (NAKAI), i, 360.
furfuryl ester (MEERWEIN and SCHMIDT), i, 1239.
Pyrone, and thio-, halochromism of halogenated derivatives of (ARNDT and PUSCH), i, 1304.
Pyrone, 4-thio- (ARNDT, SCHOLZ, and NACHTWEY), i, 58.
Pyrones, structure of (ARNDT, SCHOLZ, and NACHTWEY), i, 57.
Pyrones, 1-thio- (ARNDT, NACHTWEY, and PUSCH), i, 1307.
Pyrone colouring matters (FARBENFABRIKEN VORM F. BAYER & CO.), i, 955.
γ-Pyronecarboxylic acids, effect of boric acid on the solubility and conductivity of (VERKADE), ii, 128.
Pyroxenes, crystal structure of (WYCKOFF, MERWIN, and WASHINGTON), ii, 1126.
Pyroxonin (MAJIMA and SUGINOME), i, 1448.
Pyroxonitin, and its compound with chloroform (MAJIMA and SUGINOME), i, 1448.
Pyrroflavin (KÖNIG), i, 1184.
Pyrrole, absorption spectrum of (GALLERANI), ii, 266.
action of iodine on (G. E. K. and H. E. H. BRANCH), i, 66.
derivatives, absorption spectra of (KORSCHUN and ROLL), ii, 258.
bromination and iodination of (TERENTIEV and TSCHELINCEV), i, 295.
Pyrrole, iodo-derivatives (PIERONI and NOCENTINI), i, 1096.
4-iodo-3-nitro- (TERENTIEV and TSCHELINCEV), i, 295.
Pyrroles, action of formaldehyde and alcohols on (FISCHER and NENITZESCU), i, 834.
Pyrrole colouring matters (KÖNIG), i, 1184.

Pyrrole series, preparation of aldehydes and ketones of (KALLE & Co.), i, 297.
Pyrrolealdehyde, constitution of (RASTELLI and MINGOZZI), i, 1316.
Pyrrole-2-aldehyde, *tetra*iodo- (TERENTIEV and TSCHELINCEV), i, 295.
Pyrrole-2-carboxylic acid, *n*-propyl ester (ODDO), i, 296.
Pyrrole-2-glyoxylic acid, ethyl ester (ODDO), i, 297.
Pyrrolenephenylcarbinol-*o*-carboxylic acid, ammonium salt (ODDO and MINGOIA), i, 978.
Pyrrolenephthalides (ODDO), i, 978.
Pyrrolephthalides (ODDO and MINGOIA), i, 978.
Pyruvamide, hydrazones of (BÜLOW and SPENGLER), i, 1103.
Pyruvic acid, absorption spectra and tautomerism of (HENRI and FROMAGEOT), ii, 929.
heat of combustion of (BLASCHKO), i, 1011.
catalytic decomposition of (E. and F. MÜLLER), ii, 414.
action of *p*-aminophenylarsinic acid and, on aldehydes (ADAMS and JOHNSON), i, 319.
action of carboxylase of yeast on (NEUBERG), i, 336.
possible rôle of, in growth of bacteria (QUASTEL), i, 1216.
fate of, in the animal body (OTANI), i, 731.
esters, hydrolysis of (SKRABAL, PFAFF, and AIROLDI), ii, 139.
Pyruvic ureide, bromonitro- and nitro-, and its acetyl derivative (DAVIDSON), i, 975.
Pyruvyl bromide and chloride, hydrazones of (BÜLOW and SPENGLER), i, 1103.
Pyruvylalanine (BERGMANN, MIEKELEY, and KANN), i, 1134.
Pyrylium compounds (DILTHEY and FLORET), i, 55; (DILTHEY and RADMACHER), i, 1441.
Pyrylium salts, synthesis of (PRATT and ROBINSON), i, 422, 825, 826; (MALKIN and ROBINSON), i, 827.
Pyvuril (DAVIDSON), i, 583.

Q.

Quantum numbers and series spectra (LINDSAY), ii, 915.
and atomic numbers (HARTREE), ii, 467.
Quantum rule, Epstein–Sommerfeld (KORDYSCH), ii, 886.
Quantum theory in relation to the atomic theory and energetics (BERTHELOT), ii, 1022.
and molecular formation (BORN and FRANCK), ii, 266.
application of, to gases (PLANCK; EINSTEIN), ii, 495.
and Bohr's correspondence principle (TOLMAN), ii, 466.
of radiation (BOTHE and GEIGER; KETCHUM), ii, 1.
and resonance radiation (DARWIN), ii, 169.
Quartz, structure of (BRAGG), ii, 1131.
and its reflexion of X-rays (GIBBS), ii, 867.
spiral springs of (SMITH), ii, 818; (DRANE), ii, 995.
Quartz mercury lamp. See under Lamp.
Quebrachitolpentaphosphoric acid, salts of (CONTARDI), i, 277.
Quercetin, isolation and identification of, in apple peel (SANDS), i, 216.
5-methyl ether, and its potassium salt and tetra-acetyl derivative (KUBOTA and PERKIN), i, 1160.
Quinaketones, monocyclic (RUZICKA, SEIDEL, and LIEBL), i, 289.
Quinaldine. See 2-Methylquinoline.
Quinaldines, condensation of hydroxy and methoxy derivatives of, with aromatic aldehydes (TRÖGER and DUNKER), i, 432.
Quinatoxins, aliphatic (RUZICKA, SEIDEL, and LIEBL), i, 289.
Quinazoline, bromo-4-hydroxy-, and its methiodide (SEIDE), i, 159.
Quinhydrone, *di*cyano-, reduction potential of (RIDEAL), ii, 546.
Quinhydrones (PFEIFFER, GOEBEL, and ANGERN), i, 271.
reduction potentials of (BJILMANN, JENSEN, and PEDERSEN), ii, 404.
Quinhydrone electrode. See Electrodes.
Quinic acid, constitution of (KARRER, WIDMER, and RISO), i, 673.
utilisation of, by moulds and bacteria (BUTKEVITSCH), i, 1511.
Quinidine, determination of, spectrophotometrically (FABRE), ii, 1212.
Quinine, action of sulphuric acid on (GIEMSA and BONATH), i, 291.
compounds of cupric hydroxide and (ERBEN), i, 573.
effect of, on fermentation in the organism (SMORODINCEV and ADOVA), i, 335.
iodobismuthate (FRANÇOIS and SEGUIN), i, 1084.
salicylosalicylate (MERCK & Co.), i, 1448.

Quinine chlorostannate and chlorostannite (DRUCE), i, 1096.
arsenious tartrate (DECBUCQUET), i, 1090.
determination of, spectrophotometrically (FABRE), ii, 1212.
Quinine, amino-, and its salts and derivatives (FRÄNKEL, TRITT, MEHRER, and HERSCHMANN), i, 573.
*apo***Quinine**, and its benzoate hydrochloride (FRÄNKEL and BUHLER), i, 573.
derivatives of (SUSZKO), i, 1449.
*β-iso***Quinine**, and its derivatives, and *di*bromo- (SUSZKO), i, 1448.
Quinine series (RUZICKA, SEIDEL, and LIEBL), i, 289.
Quininetrimethylammonium picrate (FRÄNKEL, TRITT, MEHRER, and HERSCHMANN), i, 574.
*iso***Quinocyanines**, 4-chloro-, synthesis of, and their derivatives (FISCHER, MÜLLER, and VILSMEIER), i, 439.
Quinoidine extracts from animal substances (KINNERSLEY, PETERS, and SQUIRES), i, 997.
Quinol, oxidation of, in presence of aliphatic amines (HARGER), i, 24.
ethers, substitution in derivatives of (RUBENSTEIN), i, 1278.
additive compounds of aromatic amines with (HARGER), i, 23.
Quinol, *tri*bromo-, dimethyl ether (KOHN and GUTTMANN), i, 1263.
bromonitro- and chloronitro-, ethers of (KOHN and MARBERGER), i, 1264.
*tetra*chloro- (BINZ and RÄTH), i, 446.
Quinols, *mono*- and *di*-nitro-, colorimetric dissociation constants of (PRIDEAUX and NUNN), i, 24.
ψ-Quinols, preparation of (FICHTER and MEYER), i, 381.
Quinol-*om-di*hydroxybenzein (SEN, SINHA, and SARKAR), i, 916.
Quinoline, centroid structure for (FUSON), i, 1098.
arsenyl tartrate (DEBUCQUET), i, 973.
ethiodide, compounds of, with bromoform and iodoform (STEINKOPF and BESSARITSCH), i, 495.
derivatives (JOHN), i, 1317; (JOHN and NOZICZKA), i, 1451; (JOHN and WEBER), i, 1452.
Quinoline, 8-amino-, and its derivatives (SEKA), i, 587.
8-hydroxy-, salts of (ZETZSCHE, SILBERMANN, and VIRLI), i, 1411.
***iso*Quinoline** derivatives, syntheses of (HAWORTH and PERKIN), i, 968, 969, 970; (HAWORTH, PERKIN, and RANKIN), i, 969; (FORSYTH, KELLY, and PYMAN), i, 1167; (HAWORTH, PERKIN, and PINK), i, 1168.
n- and *iso*-**Quinolines**, hydroferricyanides of (CUMMING), i, 122.
Quinolines, 4-amino-, substituted (FISCHER, DIEPOLDER, and WÖLFEL), i, 438.
hydroxy-derivatives (TSCHITSCHIBABIN), i, 299.
*di*iodohydroxy- (PASSEK), i, 1170.
nitroamino- (TSCHITSCHIBABIN, WITKOVSKY, and LAPSCHIN), i, 838.
Quinoline-4-aldehyde, and its phenylhydrazone, preparation of (CHEM. FABRIK AUF AKTIEN VORM. E. SCHERING), i, 1452.
Quinolinecarboxylic acid, *di*hydroxy-, in rice husks (SAHASHI), i, 1520.
Quinolinic acid, preparation of, and its derivatives (SUCHARDA), i, 1317.
Quinolphthalein, structure and derivatives of (DOMINIKIEWICZ), i, 53.
4-Quinolyl ε-amino-α-carbethoxyamyl ketone, and its picrolonate (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl ε-benzamido-α-carbethoxyamyl ketone, and its picrate (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl δ-benzoylethylaminobutyl ketone, and its picrate (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl δ-benzoylethylamino-α-carbethoxybutyl ketone (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl ε-benzoylmethylaminoamyl ketone (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl ε-benzoylmethylamino-α-carbethoxyamyl ketone, and its salts (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl α-bromo-ε-aminoamyl ketone, and its dihydrobromide (RUZICKA, SEIDEL, and LIEBL), i, 290.
4-Quinolyl α-bromo-ε-methylaminoamyl ketone, and its dihydrobromide (RUZICKA, SEIDEL, and LIEBL), i, 289.
4-Quinolyl *N*-ethyl-2-pyrrolidyl ketone, and its dipicronolate (RUZICKA, SEIDEL, and LIEBL), i, 290.
4-Quinolyl-*N*-methyl-2-piperidylcarbinol, and its salts (RUZICKA, SEIDEL, and LIEBL), i, 290.
4-Quinolyl *N*-methyl-2-piperidyl ketone, and its salts (RUZICKA, SEIDEL, and LIEBL), i, 290.
4-Quinolyl *N*-methyl-2-pyrrolidyl ketone, and its hydrochloride (RUZICKA, SEIDEL, and LIEBL), i, 290.
4-Quinolyl 2-piperidyl ketone, and its phenylhydrazone dipicrate (RUZICKA, SEIDEL, and LIEBL), i, 290.
Quinone See Benzoquinone.
Quinones, bactericidal action of (MORGAN and COOPER), i, 207.

o-**Quinones**, oxidation of (CHARRIER and BERETTA), i, 271.
Quinone*di*chlorodi-imines, heats of formation of (BLASZKOVSKA), ii, 1042.
Quinonechloroimines, heats of formation of (BLASZKOVSKA), ii, 1042.
Quinone-imide colouring matters (KEHRMANN and CHERPILLOD), i, 302; (KEHRMANN and FALKE), i, 303; (KEHRMANN and PRUNIER), i, 304.
Quinoneimine colouring matters (KEHRMANN and STANOYÉVITCH), i, 1334; (KEHRMANN and HAENNY), i, 1330; (KEHRMANN and SAFAR), i, 1331; (KEHRMANN and LISTVA), i, 1332.
a-**Quinoquinolone**, constitution of (SEIDE), i, 159.
Quinotoxine, oxime of, and amino-, and its salts (FRÄNKEL and DIAMANT), i, 574.
phenylhydrazones (FRÄNKEL, TRITT, MEHRER, and HERSCHMANN), i, 574.
*β-iso*Quinotoxine, and its derivatives (SUSZKO), i, 1449.
Quinoxaline, 2:3:6-*tri*chloro-, and 6-chloro-2:3-*di*hydroxy- (KEHRMANN and BENER), i, 443.

R.

Rabbits, influence of histamine and tyramine on nitrogen metabolism of (IWATSURU), i, 1502.
Racemic acid, formation of, from *cis*-oxidoethylenedicarboxylic acid (BÖESEKEN), i, 1237.
Racemic compounds, liquid (AGUIRRECHE), ii, 1142.
Racemisation (LEVENE and PFALTZ), i, 795.
asymmetric catalytic (MCKENZIE and SMITH), i, 822.
Radiation, theories of (MIE), ii, 1128.
quantum theory of (BOTHE and GEIGER; KETCHUM), ii, 1; (LODGE), ii, 465, 624.
nature of (SLATER), ii, 926.
absorption of, by emitting atoms (DE BROGLIE and THIBAUD), ii, 165.
transformation of atoms into (STERN), ii, 1021.
and matter (STERN; WESTPHAL), ii, 926.
from non-luminous flames (HASLAM, LOVELL, and HUNNEMAN), ii, 475.
from incandescent solids, photo-electric action of (BECKER), ii, 1107.
emitted by high resistance conductors (REBOUL), ii, 845.
equilibria between atoms, electrons, and (DIRAC), ii, 6.
Radiation, corpuscular, from salts (VOLMER), ii, 7.
impulse (MIE), ii, 844.
resonance, polarisation of, in magnetic fields (ELLETT), ii, 628; (BREIT), ii, 629.
and the quantum theory (DARWIN), ii, 169.
visible, from solid targets (FOOTE, MEGGERS, and CHENAULT), ii, 80.
Radiation potentials (MOHLER), ii, 1113.
Radiation theory (CSÁSZÁR), ii, 733.
of chemical reactions (RICE), ii, 1076; (ORNSTEIN), ii, 1077.
Radicals, acyclic, migratory tendencies of hydrogen and (LÉVY and LAGRAVE), i, 679.
free, electrochemical relation of, to halochromic salts (CONANT, SMALL, and TAYLOR), ii, 874.
organic, degree of negativity of (KHARASCH and GRAFFLIN), i, 1107.
tenacity of (v. BRAUN, FUSSGÄNGER, and KUHN), i, 1401.
with respect to nitrogen (v. AUWERS and PFUHL), i, 1100.
migration of (TIFFENEAU and ORÉKHOV), i, 378, 679.
Radioactive compounds, fractional crystallisation of (CHLOPIN), ii, 438.
elements (HARKINS and GUY), ii, 1109.
electrolytic separation of (TÖDT), ii, 54.
minerals as indicators of geological age (ELLSWORTH), ii, 593.
particles, colloidal, electrical behaviour of (EHRENHAFT), ii, 465.
Radioactivity, measurements of (MATIGNON and MARCHAL), ii, 1110.
effect of sunlight on (MARACINEANU), ii, 348.
quantum theory of (SMEKAL), ii, 347.
Radio-luminescence, decay and regeneration of (VIOL, KAMMER, and MILLER), ii, 1117.
Radium, β-ray spectrum of (HAHN and MEITNER), ii, 9.
heat set free by, as γ-rays (THIBAUD), ii, 464.
long-range particles from (YAMADA), ii, 834.
growth of polonium in preparations of (CURIE and YOVANOVITCH), ii, 464.
coloration of rock salt by (LUDEWIG and REUTHER), ii, 21.
and its isotopes, electrolytic separation of (TÖDT), ii, 54.
emanation. See Niton.

Radium sulphate, co-precipitation of barium sulphate and (DOERNER and HOSKINS), ii, 381.
determination of, in uranium minerals (CURIE), ii, 241.
separation of groups of radiations from (LATTÈS), ii, 465.
Radium-*B* and **-*C***, β-ray spectra of (CURTISS), ii, 622.
β-particles from (D'ESPINE), ii, 622.
heating effect of γ-rays from (ELLIS and WOOSTER), ii, 622, 923.
Radium-*C*, magnetic spectrum of β-rays of (ELLIS), ii, 9.
Radium-*E*, β-particles from (EMELÉUS),
magnetic spectrum of β-particles from (CURIE and D'ESPINE), ii, 732.
half-value period of (FOURNIER), ii, 1110.
decay of (BASTINGS), ii, 9.
Radium-*F*, α-particles from (HAMMER and PYCHLAN), ii, 621.
Radon. See Niton.
Ragweed, active constituent of the pollen of (BAUMAN, CHUDNOFF, and MACKENZIE), i, 1028.
Raspberry, non-volatile acids of (NELSON), i, 762.
Rats, effect of yellow phosphorus on (BERNHARDT and RABL), i, 1357.
diet of (BOAS; HARTWELL), i, 211.
relation between diet and loss of fur in (HARTWELL), i, 464.
white, chemistry of growth of bone in (HAMMETT), i, 1001.
Rays, analysis by absorption of (LATTÈS), ii, 623.
atomic (SCHMIDT), ii, 251.
canal, Döppler effect in (KREFFT), ii, 3.
canal, slow, passage of, through hydrogen (DEMPSTER), ii, 1020.
cathode (BECKER), ii, 251.
absorption of, in aluminium (TERRILL), ii, 79; (SCHONLAND), ii, 459.
mass, photographic plates for detection of (ASTON), ii, 706.
penetrating, at sea-level (HOFFMANN), ii, 1110.
positive (WIEN), ii, 921.
from the action of ultra-violet light on metals (DU BRIDGE), ii, 251.
electromagnetic analysis of (DÖPEL), ii, 168.
Röntgen, measurements of (HUDSON), ii, 17; (WEBER), ii, 458; (BLAKE), ii, 844.
analysis by, and its use in determining constitution of organic compounds (MARK), i, 1; (ROBINSON), ii, 745.
Rays, Röntgen, quantitative analysis with (GÜNTHER and WILCKE), ii, 237; (DELAUNEY), ii, 822.
apparatus for examination by (LANGE), ii, 482.
analysis of powdered crystals by (BRENTANO), ii, 483.
absorption of (STONER and MARTIN), ii, 257.
absorption and scattering of (DUNBAR), ii, 455; (BARKLA and KHASTGIR; BARKLA), ii, 456.
scattering of (WEBSTER and ROSS; ALLISON and DUANE; COMPTON and SIMON), ii, 1034.
theory of (FRICKE), ii, 941.
Compton and Duane effects in (BECKER), ii, 17.
spectra of. See Spectra.
number of β-rays associated with (JAUNCEY and DEFOE), ii, 1128.
secondary β-rays produced in gases by (AUGER), ii, 175.
reflection of, by crystals (HARTREE; BRAGG), ii, 735; (WEBER), ii, 1034.
by crystals of alkali halides (ARMSTRONG, DUANE, and HAVIGHURST; KULENKAMPFF), ii, 1033.
by barytes (ALLISON), ii, 18.
refractive power of atoms for (MARK and TOLKSDORF), ii, 933.
diffraction of, by polymerised liquids (DE SMEDT), i, 6.
excitation of electrons by (BECKER), ii, 8; (SEITZ), ii, 168, 1034.
secondary electrons produced by (FRICKE and GLASSER), ii, 16.
K and *L* electrons expelled by (RICHTMYER), ii, 1129.
ionisation by (GREBE and KRIEGESMANN), ii, 79.
photographic and ionisation effects of (BERTHOLD), ii, 252.
intensity of, in Debye–Scherrer rings (BLUNCK and KOCH), ii, 940.
photographic blackening by (BUSSE), ii, 1080.
coagulation of colloidal solutions by (DOGNON), ii, 665.
intensity of (CLARK and DUANE; DEFOE and NIPPER), ii, 836.
J-transformation of (KHASTGIR and WATSON), ii, 836, 727; (SIEGBAHN; NIPPER), ii, 727.
K-series of (LEIDE; RÉCHOU; RAY; v. WISNIEWSKI), ii, 457.
from light elements (LEVI), ii, 456.
from hot sparks (BJÖRKESEN), ii, 830.

Rays, Röntgen, coloration of alkali halides by (BAYLEY), ii, 21.
and smectic compounds (FRIEDEL), ii, 186.
effect of, on blood (KONRICH and SCHELLER), i, 1356.
fluorescent, critical excitation frequency for (ALLISON and DUANE), ii, 930.
soft, from iron (THOMAS), ii, 336.
superposed, absorption of (WATSON), ii, 458.
coherence of (BARKLA and MACKENZIE), ii, 614.
α-Rays, decay of luminescence due to (WITMER), ii, 89.
excitation of electrons by (BECKER), ii, 8.
β-Rays, production of, in air by Röntgen rays (IKEUTI), ii, 460.
spectra of. See under Spectra.
associated with Röntgen rays (COMPTON and SIMON), ii, 347.
absorption of (FOURNIER), ii, 176, 622.
secondary, produced in gases by Röntgen rays (AUGER), ii, 175.
γ-Rays, spectra of. See under Spectra.
wave-lengths of (GRAY), ii, 84; (SKOBELTZYN), ii, 835.
photo-electric effect of (DE BROGLIE), ii, 347.
absorption and diffusion of (THIBAUD), ii, 257.
absorption and scattering of (OWEN, FLEMING, and FAGE; GRAY), ii, 84; (AHMAD), ii, 923.
scattering of (SKOBELTZYN), ii, 257.
emission of, in atomic disintegration (MEITNER), ii, 10.
heating effect of (ELLIS and WOOSTER), ii, 622.
Ray liver oil, higher alcohols of (TOYAMA), i, 4.
Reactivity of atoms and groups in organic compounds (NORRIS and ASHDOWN), i, 626.
Reagents used in analysis, specification for (COLLINS, FARR, ROSIN, SPENCER, and WICHERS), ii, 899.
Reductase, influence of colloids on the detection of (VIRTANEN), ii, 76.
of yeast (LVOV), i, 1508.
Reduction, mechanism of (PRINS), ii, 1169.
and oxidation (CADY and TAFT), ii, 1078.
biological (FERRO; NEILL and AVERY), i, 340.
with the zinc arc (STOCK, BRANDT, and FISCHER), ii, 570.
Refraction, Kerr constant of, for liquids (MARTIN), ii, 90.
double, of organic liquids (VORLÄNDER and WALTER), ii, 183.
molecular, and molecular volume (LORENZ and HERZ), ii, 356.
Refractive index, influence of arrangement of atoms on (BRAGG), ii, 92.
and critical resonance potentials (DAVIS), ii, 933.
of acids and bases, relation of, to concentration (HAMMETT), ii, 289.
of benzenoid hydrocarbons (EISENLOHR and SCHULZ), i, 17.
of doubly refracting crystals (PERRIER), ii, 1028.
of binary mixed liquids (LICHTENECKER), ii, 632.
of organic liquids, effect of pressure on (EISELE), ii, 264.
Rennin, preparation of (DE TONI), i, 200.
Reproduction, influence of fluorides and iodides on (MAZÉ), i, 870.
effect of vitamin-*B* deficiency on (PARKES and DRUMMOND), i, 1021.
diet required for (SURE) i, 212, 752.
Resins (VESTERBERG and BORGE), i, 252.
relation between capacity to form, and chemical constitution (HERZOG), i, 386.
autoxidation of (TSCHIRCH), i, 356.
from hops (WALKER), i, 1479.
American and French, constituents of (KNECHT and HIBBERT), i, 1420.
phenolic (BAEKELAND and BENDER), i, 689.
Resin acids from hops (WIELAND, MARTZ, and HOEK), i, 1422.
Resinates, lead solutions of (COFFIGNIER), i, 1294; (UZAC), i, 1295.
Resinoids, phenolic (BAEKELAND and BENDER), i, 689.
Resonance potentials, critical, and refractive indices (DAVIS), ii, 933.
Resorcinol, condensation of primary alcohols with (SEN and SARKAR), i, 812.
additive compounds of, with ketones (PFEIFFER, GOEBEL, and ANGERN), i, 271.
reactions of, with propionitriles (CHAPMAN and STEPHEN), i, 669.
derivatives, substitution in (RAO, SRIKANTIA, and IYENGAR), i, 675.
phenacyl methyl ether (FREUDENBERG, FIKENTSCHER, and HARDER), i, 420.
Resorcinolacrolein (SEN and SARKAR), i, 812.
Resorcinol-*o*-aminobenzein, and its potassium salt, and *di*bromo- (SEN and SIRCAR), i, 554.

Resorcinol-4-azopyridine-3-sulphonic acid (KOENIGS and JUNGFER), i, 154.
Resorcinolbenzein, and its derivatives (SEN and SARKAR), i, 812.
Resorcinol-*p*-cresolphthalein (SEN and SIRCAR), i, 555.
Resorcinolfluorescein (SEN and SIRCAR), i, 555.
Resorcinolgallein, and *di*bromo- (SEN and SIRCAR), i, 554.
Resorcinolglycerein, and its derivatives (SEN and SARKAR), i, 812.
Resorcinol-*op*-*di*hydroxybenzein, and *tetra*bromo- (SEN, SINHAR, and SARKAR), i, 916.
Resorcinol-β-hydroxynaphthalein (SEN and SARKAR), i, 812.
Resorcinolisatein, and *tetra*bromo- (SEN and SIRCAR), i, 555.
Resorcinolsalicylein (SEN and SIRCAR), i, 554.
Respiration, measurement of (WARBURG), i, 321.
of cells (v. SZENT-GYÖRGYI), i, 708.
effect of rubidium and selenium ions on (ROFFO and NEUSCHLOSS), i, 1006.
and fission in cells (MEYERHOF), i, 993.
of tissues (TERROINE and ROCHE), i, 709.
iron as oxygen carrier in (ELLINGER), i, 1342; (WARBURG), i, 1481.
effect of alkalinity of blood on (GOLLWITZER-MEIER), i, 177.
in avitaminosis and inanition (ROCHE), i, 462.
anaërobic, in plants (NEUBERG and GOTTSCHALK), i, 213.
Respiration apparatus for study of plants and soils (GINSBURG), i, 1120.
Respiratory centre, effect of the ionic equilibria in blood on the (GOLLWITZER-MEIER), i, 177.
exchange, apparatus for determination of (HAGEDORN), i, 177.
effect of muscular exercise on (FURUSAWA, HILL, LONG, and LUPTON), i, 92.
Rhamnicogenol (BRIDEL and CHARAUX), i, 636, 690.
Rhamnicoside (BRIDEL and CHARAUX), i, 621, 636, 690.
Rhamnosan, from water-lily blossoms (v. LIPPMANN), i, 366.
Rhamnus catharica, composition of the bark of (BRIDEL and CHARAUX), i, 621, 1224.
[illegible]nium (NODDACK, TACKE, and BERG), i, 989.
[illegible]rheumatism, lactic acid in (CAJORI, CROUTER, and PEMBERTON), i, 828.
Rhinanthus crista galli, changes in, during growth (BRAECKE), i, 619.
Rhodamines (DUTT and THORPE), i, 140.
Rhodanic acids, condensation of isatin with (HANN), i, 987.
Rhodinol, synthesis of (GRIGNARD and ESCOURROU), i, 772.
Rhodium in British Guiana (HARRISON), ii, 592.
density of (ROSE), ii, 278.
Rhodium chloride, compound of carbon monoxide and (MANCHOT and KÖNIG), ii, 1193.
Rhus glabra, tannin from (J. C. and B. L. PEACOCK), i, 1124.
Rice, β-acid from husks of (SAHASHI), i, 1520.
Ricinine, synthesis of (SPÄTH and KOLLER), i, 1446.
Rickets, experimental (MCCOLLUM, SIMMONDS, BECKER, and SHIPLEY), i, 1366.
defective ossification in (ROBISON and SOAMES), i, 462.
effect of calcium and sodium glycerophosphates and sodium dihydrogen phosphate on, in rats (KORENCHEVSKI and CARR), i, 464.
influence of piperidine in (EDERER), i, 869.
mineral constituents of blood in (ACKERSON, BLISH, and MUSSEHL), i, 609.
"**Rimu.**" See *Dacrydium cupressinum*.
Rings, formation of, in additive compounds (HIEBER, BECKER, and WAGNER), i, 1325.
four-membered, additive formation of (INGOLD and WEAVER), i, 580; (INGOLD), i, 840.
Ring compounds, isomerisation of (NAMETKIN), i, 1054.
rules for numbering (PATTERSON), i, 824.
Ring systems, fission of (MRISENHEIMER), i, 1335; (KUHN and EBEL), i, 1378.
dicyclic, stereochemistry of (HÜCKEL), i, 258.
River pebbles, manganese in (DITTLER), ii, 322.
River water. See under Water.
Robinia pseudacacia (locust tree), proteins of the bark of (JONES, GERSDORFF, and MOELLER), i, 1225.
glucoside from (HATTORI), i, 1443.
Rochelle salt. See Tartaric acid, potassium sodium salt.
Rocks, crystallisation in magmas of (DESCH), ii, 788.
iodine in (v. FELLENBERG; v. FELLENBERG, GEILINGER, and SCHWEITZER), ii, 321.

Rocks, igneous, equilibria in the formation of (NIGGLI), ii, 784.
basic volcanic, analysis of (ATHANASIU), ii, 1207.
Rock salt, electrical conductivity of (v. RAUTENFELD), ii, 639; (v. SEELEN), ii, 185.
coloration of, by radium (LUDEWIG and REUTHER), ii, 21.
density of (GEISS), ii, 278; (DEFOE and COMPTON), ii, 646.
See also Sodium chloride.
Rods, thermal conductivity of (BARRATT and WINTER), ii, 756.
iso-**Rosindulines**, and their derivatives (KEHRMANN and LISTVA), i, 1332.
iso-**Rosindulinedisulphonic acid** (ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 591.
Rotatory dispersion. See Dispersion.
power and chemical constitution (KENYON, PHILLIPS, and TURLEY), i, 507; (KENYON and SNELLGROVE), i, 771; (HEWITT and KENYON), i, 914.
and constitution of optically active compounds (RUPE and KOPP), i, 274; (RUPE and VONAESCH), i, 499; (RUPE and RINDERKNECHT), i, 533.
calculation of, from molecular structure (DE MALLEMANN), ii, 840.
and structure of sugars (HUDSON and PHELPS), i, 8; (HUDSON), i, 232, 233, 514, 636; (HUDSON and KUNZ), i, 1043.
effect of reading errors on constants of (RINDERKNECHT), ii, 357.
influence of solvents on (LUCAS), ii, 742.
of asymmetric compounds (DE MALLEMANN), ii, 935.
Rotenic acid (TAKEI), i, 761.
Rotenone (TAKEI), i, 761.
Rotenonone (TAKEI), i, 761.
Rothera's reaction, effect of different ammonium salts in (VAN URK), ii, 162.
Rottlerin, and its acetyl and benzoyl derivatives (DUTT), i, 1296.
Rubicene, constitution of (PUMMERER and ULRICH), i, 1259.
Rubidium, spectrum of (OUDT), ii, 915.
arc spectrum of (MEGGERS and LAPORTE), ii, 1101.
flame spectrum of (BLECKER and BONGERS), ii, 77.
radioactivity of (HARKINS and GUY), ii, 1109.
low-voltage arc in vapour of (NEWMAN), ii, 829.
Rubidium, quantum number of (LINDSAY), ii, 467.
Rubidium compounds, effect on, on respiration of cells (ROFFO and NEUSCHLOSS), i, 1006.
Rubidium chloroplatinate, solubility of, in water (ARCHIBALD and HALLETT), ii, 652.
magnesium chromate, optical properties of mixed crystals of ammonium magnesium chromate and (PORTER), ii, 945.
hydroxide, viscosity of solutions of (FRICKE), ii, 389.
iodide, complex compounds of stannous iodide and (AUGER and KARANTASSIS), ii, 1182.
stannic iodide (AUGER and KARANTASSIS), ii, 814.
Rubyl-3-ethosulphuric acid, 9:6′-*di*-hydroxy-, and its hydrochloride (GIEMSA and BONATH), i, 291.
Ruminants, effect of asparagine and ammonium nitrate on nitrogen metabolism of (STARZEVSKA), i, 1115.
Ruthenium, valency of, and its *tetr*oxide and halides (RUFF and VIDIC; KRAUSS and KÜKENTHAL), ii, 480.
co-ordination number of, in the chlororuthenates (BRIGGS), ii, 703.
Ruthenium bases (*ruthenium ammines*):
Rutheniumammine (AOYAMA), ii, 816.
Ruthenium chloride (WÖHLER and BALZ), ii, 424.
*penta*fluoride (RUFF and VIDIC), ii, 443.
*tri*halides, compounds of carbon monoxide with (MANCHOT and KÖNIG), ii, 149.
oxides (WÖHLER, BALZ, and METZ), ii, 149.
Hexachlororuthenic acid, ammonium and potassium salts (AOYAMA), ii, 816.
Pentachlororuthenious acid, potassium salt (AOYAMA), ii, 816.
Pentachlororuthenites (GUTBIER and NIEMANN), ii, 231.
Tetrachlorodioxyruthenic acid (AOYAMA), i, 816.
Ruthenium separation:—
separation of platinum and (RUFF and VIDIC), ii, 443.
Rutile, crystal structure of (GREENWOOD), ii, 93.
Rye, constituents of (HOLTZ and MÜLLER), i, 488.
Rye kernels, constituents of (JODIDI and WANGLER), i, 1224.
Rye straw, effect of silicic acid on the growth of (WIESSMANN), i, 488.

S.

Saccharin (*o-benzoylsulphinide*), derivatives of (HARDING), i, 670.
acetyl and benzoyl derivatives (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1324.
Saccharinic acids (GLATTFELD and SHERMAN), i, 881.
Safranine colouring matters (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 591.
Safraninedisulphonic acid (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 592.
*apo***Safranone**, 6-chloro-2-hydroxy- (KEHRMANN and SCHEDLER), i, 444.
Safroeugenol. See 4-Ethoxyallylbenzene, 3-hydroxy-.
*iso***Safroeugenol**. See 4-Ethoxypropenylbenzene, 3-hydroxy-.
n- and *iso*-**Safroles**, action of magnesium methyl iodide on (KAFUKU), i, 1413.
Salep manna, hydrolysis of (PRINGSHEIM and GENIN), i, 214.
Salicin, hydrolysis of (JOSEPHSON), i, 1359.
by emulsin (BERTRAND and COMPTON), i, 738.
ethers, tetra-acetyl derivatives (ZEMPLÉN and BRAUN), i, 1081.
Salicin, chloro-, tetra-acetyl derivative (ZEMPLÉN and BRAUN), i, 1081.
Salicylaldehyde, metallic salts (ZETZSCHE, SILBERMANN, and VIELI), i, 1411.
compound of aminomalononitrile with (GRISCHKEVITSCH-TROCHIMOVSKI and SEMENCOV), i, 1069.
Salicylaldehyde, 3:5-*di*bromo-, Schiff's bases and *p*-bromophenylhydrazone of (BREWSTER), i, 38.
Salicylaldoxime *p*-chlorophenyl ether (BAMBERGER), i, 143.
Salicylic acid (*o-hydroxybenzoic acid*), ionisation of, in alcohol–water mixtures (BRADLEY and LEWIS), ii, 868.
heat of combustion of, and its use as a standard (VERKADE and COOPS), ii, 39.
equilibrium of phenol, water, and (BAILEY), ii, 1064.
salts, diffusion potentials and ionic mobilities of (PRIDEAUX and CROOKS), ii, 42.
hydroxylamine salt (OESPER and BALLARD), i, 1233.
theobromine and theophyllin salts (KNOLL & Co.), i, 828.
esters, excretion, toxicity, and stability of (HANZLIK and PRESHO), i, 1501.
Salicylic acid (*o-hydroxybenzoic acid*), ethylene ester (CRETCHER and PITTENGER), i, 1416.
p-propenylphenyl ester (RIEDEL), i, 1423.
determination of, oxidimetrically (TÄUFEL and WAGNER), ii, 1008.
Salicylic acid, amino-, electrolytic preparation of (NORRIS and CUMMINGS), i, 668.
thio- and 5-thiocyano-, phthalidylidene ether esters (KAUFMANN and ROSSBACH), i, 1273.
5-thiol- (KAUFMANN and ROSSBACH), i, 1273.
Salicylic acids, substituted (KAUFMANN and ROSSBACH), i, 1273.
Salicylosalicylic acid, quinine salt (MERCK & Co.), i, 1448.
Salicyluric acid, synthesis of, in the organism (BALDONI), i, 330.
in urine (DRZIMAL), i, 99.
β-Salicylylpropionic acid, α-cyano- (BAKER and LAPWORTH), i, 30.
Saligenin, esters and ethers, anæsthetic and anti-spasmodic action of (JENSEN and HIRSCHFELDER), i, 467.
Saliva, effect of halides and other substances on the diastatic activity of (CLIFFORD; WALKER), i, 738.
calculus from (PETROU), i, 725.
Salivary glands, formation of lactic and phosphoric acids in (SCHMITZ and CHROMETZKA), i, 859.
"**Salluen**," effect of, in syphilis (BERING), i, 858.
Salts, emission of particles by heated (SCHMIDT), ii, 251.
corpuscular radiation from (VOLMER), ii, 7.
electrolysis of equimolar mixtures of (SAXON), ii, 984.
paramagnetism of (COTTON-FEYTIS), ii, 945.
heats of solution and dilution o (WÜST and LANGE), ii, 976.
solubility, heat of solution and lattice energy of (BUTLER), ii, 39.
vapour pressure of aqueous solutions of, from the depression of the freezing point of nitrobenzene (SIDGWICK and EWBANK), ii, 38.
absorption of, by tissues (STILES), ii, 31.
hygroscopicity of (SCHOORL), ii, 400.
hydration of, and their effect on the vapour pressure of water (SIDGWICK and EWBANK), ii, 38.
deliquescence of (SCHERINGA), ii, 296.
liquid-crystalline properties of acids, esters, and (VORLÄNDER), i, 267.
decomposition of, by colloids (HÜMMELCHEN and KAPPEN), i, 218.

Salts, bi-bivalent, solubility of, in solutions containing a common ion (WALKER), ii, 769.
coloured, rhythmic precipitation of, in gels (RIEGEL and WIDGOFF), ii, 863.
complex, magnetic properties and valency of (WELO and BAUDISCH), ii, 1031.
fused, boiling point of (LORENZ and HERZ), ii, 276.
thermal expansion of (LORENZ and HERZ), ii, 950.
equilibria in (JELLINEK and WOLFF), ii, 974; (JELLINEK), ii, 1160.
equilibria of metals with (LORENZ), ii, 536, 537.
polyatomic, dissociation of (SASAKI), ii, 399.
solid, electrical conductivity of, at high temperatures (VAILLANT), ii, 40.
uni-univalent, conductivity of, in methyl alcohol (FRAZER and HARTLEY), ii, 1163.
See also Metallic salts.
Salt solutions, effect of capillary-active substances on the surface tension of (SEITH), ii, 961.
mixed, solubility and heats of solution of (MONDAIN-MONVAL), ii, 654.
Salt vapours, ionisation of (KONDRATÉEV), ii, 615.
Salting-out effect (LINDERSTRÖM-LANG), ii, 30; (HAFNER and KÜRTHY), ii, 283.
Salvarsan (*arsphenamine*), isoelectric point of (HUNTER and PATRICK), i, 1106.
sulphur content of, and its synthesis and toxicity (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471.
and its derivatives, distribution of arsenic in the body after injection of (FORDYCE, ROSEN, and MYERS), i, 189.
action of, *in vitro* and *in vivo* (SCHUMACHER), i, 733.
silver compound of (MYERS and CORBITT; CORNWALL and MYERS; FORDYCE, ROSEN, and MYERS), i, 611.
and its derivatives (BINZ, BAUSCH, and URBSCHAT), i, 1195.
determination of arsenic in (KIRCHER and v. RUPPERT), ii, 240.
Samarium, Röntgen ray spectrum of (GLEDITSCH and BOTOLFSEN), ii, 612.
Sand cultures, effect of silica on the yield of plants in (DUCHON; LEMMERMANN), i, 767.
Sandstone, weathering of (KLANDER), ii, 821.
Sanguinarine (GADAMER and STICHEL), i, 286.
Santonin, action of, on blood sugar (STASIAK), i, 1501.
*desmotropo***Santonin**, action of iodine on (BERTOLO), i, 546.
Sapindus mukorossi and *saponaria*, sapogenin from (JACOBS), i, 1028.
Sapogenin, and its derivatives, from soap nuts (JACOBS), i, 947.
Saponins (VAN DER HAAR), i, 50, 946; (JACOBS), i, 947, 948, 1028.
dialysis of (KOFLER and WOLKENBERG), i, 1519.
toxicity of, and their detoxication by cholesterol (KOFLER and SCHRUTKA), i, 1501.
Sarcosine, preparation of the ester of (STAUDT), i, 1133.
anhydride (ABDERHALDEN and KOMM), i, 175.
Scabiosa succisa, constituents of leaves of (WATTIEZ), i, 1521.
Scandium, spectrum of (CATALÁN), ii, 724.
magnetic resolution of the spectrum of (GOUDSMIT, VAN DER MARK, and ZEEMAN), ii, 912.
arc spectrum of (PIÑA DE RUBIES), ii, 829.
arc and spark spectra of (MEGGERS), ii, 77.
ultra-violet spark spectrum of (IRETON), ii, 453.
Scandium carbide (FRIEDERICH and SITTIG), ii, 705.
nitride (FRIEDERICH), ii, 374; (FRIEDERICH and SITTIG), ii, 420.
Schiff's bases, bromine additive compounds of (BERG), i, 817.
Schoepite, structure and analysis of (SCHOEP), ii, 235.
Scleroproteins (STARY and ANDRATSCHKE), i, 1480.
Scopolamine *N*-oxide, and its derivatives (POLONOVSKI and POLONOVSKI), i, 829.
Scopolia, sterol from roots of (WINDAUS and BRUNKEN), i, 108.
Scurvy (LIOTTA), i, 1365.
biochemistry of (PALLADIN; PALLADIN and KUDRJAVZEVA), i, 330.
calcium and creatine excretion and enzymes of blood in (PALLADIN and KUDRJAVZEVA; PALLADIN and NORMARK; PALLADIN and SAVRON), i, 461.
iron in blood in (MOURIGNAND, LEULIER, and MICHEL), i, 330.
blood of guinea-pigs with (LEPPER and ZILVA), i, 1208.
Scymnus lichα, hydrocarbons from (ANDRÉ and CANAL), i, 1373.

Sea water. See under Water.
Seal, blood of. See Blood.
Secretin and insulin (PENAU and SIMONNET), i, 482.
Sedimentation, recorder for measuring distribution of particles in (LAMBERT and WIGHTMAN), ii, 1194.
Seeds, hydrogen-ion concentration in (NĚMEC), i, 871.
effect of, on hydrogen-ion concentration and reaction of nutrient solutions (RUDOLFS; HOAGLAND), i, 1368.
selective adsorption of ions by (RUDOLFS), i, 1367.
symbiosis of bacteria and (FOWLER and CHRISTIE), i, 344.
germination of (BLAGOVESCHENSKI; FODOR and REIFENBERG), i, 756.
effect of carbon dioxide on (SCHMIDT), i, 758.
action of photocatalysers on (NEITHAMMER), i, 1023.
effect of water and salt solutions on (RUDOLFS), i, 1120.
formation of vitamin-*A* during (STEPP), i, 1220.
dried, peroxydases in (COUPIN), i, 615.
germinating, alkaloids in (SABALITSCHKA and JUNGERMANN), i, 1223.
oxidation of amino-acids in (OPARIN), i, 1518.
formation of vitamin-*D* in (STEPP), i, 1221.
Selenium, atomic weight of (BRUYLANTS, LAFORTUNE, and VERBRUGGEN), ii, 174.
photo-electric emission of (DEL REGNO), ii, 81.
effect of light on the thermoelectric power of (HOLMES), ii, 811.
effect of light on thermal conductivity of (MARTIN), ii, 1117.
crystal structure of (SLATTERY), ii, 369.
optical constants of crystals of (MILLER), ii, 751.
hydrosols, coagulation of, by electrolytes (DOOLAN), ii, 293.
as carrier in chlorination (O. and C. A. SILBERRAD), ii, 1191.
Selenium compounds, acid nature of (KARVÉ), ii, 1188.
effect of, on respiration of cells (ROFFO and NEUSCHLOSS), i, 1006.
Selenium bromide and chloride, preparation of (LENHER and KAO), ii, 1206.
Selenium oxychloride, electrical conductivity of solutions of (JULIEN), ii, 872.
Selenium *di*oxide, molecular weight of, in ethyl alcohol (PRIDEAUX and GREEN), ii, 96.
additive compounds of, with halogen acids (MUEHLBERGER and LENHER), ii, 890.
Selenious acid, dissociation constants of (WILLCOX and PRIDEAUX), ii, 867.
Selenic acid, and its salts (LENHER and WECHTER), ii, 815; (LENHER and KAO), ii, 817.
preparation of (MANCHOT and WIRZ-MÜLLER), ii, 319.
Selenates, double hydrated, dissociation pressures of (FERGUSON), ii, 1063.
Selenides, preparation of (MOSER and ATYNSKI), ii, 583.
electrolytic preparation of (FISCHER), ii, 808.
Selenium determination and separation:—
determination of, and separation from tellurium (LENHER and KAO), ii, 434.
separation of tellurium and (LENHER and KAO), ii, 1199.
Selenocyanogen (BIRCKENBACH and KELLERMANN), ii, 569.
Semecarpus anacardium (marking nut), constituents of (NAIDU), i, 1224.
Semen, spermine phosphate from (ROSENHEIM), i, 180.
Semicarbazide sulphate, electrolytic preparation of (BIRCHER, INGERSOLL, ARMENDT, and COOK), i, 525.
Semicarbazide, thio-, action of aromatic amines on (MAZOUREVITSCH), i, 984.
condensation of ω-bromoacetophenone with (BOSE), i, 167.
Semicarbazides, thio-, condensation of ω-bromoacetophenone with (BOSE), i, 1465.
Semicarbazones, action of amines on (WILSON and CRAWFORD), i, 318.
action of hydrazines on (SUTHERLAND and WILSON), i, 42.
Semioxamazide, derivatives of (WILSON and PICKERING), i, 935.
ζ-Semitruxinonic acid, and its derivatives (STOERMER and KLOCKMANN), i, 928.
Sera, antimeningococcal, flocculation of (DE LA RIVIÈRE and ROUX), i, 749.
normal and luetic, chemical composition of (SOLARI), i, 858.
Sericin, preparation of, from silk (SHELTON and JOHNSON), i, 602.
***dl*-Serine,** derivatives of (BERGMANN and MIEKELEY), i, 235.

Serum, effect of irradiation on (KROETZ), i, 178.
electrical conductivity of (LASSEUR, GIRARDET, and VERMELIN), i, 853.
effect of alcohols or acetone on physical properties of (FÜRTH and PECHHOLD), ii, 1056.
complement activity of (WHITEHEAD, GORDON, and WORMALL), i, 1202.
solubility of the globulins of (SÖRENSEN), i, 1110.
proteins of (LEENDERTZ), i, 96.
precipitation of (CSAPÓ and v. KLOBUSITZKY), i, 178; (RUSZCZYNSKI), i, 322.
precipitin reactions of (HEKTOEN and WELKER), i, 323.
calcium content of (CSAPÓ and FAUBL), i, 96.
in children, acid-combining power of (BOSÁNYI and CSAPÓ), i, 188.
determination of phosphates in (ESSINGER and GYÖRGY), i, 178.
determination of sodium in (KRAMER and GITTLEMAN), i, 180.
Serum-albumin. See under Albumin.
Sesquiterpene, $C_{15}H_{25}$, and its hydrochloride from *Canarium strictum* (MOUDGILL), i, 823.
Sesquiterpenes, from extracts of the cotton plant (POWER and CHESNUT), i, 1026.
ring formation in (RUZICKA and CAPATO), i, 943.
action of formic acid on (ROBERTSON, KERR, and HENDERSON), i, 1293.
Shaking apparatus (MILLIGAN), ii, 150.
Shale oil, Kimmeridge, sulphur compounds of (CHALLENGER, JINKS, and HASLAM), i, 282.
Shark liver oil, higher alcohols of (TOYAMA), i, 4.
Sheep, bile of. See Bile.
excretion of creatine and creatinine by (PALLADIN), i, 327.
Shibuol, constitution of (KOMATSU and MATSUNAMI), i, 950.
Shrimp. See *Peneus setiferus*.
Silage, composition of, and its value as a farm food (BLACKSHAW), i, 1523.
Silane, formation of (SCHWARZ and (HOEFER), ii, 418.
Silex, hydrocarbons and carbonates in (DE LAPPARENT), ii, 821.
Silica. See Silicon *di*oxide.
Silicododecatungstic acid, and its salts (NORTH and BEAL), ii, 607.
Silicohydrocarbons, complex (KIPPING), i, 87.
Silicon, atomic weight of (HÖNIGSCHMID and STEINHEIL), ii, 174.
Silicon, spectra of (MCLENNAN and SHAVER; FOWLER), ii, 452; (LANG and SMITH), ii, 829; (MCQUARRIE), ii, 1013.
singly ionised, spectrum of (SAHA), ii, 1100.
spectral frequencies of (HOLWECK), ii, 336.
critical potential of (HOLWECK), ii, 729.
radio detector action of (CZOCHRALSKI), ii, 642.
sizes of electron-kernels of aluminium, magnesium, sodium, and (TURNER), ii, 349.
Silicon alloys with aluminium (PARRAVANO and SCORTECCI), ii, 281.
with carbon and iron (BECKER), ii, 973.
with molybdenum and nickel (PFAUTSCH), ii, 298.
Silicon nitride, spectrum of (MULLIKEN), ii, 731, 1020.
*di*oxide (*silica*), phosphorescence of, exposed to Röntgen rays (HOPWOOD and MAYNEORD), ii, 839.
effect of temperature on the hygroscopicity of (AARNIO), ii, 1157.
adsorption of acids by (JONES), ii, 382, 509; (MUKHERJEE), ii, 383, 962.
gels, adsorption by (RAY), ii, 191; (PATRICK and JONES), ii, 193; (PATRICK and OPDYCKE), ii, 656.
adsorption of butane by (PATRICK and LONG), ii, 382.
adsorption of gases by (PATRICK), ii, 509.
adsorption of water by (PATRICK and EBERMAN), ii, 284.
heats of adsorption of sulphur dioxide and of water vapour by (PATRICK and GREIDER), ii, 870.
effect of water on dried and pressed (BHATNAGAR, PRASAD, and OHRI), ii, 966.
reducing action of hydrogen adsorbed by (LATSHAW and REYERSON), ii, 412.
new type of (HOLMES and ANDERSON), ii, 518.
equilibrium of calcium and sodium metasilicates and (MOREY and BOWEN), ii, 1161.
equilibrium of sodium metasilicate with (MORLEY and BOWEN), ii, 121.
polymorphism of (LONGCHAMBON), ii, 752.
possible dynamic form of (v. WEIMARN), ii, 395.

Silicon *di*oxide (*silica*), action of, on electrolytes (JOSEPH), ii, 383.
reactions of metals and gases on vessels of (v. WARTENBERG), ii, 699.
surface devitrification of vessels of (VILBRANDT), ii, 1091.
rôle of, in plant growth (NANJI and SHAW), i, 214; (LEMMERMANN, WIESSMANN, and SAMMET), i, 766; (DUCHON; LEMMERMANN; DENSCH), i, 767.
Silicic acid gels, preparation and properties of (FELLS and FIRTH), ii, 390.
sols (PAULI and VALKÓ), ii, 521; (KRUYT and POSTMA), ii, 861.
preparation of (GRUNDMANN), ii, 775.
effect of, on plant growth and soils (WIESSMANN; NOLTE; MUKHERJEE), i, 488.
Silicic acid, detection of (LORENZ and BERGHEIMER), ii, 600.
Silicic acids (SCHWARZ and MENNER), ii, 222.
Silicates (EITEL; TAMMANN and GREVEMEYER), ii, 580.
structure of (DOMINIKIEWICZ), ii, 1036.
properties and uses of sols and gels of (VAIL), ii, 661.
colloidal, oxydase-like activity of (OTA and NODA), ii, 203.
fused, behaviour of gold and platinum with (JANDER), ii, 416.
mineral, constitution of (ISKYUL), ii, 152.
natural, constitution of (RIDLEY), ii, 1130.
determination of ferric iron in (HACKL), ii, 1004.
separation of alkalis in analysis of (CANTONI), ii, 1001.
Silicon organic compounds (KIPPING), i, 87; (VYLE and KIPPING), i, 172.
Silk, use of, in the animal organism (ABDERHALDEN), i, 726.
weighting of, with stannic chloride (FICHTER and REICHART), ii, 193.
viscose, plasticity of (VENABLE), ii, 1058.
Silk fibroin, distillation of (JOHNSON and DASCHAVSKY), i, 176.
hydrolysis of the peptone of (HATANO), i, 201.
tryptophan from (HIRATSUKA), i, 836.
Sillimanite, formation of mullite from (CRAIG), ii, 987.
crystal structure of mullite and (MAYER and DAVEY), ii, 1127.
Siloxen, reaction of halogen compounds with (KAUTSKY and THIELE), ii, 668.
Silver, atomic weight of (DEAN), ii, 255; (MOLES), ii, 346.
K_H absorption in spectrum of (RICHTMYER and SPENCER), ii, 1102.
arc spectrum of (LOWERY), ii, 4; (SHENSTONE), ii, 453; (BENGTSSON and SVENSSON), ii, 166.
spark spectrum of (L. and E. BLOCH), ii, 829.
ultra-violet absorption spectrum of (ZUMSTEIN), ii, 453.
effect of temperature on the anomalous reflexion of (DE SÉLINCOURT), ii, 275.
X-ray absorption coefficient of (WARBURTON and RICHTMYER), ii, 1103.
photo-electric sensitivity of (SUHRMANN), ii, 831.
production of optical activity in (ZOCHER and COPER), ii, 935.
electro-deposition of (SANIGAR), ii, 677.
atoms, free path of, in nitrogen (BIELZ), ii, 668.
films, emission of electrons from, exposed to Röntgen rays (SIMONS), ii, 81.
atomic heat of, at high temperature (MAGNUS and HODLER), ii, 95.
adsorption of, by hydrated manganese dioxide (PAVLOV), ii, 507.
partition of, between lead and zinc (NAISH), ii, 506.
solubility of oxygen in (PARRAVANO and MALQUORI), ii, 769, 879.
solubility of, in water (KŘEPELKA and TOUL), ii, 697.
ions, equilibrium of, with ferrous ions (TANANAEV), ii, 121.
in photography (LÜPPO-CRAMER), ii, 985.
colloidal, preparation of (MORÁVEK), ii, 775.
colour of (FEICK), ii, 1153.
dispersoid sols of (v. WEIMARN), ii, 198.
medicinal preparations of (SCHLEE and THIESSENHUSEN), i, 197; ii, 114.
sols, protected, preparation and properties of (GARARD and DUCKERS), ii, 391.
analysis and constitution of (FRIED and PAULI), ii, 390.
action of arsenious sulphide sols on (FREUNDLICH and MOOR), ii, 198.

Silver alloys, effect of various metals on the properties of (SAEFTEL and SACHS), ii, 1051.
with cadmium, electro-deposition of (ATEN and VAN PUTTEN), ii, 1166.
with lead, electrolysis of (KREMANN and BENDA), ii, 679.
with mercury (TAMMANN and STASSFURTH), ii, 377.
with mercury and tin (TAMMANN and DAHL), ii, 502.
with zinc, Röntgen ray analysis of (WESTGREN and PHRAGMÉN), ii, 746.
Silver salts, therapeutic properties of (V. NEERGAARD), i, 1212, 1357.
Silver azide, action of bromine on (SPENCER), ii, 416.
arsenate and phosphate, crystal structure of (WYCKOFF), ii, 1037.
uranyl carbonate (HEDVALL), ii, 991.
bismuthide (WEEKS and DRUCE), ii, 1188.
bromide, ultra-violet light required to develop (HELMICK), ii, 143.
photographic emulsions of, and the action of light (BAKER; LÜPPO-CRAMER; STOCK), ii, 574.
photochemical decomposition of (HARTUNG), ii, 57.
carbonate, thermal decomposition of (CENTNERSZWER and BRUŽS), ii, 803.
*per*chlorate, compounds of pyridine, water, and (MACY), ii, 536.
chloride, solubility of, in chloride solutions (KENDALL and SLOAN), ii, 1052.
mixed crystals of sodium chloride and (LE BLANC and RÖSSLER), ii, 365; (BROOMÉ; TAMMANN), ii, 366.
gelatino-halides, properties of (REYCHLER), ii, 219.
halides, photoelectric properties of (AUDUBERT), ii, 56.
photomagnetic properties of (GARRISON), ii, 371.
photochemistry of emulsions of (EGGERT and NODDACK), ii, 573.
change in mass of, on illumination (KOCH and KREISS), ii, 810.
hydroxide, precipitation of, electrometrically (BRITTON), ii, 1204.
iodide in photo-electric cells (GARRISON), ii, 212; (PRICE), ii, 680.
adsorption of silver salts by (BEEKLEY and TAYLOR), ii, 855.
hydrosols (LOTTERMOSER, SEIFERT, and FORSTMANN), ii, 514.
nitrate, equilibrium of cupric hydroxide, water, and (MALQUORI), ii, 697.
Silver oxide, solubility of, in water (REMY and KUHLMANN), ii, 119.
oxides (JIRSA), ii, 314.
higher oxides of (JIRSA), ii, 1162; (JIRSA and JELINEK), ii, 1182.
Silver organic compounds:—
Silver salvarsan (MYERS and CORBITT; CORNWALL and MYERS; FORDYCE, ROSEN, and MYERS), i, 611; (BINZ, BAUSCH, and URBSCHAT), i, 1195.
Silver detection, determination and separation:—
detection of (STEIGMANN), ii, 719.
determination of (DOUGHTY), ii, 238.
separation of, by irradiation of photographic plates (KOCH and VOGLER), ii, 941.
Sinapis alba, hexamethylenetetramine as a nutrient for (E. and G. NICOLAS), i, 623.
Sincosite (SCHALLER), ii, 152.
Sirius-yellow G. See 1:2-Benzanthraquinone.
Sitostene, nitro- (WINDAUS and BRUNKEN), i, 394.
Sitosterol (WINDAUS and BRUNKEN), i, 394.
Skatole, determination of, in bacterial cultures (FELLERS and CLOUGH), i, 1015.
Skin, osmosis of boric acid through (KAHLENBERG), i, 101.
hydrolysis of (MERRILL), i, 92.
enzymes of (WOHLGEMUTH and KLOPSTOCK), i, 203; (WOHLGEMUTH and YAMASAKI), i, 472.
absorption of potassium iodide by (CANALS and GIDON), i, 1116.
extraction of proteins from (PINESS, MILLER, and ALLES), i, 331.
substance giving the nitroprusside reaction in (KAYE), i, 180.
Sklodowskite (SCHOEP), ii, 235.
Sky, blue colour of (BUCHWALD), ii, 1117.
Smectic compounds, structure of (FRIEDEL), ii, 186, 272.
Smell, determination of thresholds of (HOFMANN and KOHLRAUSCH), i, 732.
Soaps, Röntgen ray structure of (TRILLAT), ii, 752.
as protective colloids (PAPACONSTANTINOU), ii, 393, 526; (BHATNAGAR, PRASAD, and BAHL), ii, 1155.
calcium, solubilities of (HARRISON), ii, 190.
Soap films, composition of (LAING), ii, 960.
in emulsions (RIEMAN and VAN DER MEULEN), ii, 1148.

Soap solutions, viscosity of (YAJNIK and MALIK), ii, 779.
viscosity and elasticity of (FREUNDLICH and KORES), ii, 663.
colloidal properties of (GURVITSCH), ii, 517.
alcoholic, ionisation in (PATRICK, HYDEN, and MILAN), ii, 859.
Sodamide, syntheses with (HALLER, BAUER, and RAMART), i, 260.
Sodiocyano*cyclo*hexanone (v. AUWERS, BAHR, and FRESE), i, 309.
Sodium, molecular weight of (JOUNIAUX), ii, 187.
absorption spectrum of (HARRISON and SLATER), ii, 911.
K-absorption spectrum of (ROBINSON), ii, 614.
arc spectrum of (v. WISNIEWSKI), ii, 451.
at low voltages (NEWMAN), ii, 723.
band spectrum of, and of mixtures of the vapour with potassium vapour (SMITH), ii, 86.
series spectrum of the vapour of (HARRISON), ii, 5.
vapour, low voltage arcs in (NEWMAN), ii, 450.
electrical double refraction of (LADENBURG and KOPFERMANN), ii, 917.
inverse Stark effect in (LADENBURG), ii, 79.
photo-emission from (BURT), ii, 617.
life of excited atoms of (GERLACH and SCHÜTZ), ii, 171.
atoms, transition probabilities in (HARRISON), ii, 734.
sizes of electron-kernels of aluminium, magnesium, silicon, and (TURNER), ii, 349.
deposition of, by electrolysis through glass (BURT), ii, 921.
resonance radiation, polarisation of, in magnetic fields (ELLETT), ii, 628 ; (BREIT), ii, 629.
vapour pressure of (RODEBUSH and DE VRIES), ii, 1142.
equilibrium between alkaline earth metals and, and their fused chlorides (JELLINEK and CZERWINSKI), ii, 123.
ions, action of, on the heart (HOLZLÖHNER), i, 1500.
reaction of, with aromatic aldehydes, ketones, and esters (BLICKE), i, 37, 862.
reaction between potassium and, in presence of ammonium oxalate (SCHEREFELD), ii, 1202.
Sodium alloys with lead, electrolysis of (KREMANN, KRENZL, and MARKL), ii, 132.
with mercury, preparation of (READ and LUCARINI), ii, 587.
electrolysis of (KREMANN, MÜLLER, and KIENZL), ii, 132.
interfacial tension between benzene and (BHATNAGAR, PRASAD, and MUKERJI), ii, 194.
effect of light on the action of water with (BHATNAGAR, PRASAD, and MUKERJI), ii, 811.
with mercury and zinc, velocity of reaction of aqueous solutions with (KLEIN), ii, 802.
with potassium, electrolysis of (KREMANN and v. REHENBURG), ii, 132.
Sodium antimonite and sulphite, slow oxidation of (JORISSEN and VAN DEN POL), ii, 52.
arsenite, combination of, with loosely-combined nitrogen, oxygen, and sulphur (GUTMANN), i, 1059.
action of, on azido compounds (GUTMAN), i, 84.
reactions of, with halogen organic compounds (GUTMANN), ii, 238.
azide, action of bromine on (SPENCER), ii, 416.
borate, use of, in determination of acids and bases (MELLON and MORRIS), ii, 325.
carbonate, equilibrium of sodium sulphate, water, and (CASPARI), ii, 123.
action of, on phosphates (COLANI), ii, 1001.
hydrogen carbonate, dissociation of (RANC), ii, 414.
equilibrium of hæmoglobin and (ADAIR), i, 850.
potassium carbonates (BAIN), ii, 577.
caseinate, equilibrium of solutions of sodium chloride and (SPORING), ii, 119.
chloride, absorption spectrum of photo-electric crystals of (GYULAI), ii, 837.
photo-electric properties of crystals of (GUDDEN and POHL), ii, 343 ; (GYULAI), ii, 476.
electrical conductivity of solutions of (LORENZ and VOIGT), ii, 871.
activity coefficient of (SCATCHARD), ii, 397.
dispersion of (HERZFELD and WOLF), ii, 1119.
transference numbers of, and its mixtures with potassium chloride (MACINNES), ii, 872 ; (DEWEY) ii, 873.

Sodium chloride, surface tension and adsorption of aqueous solutions of (HARKINS and MCLAUGHLIN), ii, 959.
strength and elasticity of crystals of (JOFFÉ and LEWITSKY), ii, 370; (EWALD and PÓLÁNYI), ii, 371.
mixed crystals of silver chloride and (LE BLANC and RÖSSLER), ii, 365; (BROOMÉ; TAMMANN), ii, 366.
equilibrium of magnesium sulphate with (KURNAKOV and SHEMTSCHUSHNI), ii, 299.
equilibrium of solutions of sodium caseinate and (SPORING), ii, 119.
equilibria of sodium palmitate, water, and (MCBAIN and LANGDON), ii, 537.
equilibrium of sodium sulphate, water, and (PELLING), ii, 670.
interaction of alumina and (CLEWS), ii, 577.
effect of, on solutions of chromic chloride (GUSTAVSON), ii, 1086.
See also Rock salt.
*di*chromate, reaction of potassium chloride with (ROBERTSON), ii, 121.
dithionate, detection and determination of (LITTERSCHEID and LÖWENHEIM), ii, 68.
hydroxide, activity coefficient of (HARNED), ii, 397, 398.
fused, electrical conductivity of (ARNDT and PLOETZ), ii, 127.
solubility of cellulose in (D'ANS and JÄGER), i, 1387.
equilibrium of chromium hydroxide, chromite, and (MÜLLER), ii, 124.
equilibrium of lead hydroxide, plumbite, and (MÜLLER, REISSMANN, and BALLIN), ii, 125.
equilibrium of sodium sulphite, water, and (HAMMICK and CURRIE), ii, 869.
hypochlorite, induced antiseptic action of (VARILLA and TECHOUEYRES), i, 863.
hyposulphite, reducing action of, on dyed cotton (EYMER), ii, 582.
use of, in organic analysis (CLARK), ii, 332.
nitrate, equilibrium of sodium sulphate, water, and (FOOTE), ii, 786.
nitrite, freezing point curve of aqueous solutions of (HELBERG), ii, 971.
rhodizonate, detection of barium, lead, and strontium with (KOLTHOFF), ii, 1095.
silicates, aqueous solutions of (HARMAN), ii, 1065.
Sodium aluminium silicate, crystalline forms of (BOWEN and GREIG), ii, 997.
chromosilicate, synthesis of (KARFIOL), ii, 1087.
metasilicate, equilibrium of silica with (MOREY and BOWEN), ii, 121.
equilibrium of silica, calcium metasilicate, and (MOREY and BOWEN), ii, 1161.
sulphate as a cryoscopic solvent (TURNER and PATTERSON), ii, 273.
equilibrium of sodium carbonate, water, and (CASPARI), ii, 123.
equilibrium of sodium chloride, water, and (PELLING), ii, 670.
equilibrium of sodium nitrate, water, and (FOOTE), ii, 786.
double decomposition of ammonium borate and (SBORGI and BOVALINI), ii, 206; (SBORGI, BOVALINI, and MEDICI; SBORGI), ii, 207.
*mono*sulphide, crystal structure of (CLAASSEN), ii, 845.
*tetra*sulphide, action of, on organic halides (THOMAS and RIDING), i, 113.
sulphides, behaviour of, in water and alcohol (HODGSON), i, 1104.
reactions of, with chloronitrobenzenes (HODGSON and WILSON), i, 532.
sulphite (FOERSTER, BROSCHE, and NORBERG-SCHULZ), ii, 120.
equilibrium of sodium hydroxide, water, and (HAMMICK and CURRIE), ii, 869.
thiosulphate, keeping properties of standard solutions of (COLLARD), ii, 1168.
catalysis of the reaction of ferric chloride with (HOLLUTA and MARTINI), ii, 215.
tungstate, equilibria of, with lithium tungstate and tungsten trioxide (VAN LIEMPT), ii, 421.
Sodium organic compounds:—
Sodium diethyl phosphite (NYLÉN), i, 1135.
Sodium detection, determination, and separation:—
detection of, as oxalate (WINKLER), ii, 1095.
determination of (v. DEHN), i, 855.
determination of, iodometrically (BÁLINT), ii, 158.
determination of, in aluminium (FAIRLIE and BROOK), ii, 241.
determination of, in blood (HADEN), i, 1112.
determination of, iodometrically, in serum (KRAMER and GITTLEMAN), i, 180.

Sodium detection, determination, and separation:—
determination of, in blood serum (LEBERMANN), i, 324.
determination and separation of (SMITH and ROSS), ii, 601.
Soils, mechanical composition curves of (ROBINSON), i, 224.
physical properties of (HAINES), i, 876.
heat of wetting of (BOUYOUCOS), i, 1228.
influence of bases on (PATE), i, 1528.
heat of wetting of colloids in (ANDERSON), i, 219.
relation between vapour pressure and water content of (PURI, CROWTHER, and KEEN), i, 492.
acidity of (KAPPEN), i, 221, 874; (DENSCH), i, 221; (TACKE; RAMANN), i, 875; (KURCKMANN), i, 1032; (HISSINK and VAN DER SPEK; NIKLAS and HOCK; BOBKO and DRUSCHININ; ARRHENIUS), i, 1525.
effect of drying on (ROST and FIEGER), i, 348.
effect of silicic acid on (MUKHERJEE), i, 488.
in relation to base exchange (ROBINSON and WILLIAMS), i, 222.
effect of, on absorption of phosphorus and potassium from (NĚMEC and GRAGANIN), i, 1228.
relation between the hydrogen-ion concentration, lime requirement, and thiocyanate colour of (SAINT), i, 220.
effect of hydrogen-ion concentration on micro-organisms in (RIPPEL), i, 220.
reaction of (CROWTHER), i, 875; (CROWTHER and MARTIN), i, 876.
alkalinity in relation to lithological constitution of (PRATOLONGO), i, 874.
base exchange in (HISSINK), i, 222.
adsorption of ammonium chloride by (PAVLOV), ii, 287.
adsorption of anions from solutions by (COMBER), i, 219.
adsorption of colouring matters by (WILKINSON and HOFF), i, 1227.
moisture in (MCCOOL and WEIDEMANN), i, 1527.
saturation capacity of (HISSINK), i, 490.
fixation of water in (WIEGNER, GALLEY, and GESSNER), ii, 86.
percolation of water through (WINT—), i, 1527.
Soils, dispersion of, when shaken with water (PURI and KEEN), i, 768.
relation of biological processes to concentration of cations in (BURD), i, 1527.
cation of dilute acids on (PURI), i, 1372.
aluminium in (MAGISTAD), i, 1371.
displacement of aluminium by potassium in (SMOLIK), i, 1032.
volatilisation of ammonia from (CLARKE and MORISON), i, 491.
ammonification of amino-nitrogen in (GUITTONNEAU), i, 106.
action of calcium carbonate on (GEHRING and WEHRMANN), i, 1031.
formation of carbon dioxide in (LEMMERMANN and WIESSMANN), i, 348; (REINAU), i, 1526.
clays as colloids in (JOSEPH), i, 1228.
colloids in (ROBINSON and HOLMES), i, 624; (POWELL), i, 1032.
in relation to fertility (JOFFE and MCLEAN), i, 1372.
lime requirements of (ARRHENIUS), i, 490, 766; (CROWTHER and MARTIN), i, 876; (NIKLAS and HOCK), i, 1526.
interactions of lime in (SCHEFFER), i, 624.
lime and calcium carbonate in (RAMANN; BLANCK and LOHMANN), i, 223; (BLANCK and SCHEFFER), i, 491.
occurrence of metals in (MCHARGUE), i, 1023.
formation of nitrates in (RUSSEL, JONES, and BAHRT), i, 1031.
fixation of nitrogen in (VINOGRADSKI), i, 623; (WINTERS), i, 767; (TRUFFAUT and BEZSSONOFF), i, 1227.
accumulation of nitrates in, after growth of clover or lucerne (LYON, BIZZELL, and WILSON), i, 347.
phosphorus requirements of (VAN DER SPUIJ), i, 1524.
availability of phosphorus in (AMES and SCHOLLENBERG), i, 1524.
addition of phosphorus nitride to (ALLISON), i, 218.
potassium salts in (AMES and SIMON; FRAPS), i, 1523.
effect of sodium nitrate in (ANON.), i, 347.
effect of addition of straw to (MARTIN), i, 1372.
sulphofication in (KALUSHSKI), i, 492.
sulphur as a fertiliser for (KALUSHSKI), i, 492.
urea in (BRIOUX), i, 491; (COUTURIER and PERRAUD), i, 765.

Soils, decomposition of urea in (LITTAUER), i, 218.
microbiology of (VINOGRADSKI), i, 765.
inoculation of, with *Azotobacter* (LIPMAN and TEAKLE), i, 491.
effect of alkali salts on bacteria in (GIBBS, BATCHELOR, and MAGNUSON), i, 1030.
effect of micro-organisms on absorption in (STOKLASA), i, 765.
formation of thiosulphates in, by micro-organisms (GUITTONNEAU), i, 766.
effect of carbon dioxide in air of, on growth of plants (PARKER), i, 1223.
formation and decomposition of humus in (BALKS), i, 1031.
effect of removing soluble humus from (CROWTHER), i, 1372.
humification of organic matter in (ROBINSON and JONES), i, 491.
arable, occurrence of cobalt and nickel in (BERTRAND and MOKRAGNATZ), i, 492.
manganese in (BERTRAND), i, 223.
Burma, buffer action of (CHARLTON), i, 768.
clay, electrical charge on colloids in (DAYHUFF and HOAGLAND), i, 219.
forest, air capacity and acidity of (KVAPIL and NĚMEC), i, 221.
"Hager" (KNICKMANN and HELBIG), i, 1528.
limed, retention of sulphates by (MACINTYRE and SHAW), i, 490.
marsh, hydrogen peroxide catalase in (SMOLIK), i, 1524.
moor, acidity of (ARND), i, 221.
effect of humic acids on bacteria in (ARND), i, 490.
prairie, effect of grain growing on nitrogen and organic matter in (SHUTT), i, 768.
Punjab, fixation of nitrogen in (LAUDER and ALI), i, 1524.
Rothamsted, base exchange in (PAGE and WILLIAMS), i, 222.
saline, effect of sulphur on (KALUSHSKI and SOLNIJEVA), i, 624.
analysis of (MCGEORGE), i, 348; (GEDROITZ), i, 489.
determination of acidity of (HAGER), i, 489; (ARND), i, 490; (NIKLAS and HOCK), i, 768.
determination of alkali in (JOSEPH, MARTIN, and HANCOCK), i, 222.
determination of ammonia in (MCLEAN and ROBINSON; HARPER), i, 224.
determination of colloids in (BOUYOUCOS), i, 348.
Soils, determination of hydrogen-ion concentration in (ATKINS; BARNETTE, HISSINK, and VAN DER SPEK), i, 220; (NIKLAS and HOCK), i, 348, 1526; ii, 325; (ARRHENIUS), i, 1525; (PIERRE), i, 1526.
apparatus for (TRÉNEL), i, 874.
with quinhydrone electrodes (BRIOUX and PIEN), i, 1227.
inhibition of bumping in determination of nitrogen in (HANCE), i, 1032.
determination of nutritive requirements of (DENSCH and PFAFF), i, 1371.
determination of sulphur in (WOLKOFF), i, 224.
Soil solution, composition of (MARTIN and BURD), i, 1526, 1527.
Soja beans, culture of plants of (GINSBURG), i, 1121.
constituents of, and the iodine number of their oil (ANON.), i, 346.
oxidising enzymes in (NITZESCU and COSMA), i, 471.
lecithin and cephalin of (LEVENE and ROLF), i, 487.
urease from, and its hydrolytic action (TAUBMANN), i, 744.
Sols, orientation of particles in (ZOCHER), ii, 966.
Solids, properties and structure of (FRIEDERICH), ii, 374.
fluorescence of (GYEMANT), ii, 13.
electrification by friction between gases and (PERUCCA), ii, 1028.
specific inductive capacity of (ERRERA), ii, 362.
corresponding temperatures for (BRODSKY; LAFUMA), ii, 26.
contraction constants of (BALANDIN), ii, 637.
contraction regularities in the formation of compound (SAŠLAVSKY), ii, 933.
angles of contact and polarity of surfaces of (ADAM and JESSOP), ii, 962.
internal pressure of (RICHARDS), ii, 362.
solution of, in liquid surfaces (VOLMER and MAHNERT), ii, 508.
rôle of water in (BALAREFF), ii, 409.
velocity of dissociation of (CENTNERSZWER and BRUŽs), ii, 685.
reactivity of (HEDVALL), ii, 125; (HEDVALL and HEUBERGER), ii, 306.
reactions of (BALAREFF), ii, 893.
binary, density of (PANICHI), ii, 493.
incandescent, photoelectric action of light from (BECKER), ii, 1107.

Solid state, complexity of (SMITS and SCHOENMAKER), ii, 267 ; (SMITS and RUTGERS), ii, 268.
Solid solutions. See Solutions, solid.
Solubility, determination of, at high pressures (COHEN and VAN DER BOSCH), ii, 283.
apparatus for determination of (COHEN, DE MEESTER, and MOESVELD), ii, 151.
heat of solution and lattice energy of salts (BUTLER), ii, 39.
influence of pressure on (COHEN, DE MEESTER, and MOESVELD), ii, 852.
influence of salts on (v. EULER and RUDBERG), ii, 207.
of ampholytes (v. EULER and RUDBERG), ii, 853.
of isomerides (JOHNSTON ; ANDREWS, KOHMAN, and JOHNSTON), ii, 852 ; (ANDREWS ; KOHMAN), ii, 1052 ; (KOHMAN and ANDREWS), ii, 1053.
in mixed liquids (PLEUGER), ii, 283.
of bi-bivalent salts in solutions containing a common ion (WALKER), ii, 769.
Solubility of sparingly soluble substances (REMY and KUHLMANN), ii, 30, 119.
maximum, conditions of (COLSON), ii, 37.
Solutes, ionised, interionic attraction theory of (NOYES and BAXTER ; DEBYE and PAULING), ii, 970.
Solution, contraction of volume on (RAKSHIT), ii, 238.
Solutions, potential differences of, at the boundaries of (FRICKE and ROHMANN), ii, 41.
electrons in (PISARSHEVSKI), ii, 210.
of low dielectric constant, electrolytes in (GROSS and HALPERN), ii, 1152.
specific heat of (DE KOLOSOVSKI), ii, 870.
effect of viscosity on (DE KOLOSOVSKI), ii, 653.
viscosity of (DE KOLOSOVSKI), ii, 765.
compressibility of (KAR), ii, 970.
deviations of, from van't Hoff's law (SWIENTOSLAWSKI), ii, 388.
hydrate theory of (TAYLOR), ii, 858.
molecular contraction in (RAKSHIT), ii, 765.
interaction in (ADAM and JESSOP), ii, 772.
expression for reaction of (GIRIBALDO), ii, 325.
velocity of bimolecular reactions in (CHRISTIANSEN), ii, 47.
films on surfaces of (SCHOFIELD and RIDEAL), ii, 960.
Solutions, spectroscopic determination of complexes in (JOB), ii, 389.
aqueous, absorption of ultra-violet light by (GRIEVESON), ii, 472.
specific heat of (RICHARDS and GUCKER), ii, 848.
effect of temperature on the internal friction and conductivity of (WIEN), ii, 931.
dimensions of ions in (JABŁCZYŃSKI), ii, 33.
determination of complex salts or ions in (PATTERSON and DUCKETT), ii, 389.
of strong electrolytes, theory of (HÜCKEL), ii, 513.
effect of temperature on dielectric constants of (KOCKEL), ii, 932.
surface tensions of, against oils (HOWARD and SOLLMAN), ii, 109.
dilute, electrical conductivity of (REMY), ii, 299.
very dilute, ultra-violet adsorption spectra of (SUHRMANN and HUPPERT), ii, 773.
non-aqueous, electrochemistry of (MÜLLER, HÖLZL, KNAUS, PLANISZIG, and PRETT), ii, 133 ; (MÜLLER, HÖNIG, and KONETSCHNIGG), ii, 134 ; (MÜLLER, PINTER, and PRETT), ii, 882.
decomposition potentials of (FINKELSTEIN), ii, 546.
ultrafiltration of (BECHHOLD and SZIDON), ii, 529.
of non-volatile solutes, vapour pressure of (MALI), ii, 850.
sensitive, apparatus for evaporation of (SCHMALFUSS and KALLE), ii, 320.
solid (BRUNI and LEVI), ii, 281 ; (BRUNI), ii, 380.
theory of (LASAREV), ii, 1144.
electrical conductivity of (CUY), ii, 378.
standard, preparation of (PREGL), ii, 998.
supersaturated (FISCHER), ii, 853.
true, structure of (v. WEIMARN), ii, 1055.
Solvents, theory of systems of (GERMANN), ii, 1143.
influence of, on rotatory power (LUCAS), ii, 712.
selective action of (WRIGHT), ii, 1144.
distribution of a solute between (SCHULZ), ii, 956.
mixed, velocity of reaction in (JONES, MCCOMBIE, and SCARBOROUGH), ii, 137 ; (MCCOMBIE, ROBERTS, and SCARBOROUGH), ii, 554.
organic, solubilities of metallic salts in (MÜLLER), ii, 380.

Somatoid forms (KOHLSCHÜTTER and EGG), ii, 1035.
d-**Sorbitol**, oxidation of, with bromine water (TALEN), i, 1382.
Sorbose, formation of, from formaldehyde (KÜSTER and SCHODER), i, 366.
d-**Sorbose**, preparation of, by oxidation of *d*-sorbitol (TALEN), i, 1382.
Sound, velocity of, in liquids and their heat of vaporisation (IONESCU), ii, 644.
Soy. See Soja.
Sparteine, detection of (COUCH), ii, 448.
Spathulatine, and its derivatives (COUCH), i, 61.
Spectra, complex structure of (GOUDSMIT), ii, 725.
multiplet structure in (BRAMLEY), ii, 831.
quantum theory of red displacement in (KUDAR), ii, 467.
periodicity in structure of (MEGGERS), ii, 258.
excitation of, by impact of electrons (HERTZ and DE VISSER), ii, 338.
excitation of forbidden lines in (FOOTE, TAKAMINE, and CHENAULT), ii, 916.
broadening of lines in (HOLTSMARK and TRUMPY), ii, 338.
fine structure of lines in (VALLARTA), ii, 449; (RUARK and CHENAULT), ii, 1103.
intensities of lines in (KEMBLE), ii, 178; (TAMM), ii, 1023; (FOWLER), ii, 1104.
inter-combination lines in (BOUMA), ii, 915.
multiplet lines in (RUSSELL; RAMAN and DATTA), ii, 614.
intensity of multiplet lines in (ORNSTEIN and BURGER), ii, 251; (FERMI), ii, 340; (SOMMERFELD and HÖNL), ii, 468; (KRONIG), ii, 458, 917; (RUSSELL), ii, 725; (ORNSTEIN), ii, 916; (BACK), ii, 917.
Zeeman patterns in (Hicks), ii, 3.
influence of an electric field on Zeeman effect in (UREY), ii, 170.
doublets and triplets in (SUGIURA), ii, 726.
absorption maxima in, determined spectroscopically and spectrophotometrically (GOMBOS), ii, 178.
in relation to the polarisability of the atom-core (SCHRÖDINGER), ii, 722.
of atoms of the same electronic structure (HARTREE), ii, 2; (BOWEN and MILLIKAN), ii, 916.
of elements from scandium to nickel (HUND), ii, 912.
of the lighter elements, primed terms in (LAPORTE), ii, 1104.
Spectra of explosive mixtures of oxygen, nitrogen, and acetylene (GARNER and SAUNDERS), ii, 627.
of exploded wires (SMITH), ii, 1017.
absorption, of aldehydes and ketones (LECOMTE; PURVIS), ii, 627.
and constitution of colouring matters (KEHRMANN and SANDOZ), i, 983.
dispersion and density of homologous compounds (KRETHLOW), ii, 1029.
of ketones (PLOTNIKOV), ii, 837; (LANGEDIJK), ii, 1116.
of mixed metal vapours (BARRATT), ii, 927.
of non-polar compounds and unsaturated ketones (SCHEIBE, RÖSSLER, and BACKENKÖHLER), ii, 352.
infra-red (MÁRTON), ii, 1025.
of alcohols (LECOMTE), ii, 351.
of organic ammonia compounds (BELL), ii, 928.
ultra-red (BONINO), ii, 838.
ultra-violet, photography of (CROSS), ii, 351.
photometric measurement of (LEY and VOLBERT), ii, 78.
of very dilute solutions (SUHRMANN and HUPPERT), ii, 773.
of organic acids (VLÈS and GEX), ii, 472.
of benzene derivatives (KLINGSTEDT), ii, 929.
of metallic halides (GETMAN), ii, 837.
of organic compounds (MARCHLEWSKI and MOROZ), ii, 353.
K-absorption, and chemical constitution (STELLING), ii, 935, 936.
L-absorption (NISHINA), ii, 457.
arc, broadening of lines in (LOWERY; JOHNSON), ii, 614.
complexity of lines in (ROYDS), ii, 249.
excitation of forbidden lines in (FOOTE, TAKAMINE, and CHENAULT; TAKAMINE and FUKUDA), ii, 166.
Stark effect in (NAGAOKA and SUGIURA), ii, 171.
of the platinum metals (MEGGERS), ii, 454.
arc and spark, *s*-terms in (v. WIŚNIEWSKI), ii, 449.
displacement law for (MEGGERS, KIESS, and WALTERS), ii, 77.
Döppler effect in (KREFFT), ii, 78.
band (DALTA), ii, 86.

Spectra, band (MECKE), ii, 259, 351, 736; (DESLANDRES), ii, 736, 1023, 1114; (DUFFIEUX), ii, 1023; (DUFFENDACK), ii, 1114.
quantum theory of (BLACKBURN), ii, 260.
structure and distribution of (DESLANDRES), ii, 626, 930.
nature of (NICHOLSON), ii, 930.
isotope effect in (MULLIKEN), ii, 259, 346, 833, 1020.
intensities in (FOWLER), ii, 623; (MECKE), ii, 626; (DIEKE), ii, 626, 836; (HÖNL and LONDON), ii, 1024.
in relation to molecular properties (KRATZER), ii, 836.
band emission, of aromatic compounds (MARSH), ii, 470, 625.
cathode, of metals and their salts (KIMURA and NAKAMURA), ii, 166, 167.
comet tail (LEMON), ii, 249.
complex (HUND), ii, 1104.
continuous, of halogens (STEUBING), ii, 452.
diffraction, oscillation phenomena in (BUCHWALD), ii, 1117.
flame, intensity measurements in (BLEEKER and BONGERS), ii, 77; (BLUKER), ii, 1025.
fluorescence (BAYLE, FABRE, and GEORGE), ii, 260; (NUNAN and MARSH), ii, 353.
infra-red (WITT; TROWBRIDGE), ii, 335.
band, constants of (FERMI), ii, 471.
magnetic, study of (NIKITIN), ii, 173.
mass (ASTON), ii, 618.
of light elements (COSTA), ii, 1021.
β-ray (THIBAUD), ii, 622.
γ-rays, study of, by crystal diffraction (THIBAUD), ii, 176.
Röntgen ray (LEVI), ii, 456; (LEIDE; RÉCHOU; RAY; v. WIŚNIEWSKI), ii, 457; (BÄCKLIN, SIEGBAHN, and THORÆUS), ii, 614.
intensities in (ROBINSON), ii, 728.
energy levels of (COSTER), ii, 458.
semi-optical lines in (BÄCKLIN, SIEGBAHN, and THORÆUS), ii, 457; (DE BROGLIE and DAUVILLIER), ii, 458.
$L\alpha$-doublets in (RAY), ii, 78.
from a ruled reflection grating (COMPTON and DOAN), ii, 1103.
effect of a surrounding box on (COMPTON and BEARDEN), ii, 1167.
Spectra, Röntgen ray, of aliphatic acids (DE BROGLIE and TRILLAT), ii, 640.
of elements from aluminium to calcium (BÄCKLIN), ii, 914.
of light elements, K lines in (TURNER), ii, 915.
of long-chain organic compounds (SHEARER), ii, 938.
quantitative analysis by means of (COSTER and NISHINA), ii, 324.
continuous (MARCH), ii, 614; (BRONSTEIN), ii, 727.
doublet (WENTZEL), ii, 728.
Röntgen-spark (WENTZEL), ii, 251.
resonance fluorescence, Döppler effect in (RUMP), ii, 473.
series (BOWEN and MILLIKAN), ii, 252.
quantum numbers and (LINDSAY), ii, 915.
spark (WERNER), ii, 165.
in the Schumann region (L. and E. BLOCH), ii, 726.
classification of enhanced lines in (KIMURA and NAKAMURA; KIMURA), ii, 726.
Tesla-luminescence (MCVICKER, MARSH, and STEWART), ii, 12, 86, 630.
ultra-violet, visual perception of lines in (STEUBING), ii, 449.
screening doublets in (UNSÖLD), ii, 1016.
intensity of (DORGELO), ii, 335.
of alkali metal (SHAVER), ii, 451.
emission, of halogens (LUDLAM and WEST), ii, 350.
spark (LANG), ii, 609.
Spectrochemistry of aromatic polynuclear hydrocarbons (v. AUWERS and KRAUL), i, 900.
of nitrogen compounds (v. AUWERS and KRAUL), ii, 847.
ultra-red (BONINO), ii, 1032.
Spectrograph, Röntgen ray (CORK), ii, 250; (MÜLLER), ii, 895.
Spectrometer, colour vision (PEDDIE), ii, 1118.
Spectrophotometer, direct-reading (KEUFFEL), ii, 1193.
Spectroscope, lighting unit for (FREDERICK and WEBSTER), ii, 588.
Spectroscopy, shift law in (FUES), ii, 340.
new apparatus for (LEISS), ii, 341.
electric and magnetic (ARKADIEV), ii, 750.
Sperm oil, constitution of tetradecenoic acid from (TSUJIMOTO), i, 1128.
Arctic, unsaponifiable matter of (TSUJIMOTO), i, 772.

Spermine, isolation of, and its salts and derivatives (DUDLEY, M. C. and O. ROSENHEIM), i, 294.
phosphate, isolation of, from semen and testis (ROSENHEIM), i, 180.
Sphagnum, acidity of salt solutions after shaking with (SKENE and STUART), i, 765.
Sphingosine (LEVENE and HALLER), i, 890.
Spiræa, monotropitin in roots of species of (BRIDEL), i, 347.
Spirans (LEUCHS and SANDER), i, 1432.
synthesis of (RADULESCU and GEORGESCU), i, 819.
colour of (RADULESCU), i, 1159.
Spleen, formation of bile pigments in (ERNST and SZAPPANYOS; ERNST; ERNST and FÖRSTER), i, 732.
production of urea in autolysis of (McCANCE), i, 472.
effect of removal of, on blood-sugar (BIERRY, RATHERY, and LEVINA), i, 857.
Splenomegaly. See Gaucher's disease.
Squill, African. See *Urginea Burkei*.
Stability of organic compounds (BOLIN), ii, 411.
Staining of tissues (GICKLHORN and KELLER), i, 468.
Standard solutions. See Solutions, standard.
Stannic salts. See under Tin.
Stannous salts. See under Tin.
Staphylococcus, action of bismuth on (LEMAY and JALOUSTRE), i, 206.
Starch (LING and NANJI), i, 516, 517; (PRINGSHEIM and LEIBOWITZ), i, 1043; (PRINGSHEIM, LEIBOWITZ, and SILMANN), i, 1244.
formation of, from arabinose by plants (POLONOVSKI and MORVILLEZ), i, 1222.
constitution of (KUHN), i, 11, 636.
elasticity and tensile strength of (NEALE), ii, 783.
hydrolysis of (BIEDERMANN and JERNAKOFF), i, 11; (KARRER), i, 1370.
action of polarised light on (BALY and SEMMENS), i, 12; (JONES), i, 1212.
adsorption of iodine by (ANGELESCU and MIRCESCU), ii, 1149.
absorption of water by films of boiled (FARROW and SWAN), ii, 506.
swelling of, in cells (LEPESCHKIN), i, 1004.
swelling of granules of (ARZICHOVSKI), ii, 967.
saccharification of, by amylase (PETIT and RICHARD), i, 1504.
Starch, decomposition of, by bacteria (SIEDICH), i, 1510.
action of diastase on (LECOQ; DE HOOP and VAN LAER), i, 470.
colloidal, properties of (SAMEC), ii, 1153.
paste, liquefaction of (PETIT), ii, 967.
capillary flow of (FARROW and LOWE), ii, 509.
sols, properties of (KRUYT and TENDELOO), ii, 113.
iodide, composition of (MURRAY), i, 889.
determination of (CHRZASZCZ), ii, 74.
Stearaldehyde *p*-nitrophenylhydrazone (STEPHEN), i, 1131.
Stearic acid, crystal structure of (MULLER), ii, 748.
mixtures of eicosoic acid and (MORGAN and BOWEN), i, 114.
calcium salt (KLIMONE, v. MOLTINI, and BENEDIK), i, 506.
solubility of (HARRISON), ii, 190.
sodium salt, emulsifying power of (YAJNIK and ILAHI), ii, 968.
thallium salt (HOLDE and SELIM), i, 504.
Stearic acid, *di*bromo*di*iodo- and *di*iodo*di*hydroxy- (HOLDE and GORGAS), i, 883.
β-hydroxy-, and its ethyl ester, and hydrazide (LEVENE and HALLER), i, 890.
γ-hydroxy- (CLUTTERBUCK), i, 5.
*di*hydroxy-, oxidation of (LAPWORTH and MOTTRAM), i, 1234.
Stearolic acid, crystal structure of (MULLER), ii, 748.
hydration of (ROBINSON), ii, 745.
N-**Stearylpropylenediamine** (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 1133.
Stereochemistry (WALDEN), i, 349.
studies in (HOLMBERG and MÜLLER), i, 1236; (HOLMBERG), i, 1238; (HOLMBERG and ROSÉN), i, 1291.
of aromatic compounds (KUHN and JACOB), i, 1404.
Stereoisomerism and permeability (OKAGAWA), i, 711.
of aromatic compounds (KUHN and JACOB), i, 1260.
Steric hindrance (FREUDENBERG and HUBER), i, 229.
Steric series (FREUDENBERG and MARKERT), i, 1275.
Sterol, $C_{34}H_{58}O$, and its acetate, from American cotton wax (CLIFFORD and PROBERT), i, 879.
Stibinic acids, aromatic, complex metallic compounds of (CHEMISCHE FABRIK VON HEYDEN), i, 87.

Stigmastane (WINDAUS and BRUNKEN), i, 394.
Stigmastanol. See Tetrahydrostigmasterol.
Stigmastanone, and its derivatives (WINDAUS and BRUNKEN), i, 394.
Stigmasterol (WINDAUS and BRUNKEN), i, 394.
Stilbazole methiodide (KOENIGS, KÖHLER, and BLINDOW), i, 834.
2-Stilbazole, *cis-* and *trans*-2′-amino-, and -2′-nitro-, and their derivatives (RÄTH and LEHMANN), i, 432.
Stilbene hydrate (ISHIBASHI), i, 1432.
Stilbene, 4-iodo-2-nitro-, and 2:4-*di*-nitro-2′-hydroxy- (GULLAND and ROBINSON), i, 1188.
2-nitro-4′-amino-4-cyano-, and its hydrochloride and derivatives (PFEIFFER, KALCKBRENNER, and BEHR), i, 549.
2′:4′-*di*nitro-3:4-*di*hydroxy-, methylene ether (DEY and ROW), i, 954.
Stilbene-α-carboxylic acid, derivatives of (DEY and ROW), i, 954.
Stilbene-4-carboxylic acid, 2-nitro-4′-amino-, and its salts and derivatives (PFEIFFER, KALCKBRENNER, and BEHR), i, 549.
Stilbenediazonium hydrogen sulphate, nitro- (GULLAND and ROBINSON), i, 1188.
Stilbenediol, potassium salt (SCHEUING and HENSLE), i, 27.
Stirring apparatus, test of efficiency of (ROTH), ii, 150.
Strawberry, non-volatile acids of (NELSON), i, 762.
Streptococcus, action of bismuth on (LEMAY and JALOUSTRE), i, 206.
Strontium, structure of (COLLINS), ii, 733.
pure, preparation of (DANNER), ii, 62.
photo-electric effect on (DÖPEL), ii, 832.
Strontium alloys with mercury, electrodes of. See Electrodes.
Strontium chloride, refractive power of, for *X*-rays (MARK and TOLKSDORF), ii, 933.
selenide, crystal structure of (SLATTERY), ii, 369.
Strontium detection:—
detection of (KOLTHOFF), ii, 1095.
detection of, in presence of barium (FEIGL), ii, 435.
Strophanthidin, structure of (JACOBS and COLLINS), i, 1082.
ψ-Strophanthidin (JACOBS and COLLINS), i, 567.
Strophanthin (JACOBS and COLLINS), i, 566, 1082.
toxicity of (Tocco-Tocco), i, 613.
Strophanthus letei, saponin from (WELLS and GARCIA), i, 614.
Strychnine (LIONS, PERKIN, and ROBINSON), i, 831.
arsenious tartrate (DEBUCQUET), i, 1090.
Strychnos, determination of alkaloids in preparations of (SABALITSCHKA and JUNGERMANN), ii, 608.
Strychnos alkaloids (LEUCHS and KANAO), i, 61; (LEUCHS and TAUBE), i, 1314.
Sturgeon. See *Acipenser sturio*.
Styphnic acid, methyl ester, pyridine and quinoline salts (KÖHN and LÖFF), i, 1265.
Styrene (*phenylethylene*), α-chloro- (DUFRAISSE and VIEL), i, 1138.
Styrylacrolein. See ε-Phenyl-$\Delta^{\beta\delta}$-pentadien-α-al.
Styryl amyl ketone, and its oxime (RYAN and SHANNON), i, 558.
2-Styryl-3-*o*-anisolesulphonyl-2-methylquinoline, and its hydrochloride (TRÖGER and BROHM), i, 1453.
Styrylbenzopyrylium salts (WALKER and HEILBRON), i, 693; (HEILBRON, WALKER, and BUCK), i, 694.
Styryl*di*chloroarsine, α-chloro- (HUNT and TURNER), i, 844.
2-Styrylchromanol, derivatives of (ROBINSON and SHINODA), i, 1301.
2-Styrylchromone, 3:7-*di*- and 3:5:7-*tri*-hydroxy- (ROBINSON and SHINODA), i, 1301.
Styryl *p*-methoxystyryl ketone, *m*-amino- and *o*- and *p*-nitro- (PFEIFFER, PRAHL, FITZ, and STOLL), i, 680.
Styryl *p*-methoxystyryl ketones, amino-, and their *per*chlorates (PFEIFFER), i, 410.
2-Styryl-4-methylbenzopyrylium chloride, 4′:7-*di*- and 3′:4′:7-*tri*-hydroxy- (HEILBRON, WALKER, and BUCK), i, 694.
Styryl methyl ketone (*benzylideneacetone*), absorption spectra of (PURVIS), ii, 627.
oxide (WEITZ), i, 408.
and *o*-chloro-, and *o*-hydroxy-, hydrazones of (v. AUWERS and KREUDER), i, 1455.
Styryl methyl ketone, chloro-oximino-, and its derivatives (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132
α-thiocyano-, and its *di*bromide (CHALLENGER and BOTT), i, 936.
Styryl methyl ketone-*p*-arsinic acid, semicarbazone (MARGULIES), i, 448.
2-Styryl-1-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), i, 1321.

Styryl nitrocinnamylidenemethyl ketones (PFEIFFER), i, 409.

2-Styrylpyridine, 4:6-*di*chloro-5-cyano-, and its dimeride (SPÄTH and KOLLER), i, 1446.

2-Styrylquinoline, derivatives of (PFEIFFER, RHEINBOLDT, and WOLF), i, 412.

2- and **4-β-Styrylquinolines**, hydroxy-derivatives, and their salts (TRÖGER and DUNKER), i, 433.

Sub-electrons (DAECKE), ii, 258, 349.

Sublimation, devices for (JOHN and FISCHL), ii, 897.

Submaxillary glands, metabolism of phosphoric acid in (CAMIS), i, 191.

Substance, $C_3H_5O_3NS$, from lactamide and thionyl chloride (BERGMANN and MIEKELEY), i, 235.

$C_3H_4O_2NCl$, from dichlorourethylane and hydrogen chloride (MELDRUM and ALIMCHANDANI), i, 1273.

$C_4H_4O_3N_2$, from diketopiperazine and hypobromite (GOLDSCHMIDT and STEIGERWALD), i, 1109.

$C_5H_3OCl_5$, from *m*-aminophenol and sulphuryl chloride (ELLER and LORENZ), i, 538.

$C_5H_9O_4ClS$, from ethyl lactate and thionyl chloride (BERGMANN and MIEKELEY), i, 235.

C_6H_9OCl, from chlorine monoxide and *cyclo*hexene (GOLDSCHMIDT and SCHÜSSLER), i, 498.

$C_{10}H_{18}O_2$, from lemon oil (ROMEO), i, 1293.

$C_{10}H_{13}ON_2Br$, from α-bromocinnamaldehyde and methylhydrazine (v. AUWERS and OTTENS), i, 1429.

$C_{11}H_{18}O_2Cl_6$, from condensation of acetone and chloroform (TAFFE), i, 2.

$C_{12}H_{16}O_2$, from oil of Appa grass (MOUDGILL), i, 945.

$C_{13}H_{10}ON_2Se$, from phenylpiaselenazonium chloride and alkalis (BATTEGAY and VÉCHOT), i, 1467.

$C_{13}H_{14}O_5N_2$, from tryptophan in the body (MATSUOKA and YOSHIMATSU), i, 731.

$C_{14}H_{14}O_2$, from chloroacetic acid and magnesium phenyl bromide (PETERS, GRIFFITH, BRIGGS, and FRENCH), i, 544.

$C_{14}H_{18}O_7$, from carbon dioxide and dimethylketen (STAUDINGER, FELIX, and HARDER), i, 786.

$C_{14}H_{19}N_3$, from 2:4-dimethylpyrrole, hydrogen chloride, and hydrogen cyanide (FISCHER and NENITZESCU), i, 835.

Substance, $C_{14}H_{12}O_5Cl_6$, and its derivatives, from *m*-hydroxytoluic acid and chloral hydrate (MELDRUM and ALIMCHANDANI), i, 1272.

$C_{15}H_{16}O_3$, from α-bromopropionic acid and magnesium phenyl bromide (PETERS, GRIFFITH, BRIGGS, and FRENCH), i, 544.

$C_{15}H_{14}ON_2$, from phenylhydrazine and derivatives of phenyl β-hydroxyvinyl ketone (v. AUWERS and SCHMIDT), i, 585.

$C_{15}H_{20}O_2N_2$, and its salts, from oxidation of eserethole (STEDMAN and BARGER), i, 293.

$C_{16}H_9ONS$, from oxidation of 4-hydroxy-2-nitrophenyl α-naphthyl sulphide (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 596.

$C_{16}H_{10}O_3N_2$, from 2-hydroxyanthraquinonyl-3-hydrazine and acetic anhydride (TANAKA), i, 1434.

$C_{16}H_{11}ON_3$, from oxidation of 1-benzeneazo-2-aminonaphthalene (CHARRIER, CRIPPA, TOIA, and BIANCHESSI), i, 590.

$C_{16}H_{28}ON_2$, and its dipicrate, from methylation of esoline ethyl ether (STEDMAN and BARGER), i, 293.

$C_{17}H_{28}O_3$, from bacterial decoompsition of cholic acid (KAZIRO), i, 1363.

$C_{17}H_{13}ON_3$, from *o*-nitro-α-phenylcinnamonitrile and potassium cyanide (BRAND and LOEHR), i, 684.

$C_{18}H_{24}O_{10}Cl_8$, from indene and chlorine monoxide (GOLDSCHMIDT and SCHÜSSLER), i, 498.

$C_{18}H_{30}O_3N_2$, and its salts, from methylation of esoline ethyl ether (STEDMAN and BARGER), i, 293.

$C_{19}H_{24}O_{10}$, from carbon dioxide and dimethylketen (STAUDINGER, FELIX, and HARDER), i, 786.

$C_{20}H_{11}O_3N$, from isatin and 4:5-benzcoumaran-3-one (FRIES and PUSCH), i, 569.

$C_{20}H_{27}O_3N_2P$, from lactophenine, anæsthesin, and phosphoryl chloride (WEIL), i, 157.

$C_{21}H_{18}N_4$, and its derivatives from aniline and 5-chloro-4-phenyl-1-*p*-tolyl-1:2:3-triazole and also from *p*-toluidine and 5-chloro-1:4-diphenyl-1:2:3-triazole (CARNELLEY and DUTT), i, 166.

$C_{21}H_{32}O_4$, from oxidation of methyl abietate (RUZICKA, MEYER, and PFEIFFER), i, 1420.

$C_{22}H_{26}O_4N_4$, from aminoantipyrine and acetylanæsthesin (WEIL), i, 157.

Substance, $C_{26}H_{38}N_4I_2$, from action of methyl iodide on calycanthine (SPÄTH and STROH), i, 1447.
$C_{27}H_{24}O$, from $\beta\beta$-diphenylpropionic acid and magnesium phenyl bromide (PETERS, GRIFFITH, BRIGGS, and FRENCH), i, 544.
$C_{28}H_{22}O_6$, from piperonal and *p*-methoxystyryl ethyl ketone (RYAN and CAHILL), i, 558.
$C_{28}H_{24}N_4$, from phenylacetonitrile and 3-cyano-2-methylindole (SEKA), i, 67.
$C_{28}H_{25}N_3$, and its derivatives, from 2-benzyl-1-hydrindone and phenylhydrazine (LEUCHS and WINZER), i, 1281.
$C_{28}H_{26}O_4$, from anisaldehyde and ketones (RYAN and CAHILL), i, 558.
$C_{28}H_{37}O_9N$, from oxidation of delphinin (KELLER), i, 831.
Substitution, influence of, on physical and chemical properties (RULE and PATERSON), i, 29.
effect of, on equilibria in binary systems (KREMANN and DRAZIL), ii, 649; (KREMANN, ZECHNER, and WEBER; KREMANN, ZECHNER, and DRAZIL), ii, 650.
in aromatic compounds (BARNETT, COOK, and MATTHEWS), i, 648.
influence of α-methoxyvinyl groups in (C. K. and E. H. INGOLD), i, 657.
directive influence of nitrogen and oxygen atoms in (HOLMES and INGOLD), i, 1142.
influence of nitroso groups in (INGOLD), i, 646.
in the aromatic nucleus (BARNETT and MATTHEWS), i, 18; (PRINS), i, 18, 379; (BARNETT and COOK), i, 123; (BARNETT, COOK, and MATTHEWS), i, 900, 1140, 1398.
in the benzene nucleus (FRANCIS, HILL, and JOHNSTON), i, 1141.
Succinamic acid, *d*-thiol- (LEVENE and MIKESKA), i, 6.
Succinic acid, electrolytic preparation of (NORRIS and CUMMINGS), i, 668.
dissociation constants of (BRITTON), ii, 977.
radical dissociation of aryl derivatives of (LÖWENBEIN and FOLBERTH), i, 552.
equilibria of, with phenols (KREMANN, ZECHNER, and DRAZIL), ii, 650.
oxidation of, in tissues (v. SZENT-GYÖRGYI), i, 93.
alkaline earth salts, solubilities of (WALKER), ii, 769.
Succinic acid, aniline trihydrogen salt (RAMBECH), i, 385.
lead salt, solubilities of (AUERBACH and WEBER), i, 1130.
di-*p*-tolyl and di-*m*-xylyl esters, and *di*bromo-, di-*p*-tolyl ester (FRIES and BARTENS), i, 568.
detection of, in tissues (KLEIN and WERNER), i, 871.
Succinic acid, thiol-, and its sodium salts (LEVENE and MIKESKA), i, 512.
d-thiol- (LEVENE and MIKESKA), i, 6.
Succinic acids, substituted, synthesis of (BAKER and LAPWORTH), i, 670.
Succinic acids, $\alpha\beta$-*di*amino-, stereoisomeric, and the dibenzoyl derivative of the *meso*-form (KUHN and ZUMSTEIN), i, 1249.
Succinimide, mercury derivatives of (LYONS), i, 645.
Succinimide, amino-, derivatives of (CHERBULIEZ and CHAMBERS), i, 1046.
iodo-, structure and crystallography of (YARDLEY), ii, 746; (TUTTON), ii, 747.
Succinimides, tetra-alkyl derivatives, and their pharmacological action (DOX), i, 796.
CC-substituted, preparation of (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING), i, 376.
Succinodehydrogenase, effect of potassium salts on (SAHLIN), i, 743.
Succinylfluorescein (DUTT and THORPE), i, 141.
Succinylrhodamine hydrochloride (DUTT and THORPE), i, 142.
Succinyl-*p*-tolil, nitration of (BRADY, QUICK, and WELLING), i, 1400.
Sucrose (*saccharose; cane-sugar*), rotatory dispersion of (LOWRY and RICHARDS), ii, 265.
configuration of (SCHLUBACH and RAUCHALLES), i, 1243.
effect of inorganic salts on the polarisation of solutions of (BROWN), ii, 372.
osmotic pressure of (APPLEBEY and DAVIES), ii, 964.
inversion coefficient of (SAILLARD), i, 1133.
catalysis and inversion of, by acetic acid (SAILLARD), ii, 307.
effect of dextrose and lævulose on the inversion of, by honey invertase (NELSON and SOTTERY), i, 104.
hydrolysis of (NELSON and BODANSKY), i, 1008.
hydrolysis constant of (COLIN and CHAUDUN), i, 233.

Sucrose (*saccharose; cane-sugar*), hydrolysis of, by invertase in presence of α-methylglucoside (NELSON and FREEMAN), i, 739.
solubility of (MONDAIN-MONVAL), ii, 769.
effect of catalysts on carbonisation of (LESSING and BANKS), i, 9.
acids resulting from yeast fermentation of (KOSTYTSCHEV and FREY), i, 1214.
determination of, oxidimetrically (TÄUFEL and WAGNER), ii, 1007.
Sugars, preparation of, by means of diphenylmethanedimethyldihydrazine (v. BRAUN and BAYER), i, 1382.
and their derivatives, rotation and structure of (HUDSON and PHELPS), i, 8; (HUDSON), i, 232, 233, 514, 636; (HUDSON and KUNZ), i, 1043.
theory of protective action of (SHRIVASTAVA, GUPTA, PRASAD, and BHATNAGAR), ii, 293.
nomenclature of isomeric (WOHL and FREUDENBERG), i, 366.
adsorption of, by colloidal solutions (PRASAD, SHRIVASTAVA, and GUPTA), ii, 957.
condensation of, with dilute mineral acids (LEVENE and ULPTS), i, 1042.
oxidation of alcohols from (VOTOČEK and LAKES), i, 773.
oxidation of, by permanganates (KUHN and WAGNER-JAUREGG), i, 1241.
relative reducing powers of (ROWE and WIENER), i, 885.
reduction of, by aluminium alloys (NANJI and PATON), i, 117.
unsaturated reduction products of (BERGMANN, MIEKELEY, and STATHER), i, 227; (BERGMANN), i, 887.
acetone fermentation of (SPEAKMAN), i, 1013.
fermentation of, by microbes (KLUYVER and DONKER), i, 1215.
constitution of the monocarboxylic acids derived from (PRYDE, HIRST, and HUMPHREYS), i, 865.
lactone formation from carboxylic acids of (LEVENE and SIMMS), i, 1380.
phosphorylation of (NEUBERG and KOBEL), i, 1508.
compounds of sulphuric acid with (OHLE and BOURJAN), i, 634.
and their derivatives, bismuth nitrates of (MASCHMANN), i, 527.
halogen acetyl derivatives of, and their optical rotation (BRAUNS), ii, 633.
Sugars, in blood. See under Blood.
in cerebro-spinal fluid, in relation to sugar in blood (GOODWIN and SHELLEY), i, 853.
in liver, effect of alcohols on (LESSER), i, 613.
in urine. See under Urine.
colloidal (v. WEIMARN), ii, 290, 390.
polymethylated, action of emulsin on (KUHN and SCHLUBACH), i, 863.
reducing, analysis of (RUOSS), ii, 244.
determination of (PICK), ii, 906.
determination of, volumetrically (LANE and EYNON), ii, 445.
analysis of (HILDT), ii, 244; (KLASON), ii, 331.
determination of, by Benedict's method (QUICK), i, 1115.
determination of, volumetrically (VAN DER HOEVEN), ii, 331.
Sulphæmoglobin, formation of (VAN DEN BERGH and WIERINGA), i, 1475.
Sulphatase (NEUBERG and SIMON; ROSENFELD), i, 743.
Sulphates. See under Sulphur.
Sulphinic acids, and their derivatives, action of hydroxylamine on (WHALEN and JONES), i, 802.
"**Sulphisatyd**," identity of 3-thioloxindole and (SANDER), i, 977.
Sulphites. See under Sulphur.
Sulphoacetaldehyde, chloro-, barium salt (LEPOUSE), i, 784.
Sulphoacetic acid, complex salts of (HAHN and WOLF), ii, 578.
Sulphoacetic acid, bromo-, resolution of (BAEKER and MOOK), i, 632.
chloro-, resolution of, and its salts (BACKER and BURGESS), i, 359, 631.
potassium salt, crystallography of (JAEGER), ii, 948.
3-Sulpho-5-arsinobenzenesulphamic acid, 2-hydroxy, barium salt (CHRISTIANSEN, NORTON, and SHOHAN), i, 1471.
Sulphobenzoic acid, metallic and triamine salts of (HAHN and WOLF), i, 814.
complex salts of (HAHN and WOLF), ii, 578.
α-Sulpho-β-benzoylpropionic acid, and its disodium salt (BOGERT and RITTER), i, 816.
Sulphonamides, aromatic *N*-halogenated, alkali salts (CHEMISCHE FABRIK VON HEYDEN), i, 380.
1-4′-Sulphonaphthaleneazo-2:4-*di*-hydroxynaphthalene, 1-amino- (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 988.

Sulphonium compounds, physiological activity and mobility of -onium ions in (BENCOWITZ and RENSHAW), ii, 872.
effect of, on the nervous system (HUNT and RENSHAW), i, 861.
2-*p*-Sulphophenyl-5-amino-6-methyl-1:3-benzotriazole, and its salts (BERETTA and JACOOB), i, 589.
1-*p*-Sulphophenyl-3-methyl-5-pyrazolone, preparation of (REEVES), i, 699.
1-*p*-Sulphophenyl-1:2:5-triazole-3:4-dicarboxylic acid, and its strontium salt (BERETTA and JACOOB), i, 589.
***d*-α-Sulphopropionic acid**, and its sodium salts (LEVENE and MIKESKA), i, 512.
5-Sulphopyrocatechol-4-carboxylic acid, barium salt (FICHTER and STOCKER), i, 240.
Sulphosuccinic acid, and its potassium salts (LEVENE and MIKESKA), i, 512.
***d*-Sulphosuccinic acid**, salts of (LEVENE and MIKESKA), i, 6.
***d*-Sulphosuccinmonoamide**, barium salt (LEVENE and MIKESKA), i, 6.
Sulphoxyl compounds (BINZ and BAUSCH), i, 991.
Sulphur, spectrum of (BUNGARTZ), ii, 609.
K-absorption spectrum of (ROBINSON), ii, 614.
absorption spectra and constitution of the vapour of (HENRI and TEVES), ii, 19, 87.
spectrum of electrodeless discharge in vapour of (SHAVER), ii, 471.
Röntgen ray spectra of, and its compounds (RAY), ii, 914.
series spectra of (BOWEN and MILLIKAN), ii, 342, 610.
spectral frequencies of (HOLWECK), ii, 336.
critical potential of (HOLWECK), ii, 729.
liquid, electrical properties of (BLACK), ii, 24.
valency of (LECHER), i, 390; (LECHER, KÖBERLE, and STÖCKLIN), i, 391; (STEINKOPF), i, 657.
colloidal, surface tension of (JOHLIN), ii, 1054.
sols, effect of salts on stability of (v. WEIMARN and UTZINO), ii, 664.
velocity of transformation of (FRAENKEL and GOEZ), ii, 557.
affinity of metals for (JELLINEK and ZAKOVSKI), ii, 401.
and its compounds, corrosion of metals by naphtha solutions of (WOOD, SHEELY, and TRUSTY), ii, 980.
interaction of nitrogen sulphide and (USHER), ii, 581.
Sulphur, as a fertiliser (KALUSHSKI), i, 492.
nacreous, physical properties of (WHITAKER), ii, 486.
precipitated, separation of, in analysis (AWSCHALOM), ii, 823.
Sulphur compounds, acid nature of (KARVÉ), ii, 1188.
Sulphur *monochloride*, decomposition of, by water (NOACK), ii, 989.
action of, on organic acid amides (NAIK and PATEL), i, 121.
action of, on thioamides (ISHIKAWA), i, 1149.
Disulphur *di*chloride, decomposition of, by water (NEUMANN and FUCHS), ii, 410.
Sulphuryl chloride (O. and C. A. SILBERRAD and PARKE), i, 1137.
catalysis of the formation of (CUSMANO), ii, 690.
thermal decomposition of (SMITH), ii, 876.
Disulphur *di*fluoride, preparation and properties of (CENTNERSZWER and STRENK), ii, 701.
Sulphur hydride. See Hydrogen Sulphide.
Sulphides, electrolytic preparation of (FISCHER), ii, 807.
analysis of mixtures of sulphites, thiosulphates and (KURTENACKER and BITTNER), ii, 239.
determination of, in alkali and alkaline earth sulphides (SCHULEK), ii, 327.
Sulphur *di*oxide, electrolysis in (CADY and TAFT), ii, 1073.
electrochemistry of oxidation by (CARTER and JAMES), ii, 134.
adsorption of, by glass (BANGHAM and BURT), ii, 657.
heat of adsorption of, by silica gels (PATRICK and GREIDER), ii, 870.
adsorption of, in water (WHITMAN and DAVIS), ii, 106; (SHERWOOD), ii, 852.
solubility of, in water and aqueous solutions of potassium chloride and sodium sulphate (HUDSON), ii, 768.
equilibrium of water and (TAMMANN and KRIGE), ii, 869.
solubility of mixtures of cetene and (SEYER and HUGGETT), ii, 504.
solubility of mixtures of *n*-hexane and (SEYER and GILL), ii, 504.
gaseous, photochemical decomposition of (HILL), ii, 56.
detection of (EEGRIWE), ii, 156.

Sulphur *sesqui*oxide (VOGEL and PARTINGTON), ii, 890.
*tri*oxide, pure, melting point and vapour pressure of (SMITS and SCHOENMAKER), ii, 267; (SMITS), ii, 268.
Sulphurous acid, and its salts (FOERSTER and KUBEL; FOERSTER, BROSCHE and NORBERG-SCHULZ), ii, 120.
absorption spectra of (DIETZEL and GALANOS), ii, 1115.
action of, on hydroxylamine (RASCHIG), ii, 225.
reactions of nitrous acid with (RASCHIG), ii, 146.
Sulphites, catalytic oxidation of (REINDERS and VLÈS), ii, 567.
action of, on nitro and nitroso compounds (RASCHIG), i, 239.
analysis of mixtures of sulphides, thiosulphates and (KURTENACKER and BITTNER), ii, 239.
determination of, by the action of oxidising agents (HENDRIXSON), ii, 1001.
acid, combination of ethylenic hydrocarbons with (KOLKER and LAPWORTH), i, 353.
action of, on nitro and nitroso compounds (RASCHIG), i, 239.
Sulphuric acid, catalytic action of platinum in the contact process for (CLARK, MCGRATH, and JOHNSON), ii, 1176.
passage of an alternating current through (LATTEY), ii, 979.
partial pressures of water in aqueous solutions of (GREENEWALT), ii, 493.
vapour pressure of aqueous solutions of (GROLLMAN and FRAZER), ii, 398.
absorption of hydrochloric acid by (CUPR), ii, 655.
free energy of, in sulphate solutions (HARNED and STURGIS), ii, 538.
solvolysis of salts in (DAVIDSON), ii, 505.
reduction of, to hydrogen sulphide (VILA), ii, 148.
Sulphates, formation of, from thiosulphates by soil bacteria (GUITTONNEAU), i, 1218.
viscosity of solutions of (GRUNERT), ii, 859.
action of oxidising agents on, and their determination (HENDRIXSON), ii, 712.
determination of, volumetrically (KLINKE), ii, 239.
determination of, in plant sap (GORTNER and HOFFMAN), i, 485.
Sulphur:—
Persulphuric acid, electrolytic preparation of (MAZZUCCHELLI), ii, 214.
Persulphates, reaction between iodides and, in gelatin (RAWLING and GLASSETT), ii, 561.
Thiosulphates, formation of, by microorganisms in soils (GUITTONNEAU), i, 766.
conversion of, into sulphates by soil bacteria (GUITTONNEAU), i, 1218.
reduction of ferric salts by (HOLLUTA and MARTINI), ii, 305, 702.
standardisation of solutions of (DIMITROV), ii, 598.
analysis of mixtures of sulphides, sulphites, and (KURTENACKER and BITTNER), ii, 239.
determination of, in alkali and alkaline earth sulphides (SCHULEK), ii, 327.
Thionic acids, constitution of (VOGEL), ii, 1189.
Polythionic acids, preparation, constitution, and properties of (RASCHIG), ii, 229, 230.
determination of (KURTENACKER and BITTNER), ii, 434.
Polythionates (KURTENACKER and KAUFMANN), ii, 1189, 1190.
formation and decomposition of (FOERSTER), ii, 148, 701; (FOERSTER and RIESENFELD), ii, 229.
Dinitrososulphonates (RASCHIG), ii, 226.
Sulphur organic compounds (SCHÖNBERG, ROSENBACH, KRÜLL, and OSTWALD), i, 1300.
Sulphur phenyl chloride. See Benzene, chlorothiol-.
Sulphides, cyclic (v. BRAUN, BAYER, and KAISER), i, 1445.
Polysulphides, organic (THOMAS and HARDING), i, 4, 113.
Sulphurous acid, organic derivatives, constitution of (RASCHIG), i, 245.
Thiosulphates, organic (HELLER), i, 313.
Sulphur determination:—
determination of (KÜHL), ii, 156.
determination of, microchemically (GEILMANN), ii, 1000.
determination of, in polysulphides (KURTENACKER and BITTNER), ii, 433.
determination of, in soils (WOLKOFF), i, 224.
Sulphur-blue, constitution of (BINZ and RÄTH), i, 445.
Sulphuric and **Sulphurous acids**. See under Sulphur.

Sunlight, tropical, photosynthesis in (DHAR and SANYAL), ii, 884.
Suprarenals, cholesterol content of (PARHON and MARZA), i, 1346.
Suprarenal powders, detection and determination of adrenaline in (BAILLY), ii, 248.
Surfaces, thermodynamics of (GAY), ii, 539.
Surface energy and adsorptive power of solids (ILJIN), ii, 856.
and adsorption at phase boundaries (ILJIN), ii, 958.
Surface tension (BRILLOUIN), ii, 496.
determination of (DU NOÜY), ii, 279; (CARVER and HOVORKA), ii, 647; (MOLODYI and PAVLOV), ii, 1142.
from capillary rise (SUGDEN), ii, 497.
cause of (KENNARD), ii, 1046, 1148; (ADAM), ii, 1046.
and the scattering of light by liquids (RAMAN and RAMDAS), ii, 952, 1046.
relation between heat of vaporisation and (PLÁCINTEANU), ii, 89.
relation between foaming power and (OSTWALD and STEINER), ii, 771.
effect of concentration on (SCHECHTMANN), ii, 1148.
and surface energy (WILLIAMS), ii, 386.
during esterification (CAUQUIL), ii, 964.
of aqueous solutions against oils (HOWARD and SOLLMAN), ii, 109.
of higher fatty acids (FRUMKIN), ii, 856.
measurement of, in biological fluids (BRINKMAN and VON DER VELDE), i, 468.
of crystals against saturated solutions (SOEP), ii, 1046.
of dilute electrolytes (WAGNER), ii, 387.
of liquid films (MARCELIN; DELAPLACE), ii, 772.
at interface of liquids (DU NOÜY), ii, 647.
of salt solutions, effect of capillary-active substances on (SEITH), ii, 961.
negative (ADAM and JESSOP), ii, 772.
Swelling (CLARKE), ii, 863.
measurement of (THIESSEN and CARIUS), ii, 520.
effect of alcohol on (LOEBENSTEIN), ii, 520.
of colloids (BILTZ), ii, 520; (KATZ and MARK), ii, 666.
[illegible] MOLENGRAAFF and HALL), ii, 64[illegible].
Symmetry, tetrahedral and octahedral, tridentate groups in (SMITH), ii, 841.
Syphilis (FORDYCE, ROSEN, and MYERS), i, 189, 611.
action of bismuth in (LEVADITI, NICOLAU, SALGUE, and SCHOEN), i, 463.
effect of "salluen" in (BERING), i, 858.
Systems; critical state for (GAY and PERRAKIS), ii, 669.
binary. See Binary systems.
disperse, viscosity of (OSTWALD), ii, 392.
giving colour changes (v. WEIMARN), ii, 390.
heterogeneous, velocity of reaction in, in relation to rate of stirring (KLEIN), ii, 802.
conjugated, additive character of (JONESCU), i, 1153.
metastable, velocity of transformation of, in relation to temperature (STEPANOV), ii, 645.

T.

Tadpoles, effect of carbamide on the nutrition of (KŘIŽENECKÝ and PODHRADSKÝ), i, 612.
Taka-diastase, hydrolysis by (HATANO), i, 201.
lipase from (OGAWA), i, 103.
Taka-esterase (WILLSTÄTTER and KUMAGAWA), i, 1213.
Taka-rennin (HATANO), i, 102.
Talc from Armenia (DITTLER), ii, 323.
Tallow, Rambutan, *n*-eicosoic acid from (MORGAN and HOLMES), i, 777.
***d*(-)-Talose**, and its derivatives (v. BRAUN and BAYER), i, 1382.
Talosebisdiphenylmethanedimethyldihydrazone (v. BRAUN and BAYER), i, 1382.
Tangentimeter (LATSHAW), ii, 428.
Tannins (FREUDENBERG and BLÜMMEL), i, 51; (FREUDENBERG, FIKENTSCHER, and HARDER), i, 419; (FREUDENBERG, FIKENTSCHER, and WENNER), i, 692; (FREUDENBERG, FIKENTSCHER, HARDER, and SCHMIDT), i, 1165.
autoxidation of (TSCHIRCH), i, 856.
reaction between carbohydrates and (STOCKS and GREENWOOD), i, 1165.
precipitation of gelatin by (SMORODINCEV and ADOVA), i, 847.
oakwood (FEIST and BESTEHORN), i, 566.
in ripening vine-shoots (PICARD), i, 346.

Tannins, analysis of, with ferrous tartrate reagent (WARE), ii, 444.
detection of, by the ferric citrate test (WARE), ii, 905.
detection of, in drugs (WARE), ii, 1209.
determination of, with cinchonine (HOOPER), ii, 443.
Tantalum, electron emission from (DUSHMAN, ROWE, EWALD, and KIDNER), ii, 345.
Tantalum *tri*chloride, derivatives of (RUFF and THOMAS), ii, 1187.
*penta*chloride, reduction of (RUFF and THOMAS), ii, 1187.
Tantalic acid, and its alkali salts (JANDER and SCHULZ), ii, 701.
Tantalum detection, determination, and separation :—
detection and determination of, and its separation from niobium (POWELL and SCHOELLER), ii, 1096.
determination of, and separation from iron (PIED), ii, 442.
Tar, low temperature, aromatic hydrocarbons in (KRUBER), i, 1137.
Taraktogenic acid, and its silver salt (HASHIMOTO), i, 1234.
Tartaric acid, preparation of (MILAS and TERRY), i, 780.
rotatory power of (VLÈS and VELLINGER), ii, 964.
in relation to hydrogen-ion concentration (VLÈS and VELLINGER), i, 356.
rotatory dispersion of derivatives of (AUSTIN and PARK), ii, 1028.
dissociation constants of (BRITTON), ii, 977.
second dissociation constant of (PAUL), ii, 116.
photochemical reaction between bromine and (GHOSH and MUKHERJEE), ii, 1179.
salts, administration and excretion of (SIMPSON), i, 1211.
amine antimonyl salts (CHRISTIANSEN and NORTON), i, 654.
aniline trihydrogen salt (RAMBECH), i, 385.
arsenyl salts with organic bases (DEBUCQUET), i, 973.
lead salt, solubilities of (AUERBACH and WEBER), i, 1130.
potassium and sodium salts, hydrates of (LOWRY and MORGAN), ii, 26.
potassium sodium salt (*Rochelle salt*), dielectric fatigue in (VALASEK), ii, 1118.
vapour pressure of (LOWRY and MORGAN), ii, 26.
properties of crystals of (ISELY; VALASEK), ii, 23.
Tartaric acid, sodium tribismuthyl salt (MASCHMANN), i, 527.
distinction of citric acid from (PARRI), ii, 162.
detection of, in tissues (KLEIN and WERNER), i, 871.
determination of (FRANÇOIS and LORMAND), ii, 75.
determination of, oxidimetrically (TÄUFEL and WAGNER), ii, 1007.
meso-**Tartaric acid**, hydrate of (AMADORI), i, 511.
Tartarobismuthic acid, sodium potassium salt, action of, on liver catalase (MAUBERT, JALOUSTRE, LEMAY, and ANDREOLY), i, 614.
Taurine, methylation and acetylation of (TERAOKA), i, 1390.
Tautomerism and additive reactions (INGOLD), i, 357.
and the mobility of hydroxyl groups (FARROW and INGOLD), i, 155.
of dyads (INGOLD), i, 779; (GRIFFITHS and INGOLD), i, 1190.
of heterocyclic compounds (HELLER, BUCHWALDT, FUCHS, KLEINICKE, and KLOSS), i, 1323.
keto-enolic (KAUFMANN and LIEPE), i, 1241.
ring-chain (DUTT and THORPE), i, 140; (KON, SMITH, and THORPE), i, 509; (ROTHSTEIN, STEVENSON, and THORPE), i, 884; (BAKER), i, 916.
three-carbon (KON and LINSTEAD), i, 506.
three-carbon, in the *cyclo*propane series (GOSS, INGOLD, and THORPE), i, 549.
Teeth, calcium salts in (LIESEGANG), i, 607.
effect of fluorides in diet of rats on (MCCOLLUM, SIMMONDS, BECKER, and BUNTING), i, 861.
Telluridiacetic acid, *di*chloro- (MORGAN and DREW), i, 530.
Tellurium, molecular weight of (JOUNIAUX), ii, 187.
optical constants of (MILLER), ii, 751.
reduction potential of, and the energy and heat of formation of the dioxide (SCHUMANN), ii, 670.
vapour pressure of (DOOLAN and PARTINGTON), ii, 278.
crystal structure of (SLATTERY), ii 369.
hydrosols, coagulation of, by electrolytes (DOOLAN), ii, 293.
Tellurium compounds, acid nature of (KARVE), ii, 1188.
Tellurium *tetra*chloride, interaction of acetic anhydride with (MORGAN and DREW), i, 530.

Tellurium *sub*oxide (DAMIENS), ii, 316.
*di*oxide, fused, electrocapillarity of (SIMEK and KADLCOVA), ii, 678.
Tellurium organic compounds (MORGAN and TAYLOR), i, 634.
Tellurium β-diketones, bactericidal action of (MORGAN, COOPER, and CORBY), i, 206.
O-ethyldi*iso*butyrylmethane trichloride (MORGAN and TAYLOR), i, 634.
n-nonylacetone trichloride (MORGAN and TAYLOR), i, 634.
Tellurium determination and separation:—
determination of, and separation from selenium (LENHER and KAO), ii, 434.
Tellurodiacetic acid, and its salts (MORGAN and DREW), i, 530.
Temperature, relation of, to density (HERZ), ii, 494, 1141.
corresponding, of solids (BRODSKY; LAFUMA), ii, 26.
high, equilibria at (PUSHIN and GREBENSHCHIKOV), ii, 38; (v. WARTENBERG), ii, 576.
low, constant (SLIGH), ii, 756.
thermodynamic, of gases (WERTHEIMER), ii, 784.
Temperature coefficients and mechanism of chemical reactions (RICE, FRYLING, and WESOLOWSKI), ii, 48.
Terephthalic acid, 2-amino- and 2-nitro-, diethyl and diethylaminoethyl esters, and their hydrochlorides (SODERMAN and JOHNSON), i, 814.
Terephthaloyl chloride, nitro- (SODERMAN and JOHNSON), ii, 814.
Ternary systems, equilibria in (SCHREINEMAKERS), ii, 869.
graphic representation of (URAZOV), ii, 788.
Terpenes (VESTERBERG and BORGE), i, 252; (KONDAKOV and SAPRIKIN), i, 1163, 1292.
Terpenes, and their derivatives, catalytic hydrogenation of (ARMSTRONG and HILDITCH), ii, 563.
autoxidation of (TSCHIRCH), i, 356.
catalytic oxidation of (RAO), i, 687.
dicyclic, structure of (SŁAWINSKI), i, 48.
Terpene compounds (RUZICKA and CAPATO), i, 943.
higher (RUZICKA and PFEIFFER; RUZICKA, MEYER, and PFEIFFER), i, 1419.
α-Terpineol, resolution of, and its esters (FULLER and KENYON), i, 48.
Terpineols, relation between pinenes and (DUPONT), i, 564.
Testicles of cattle, lipoids in (SORG), i, 457.
Testicles, cholesterol content of (PARHON and MARZA), i, 1346.
effect of injection of emulsions of, on metabolism (KORENCHEVSKY and CARR), i, 1513.
spermine phosphate from (ROSENHEIM), i, 180.
Test-tube stand, improved (PATTERSON), ii, 151.
Tetany, etiology of, in children (ANDERSON and GRAHAM), i, 330.
effect of cod-liver oil on metabolism in (LIU), i, 725.
parathyroid, and its effect on calcium of the blood (CAMERON and MOORHOUSE), i, 857.
Tetra-acetoxy*di*chlorodititanium chloride (GIUA and MONATH), i, 531.
Tetra-acetoxy*di*hydroxydititanium chloride (GIUA and MONATH), i, 531.
Tetra-acetyldextrose-1-pyridinium tetra-acetyldextrose ζ-sulphate (OHLE and BOURJAN), i, 634.
Tetra-acetylmucic acid, salts and methyl ester of (SIMON and GUILLAUMIN), i, 116.
Tetra-allylammonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 495.
α-Tetra-amylose nitrates (PRINGSHEIM, LEIBOWITZ, and SILMANN), i, 1244.
Tetra-anhydrotetrakisdiphenylgermanediol (MORGAN and DREW), i, 1197.
Tetra-anisylethylene sulphide (SCHÖNBERG, ROSENBÄCH, KRÜLL, and OSTWALD), i, 1301.
Tetra-arsenoacetic acid, sodium salt, therapeutic action of (BARBOUR, RIDOUT, and CLAYDON), i, 733.
Tetrabenzylmethane (TROTMAN), i, 383.
Tetra-(4-carbethoxy-2:3-dimethylpyrryl) ethane (FISCHER and BELLER), i, 1333.
Tetra-(4-carbethoxy-2:3-dimethylpyrryl) ethylene (FISCHER and BELLER), i, 1333.
Tetracarbethoxyellagic acid (FEIST and BESTEHORN), i, 566.
Tetrachlorodioxyruthenic acid. See under Ruthenium.
Tetradecenoic acid from sperm oil (TSUJIMOTO), i, 1128.
9:10-Tetraethyl*di*amino-9:10-dihydroanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
Tetraethylammonium iodide, concentration cells containing (GRANT), ii, 301.
compound of iodoform and (STEINKOPF and BESSARITSCH), i, 495.

βγε(ζ)-6-Tetraethylglucose (HESS and SALZMANN), i, 1383.
Tetraethylmethane. See γγ-Diethylpentane.
Tetraethylsuccinic acid, imide and nitrile of (DOX), i, 797.
Tetrahydroacridine, and amino-, chloro-, and nitro-, and their derivatives (PERKIN and SEDGWICK), i, 63.
Tetrahydroacridone, amino- and nitro-derivatives, and their derivatives (PERKIN and SEDGWICK), i, 64.
1:2:3:4-Tetrahydroanthracene, derivatives of (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 128.
Tetrahydroanthranil, *C*-amino-, and its derivatives (v. AUWERS, BAHR, and FRESE), i, 312.
1:2:3:4-Tetrahydroanthraquinone (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 128.
Tetrahydrobenzothiochromanones (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
Tetrahydrobenz*iso*oxazoles (v. AUWERS, BAHR, and FRESE), i, 308.
Tetrahydroberberine, 6-nitro- (HAWORTH and PERKIN), i, 970.
Tetrahydrocarbazole, derivatives of (LINNELL and PERKIN), i, 62.
Tetrahydrofurfuraldehyde (SCHEIBLER, SOTSCHEK, and FRIESE), i, 1298.
Tetrahydrofurylbutylcarbinol, and its acetate (PIERCE and ADAMS), i, 825.
Tetrahydro-ψ-glucal diacetate (BERGMANN), i, 887.
Tetrahydroindazoles (v. AUWERS, v. SASS, and WITTEKINDT), i, 1181.
Tetrahydroindene (ZELINSKI and BORISSOV), i, 122.
Tetrahydrojatrorrhizine, derivatives of (SPÄTH and DUSCHINSKY), i, 1313.
Tetrahydrolupulon, and its salts (WÖLLMER), i, 691.
Tetrahydro-α-methylmorphimethine, chloro-, salts of (SPEYER and KOULEN), i, 59.
Tetrahydro-γ-methylmorphimethine, and its derivatives (SPEYER and KOULEN), i, 60.
Tetrahydro-α-methylmorphimethine-*N*-oxide-sulphonic acids (SPEYER and KOULEN), i, 60.
1:2:3:4-Tetrahydro-1-methyl-2-naphthoic acid (v. AUWERS and MÖLLER), i, 404.
Tetrahydronaphthalene, action of aluminium chloride with (SCHROETER, VAN HULLE, GLUSCHKE, STIER, and MÜLLER), i, 125.
Tetrahydronaphthalene, *ac*-2-nitro-1-oximino- (STRAUS and EKHARD), i, 1138.
Tetrahydronaphthalenes, bromonitro- (VESELÝ and CHUDOZILOV), i, 1056.
4-*ar*-Tetrahydronaphthalene, 4-α-nitro- (ROWE and TARBETT), i, 317.
α-*ar*-Tetrahydronaphthaleneazo-α-naphthylamine (ROWE and TARBETT), i, 317.
α-*ar*-Tetrahydronaphthaleneazo-*ar*-tetrahydro-α-naphthylamine (ROWE and TARBETT), i, 317.
1:2:3:4-Tetrahydronaphthalene-1:2-carboxylic acid, and its anhydride (v. AUWERS and MÖLLER), i, 404.
***cis*Tetrahydronaphthalenediols,** borates of (HERMANS), i, 501.
***ar*-Tetrahydro-β-naphthol,** derivatives of (CHEMISCHE FABRIK VON HEYDEN), i, 1407.
1-Tetrahydronaphthoylmethylmalonic acid, potassium hydrogen salt (SCHROETER, VAN HULLE, and MÜLLER), i, 130.
2-Tetrahydronaphthoylmethylmalonic acid, and its salts and ethyl ester (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 128.
β-1-Tetrahydronaphthoylpropionic acid, (SCHROETER, VAN HULLE, and MÜLLER), i, 130.
β-2-Tetrahydronaphthoylpropionic acid, salts of (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 128.
1:2:3:4-Tetrahydronaphthyl-1-acetic acid, and its copper salt and ethyl ester (SCHROETER, ZADEK, and HOFFMANN), i, 677.
1:2:3:4-Tetrahydronaphthyl-1-acetic acid, 1-hydroxy-, and its ethyl ester and hydrazide (SCHROETER, ZADEK, and HOFFMANN), i, 677.
γ-1-Tetrahydronaphthyl-*n*-butyric acid (SCHROETER, VAN HULLE, and MÜLLER), i, 131.
γ-Tetrahydronaphthylcrotonolactone (SCHROETER, GLUSCHKE, VAN HULLE, and GÖTZKY), i, 128.
β-1-Tetrahydronaphthylthiolpropionic acid (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
Tetrahydronaphthylylene-1-acetic acid, and its ethyl ester (SCHROETER, ZADEK, and HOFFMANN), i, 677.
1:2:3:4-Tetrahydrophenanthrene, spectrochemistry and structure of (v. AUWERS and KRAUL), i, 900.
and its picrate (SCHROETER, VAN HULLE, and MÜLLER), i, 131.

4-Tetrahydroquinolone, preparation of (BRITISH DYESTUFFS CORPORATION, LTD., PERKIN, and CLEMO), i, 697.
Tetrahydrostigmasterol, and its acetate (WINDAUS and BRUNKEN), i, 394.
Tetrakistrimethylstibinepalladous chloride (MORGAN and YARSLEY), i, 378.
Tetrakistrimethylstibineplatinous salts (MORGAN and YARSLEY), i, 378.
"Tetralin," surface tension of (GRUNMACH and SCHWEIKERT), ii, 31.
5-Tetralone. See 1-Keto-1:2:3:4-tetrahydronaphthalene.
Tetramercuriaceto-*o*-toluidide acetate (ROSSI and BOCCHI), i, 601.
ω:3:4:5-Tetramethoxyacetophenone, and its semicarbazone (PRATT and ROBINSON), i, 423.
1:2:6:7-Tetramethoxy-9-anthrone (JACOBSON and ADAMS), i, 1077.
3:3′:4′:5′-Tetramethoxybenzoylcoumaranone, bromo- (DEAN and NIERENSTEIN), i, 953.
Tetramethoxybenzoyldihydrocoumarones, and their phenylhydrazones (DEAN and NIERENSTEIN), i, 281.
6:7:2′:3′-Tetramethoxy-2-benzoyl-1:2-dihydro*iso*quinoline, 1-cyano- (HAWORTH and PERKIN), i, 968.
Tetra-*p*-methoxybenzpinacolin (TIFFENEAU and ORÉKHOV), i, 680.
Tetramethoxybenzyldihydrocoumarones, α-hydroxy-, and their acetyl derivatives (DEAN and NIERENSTEIN), i, 281.
6:7:2′:3′-Tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline, 1-cyano- and 1-hydroxy- (HAWORTH and PERKIN), i, 968.
6:7:3′:4′-Tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline, 1-cyano- and 1-hydroxy- (HAWORTH, PERKIN, and RANKIN), i, 969.
6:7:2′:3′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium iodide (HAWORTH and PERKIN), i, 968.
6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium salts (HAWORTH, PERKIN, and RANKIN), i, 969.
6:7:2′:3′-Tetramethoxy-2-benzyl-3:4-dihydro-1-*iso*quinolone (HAWORTH and PERKIN), i, 968.
3:3′:4′:5′-Tetramethoxybenzylidenecoumaranone, and bromo-, and its dibromide (DEAN and NIERENSTEIN), i, 952.
6:7:2′:3′-Tetramethoxy-2-benzyl-1-methyl-1:2:3:4-tetrahydro*iso*quinoline, and its picrate (HAWORTH and PERKIN), i, 968.
6:7:2′:3′-Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH and PERKIN), i, 968.
6:7:3′:4′-Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH, PERKIN, and RANKIN), i, 969.
6:7:2′:3′-Tetramethoxy-2-benzyl-1-*iso*quinoline (HAWORTH and PERKIN), i, 968.
6:7:3′:4′-Tetramethoxy-2-benzyl-1-*iso*quinoline (HAWORTH, PERKIN, and RANKIN), i, 969.
6:7:3′:4′-Tetramethoxy-2-benzyl*iso*quinolinium bromide and iodide (HAWORTH, PERKIN, and RANKIN), i, 969.
6:7:2′:3′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline, and 1-cyano- and 1-hydroxy-, and their salts (HAWORTH and PERKIN), i, 968.
6:7:3′:4′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline, and 1-cyano- and 1-hydroxy- (HAWORTH, PERKIN, and RANKIN), i, 969.
6:7:2′:3′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline-1-carboxylamide (HAWORTH and PERKIN), i, 969.
Tetramethoxydibenzoyldimethylbenzenes (DE DIESBACH and STREBEL), i, 1436.
5:7:3′:4′-Tetramethoxyflavan, 4-hydroxy-, and its acetyl derivative (NIERENSTEIN), i, 279.
4:3′:4′:5′-Tetramethoxyflavanone, and *iso*nitroso- (DEAN and NIERENSTEIN), i, 952.
5:7:2′:4′-Tetramethoxyflavylium salts (PRATT and ROBINSON), i, 825.
4:4′:7:7′-Tetramethoxyindigotin (RUBENSTEIN), i, 1279.
3:7:3′:4′-Tetramethoxy-2-styrylchromone, 5-hydroxy- (ROBINSON and SHINODA), i, 1302.
Tetramethylacetonedicarboxylic anhydride. See β-Keto-αaγγ-tetramethylglutaric anhydride.
4:4′-Tetramethyl*di*aminobenzophenone, additive compounds of, with resorcinol and α-naphthol (PFEIFFER, GOEBEL, and ANGERN), i, 262.
9:10-Tetramethyl*di*amino-9:10-dihydroanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.
pp′-Tetramethyl*di*aminodiphenyl (VORLÄNDER), i, 1258.
9:10-Tetramethyl*di*aminodiphenyl-9:10-dihydroanthracene (BARNETT, COOK, and MATTHEWS), i, 648.
9:10-Tetramethyl*di*aminodiphenyl-9:10-dihydroanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1140.

Tetramethylammonium *tetra*chloroferrate (REMY and ROTHE), ii, 1039.
Tetramethylarsonium stannic iodide (AUGER and KARANTASSIS), ii, 814.
Tetramethylbenzopyrans (CLAISEN), i, 277.
9:10-Tetramethyldianilinoanthracene, 1:5-*di*chloro- (BARNETT, COOK, and MATTHEWS), i, 1399.
2:2′:5:5′-Tetramethyl-4:4′-dipyrrylmethane-3:3′-dicarboxylic acid, ethyl ester (FISCHER and NENITZESCU), i, 833.
Tetramethyldistannane, disodium derivative (KRAUS and GREER), i, 1394.
***N*:*N*″:*N*‴:*N*‴-Tetramethyl-*N*-ethylguanidine** (LECHER, GRAF, and GNÄDINGER), i, 1393.
Tetramethylgalactose (HAWORTH, RUELL, and WESTGARTH), i, 117.
Tetramethylglucose, mutarotation of, in various solvents (LOWRY and RICHARDS), i, 886.
Tetramethylguanidines, preparation of (SCHENCK and v. GRAEVENITZ), i, 377.
Tetramethylhæmatoporphyrin ester, isomerism of (FISCHER and MÜLLER), i, 846.
Tetramethylmethylgalactoside (HAWORTH, RUELL, and WESTGARTH), i, 117.
3:3′:4′:5′-Tetramethylmyricetin, and its diacetyl derivative (KALFF and ROBINSON), i, 423.
Tetramethylnaphthalene, and its picrate (BRINER, PLÜSS, and PAILLARD), i, 249.
Tetramethylquinamide (KARRER, WIDMER, and RISO), i, 673.
1:3:7:9-Tetramethyluric acid, action of alkalis on (GATEWOOD), i, 1189.
Tetranaphthylene*cyclo*octatetraene. See Dehydrofluorocyclene.
Tetra-oxymethylene, and its diacetate (STAUDINGER and LÜTHY), i, 361.
Tetraphenylcarbazide (FEIGL), i, 170.
1:3:4:6-Tetraphenyl-1:4-dihydro-1:2:4:5-tetrazine, 1:4-*di*-*p*-bromo-, and 1:4-*ω*-2′:4′-*tetra*bromo- (CHATTAWAY and WALKER), i, 930.
Tetraphenyldipyroxonium *per*bromide (ARNDT, SCHOLZ, and NACHTWEY), i, 58.
2:6:2′:6′-Tetraphenyl-4:4′-dipyrylene (ARNDT, SCHOLZ, and NACHTWEY), i, 58.
Tetraphenylgermane (MORGAN and DREW), i, 1197.
Tetraphenyl-1-methylpyrrole (PERKIN and PLANT), i, 843.
Tetraphenylsuccinodilactones, 2:2-*di*hydroxy-. See 2:2′-Diketo-3:3′-diphenyl-3:3′-dicoumaranyls.
Tetraphenyl*di*thiopyrylene (ARNDT, NACHTWEY, and PUSCH), i, 1312.
Tetrapropylammonium iodide, compounds of, with bromoform, chloroform, and iodoform, and the *tri*iodide (STEINKOPF and BESSARITSCH), i, 495.
Tetrazole, cyano-, action of hydrazine on (OLIVERI-MANDALÀ), i, 78.
Tetrolaldehyde *p*-nitrophenylhydrazone (v. AUWERS and DANIEL), i, 1181.
Tetryl. See Phenylmethylnitroamine, *tri*nitro-.
Textiles, action of ultra-violet light on (HEERMANN), ii, 144.
absorption of water by (SHORTER), ii, 789.
Thallium, absorption spectrum and dispersion of the vapour of (NARAYAN, GUNNAIYA, and RAO), ii, 5; (RAO), ii, 455.
spark spectrum of (RAO), ii, 610; (CARROLL), ii, 1101.
vapour, resonance radiation from (NARAYAN and RAO), ii, 338.
transformation of *α*- into *β*- (ASAHARA), ii, 488, 645.
effect of allotropy on growth of crystals of (ASAHARA), ii, 637.
possible transformation of lead into (RUSSELL), ii, 924.
Thallium alloys with cadmium and lead (DI CAPUA), ii, 787.
Thallium compounds, isomorphism of, with those of rare earth metals (ZAMBONINI and CAROBBI), ii, 272
Thallous bromide and chloride, crystal structure of (LUNDE), ii, 941.
chloride, activity coefficient of aqueous solutions of (RANDALL and VANSELOW), ii, 33.
double selenates (LINDSLEY and DENNIS), ii, 584.
selenide (MOSER and ATYNSKI), ii, 583.
sulphate, double salts of neodymium sulphate and (ZAMBONINI and CAGLIOTI), ii, 1185.
cobalt and nickel sulphates (TUTTON), ii, 749.
Thallous lanthanum sulphates (ZAMBONINI and CAROBBI), ii, 579.
sulphide, equilibria of, with arsenic and lead sulphides (CANNERI and FERNANDES), ii, 887.
telluride (BRUKL), ii, 895.
Thallic thallous halides (BERRY), ii, 59.

Thallium organic compounds:—
Thallium alkyl and aryl halides and salts (KRAUSE and V. GROSSE), i, 378, 1252.
Thebaine, constitution of (WIELAND and KOTAKE), i, 1448.
action of cyanogen bromide on (SPEYER and ROSENFELD), i, 962.
Thebenone, and its derivatives (WIELAND and KOTAKE), i, 1093.
Theobromine, and its derivatives, salts of (KNOLL & Co.), i, 828.
Theophylline, salts of (KNOLL & Co.), i, 828.
riboside, triacetylriboside, xyloside, and triacetylxyloside (LEVENE and SOBOTKA), i, 1463.
Therapeutic compounds (WELLCOME FOUNDATION, LTD., GRAY, and HENRY), i, 1446.
Thermal conductivity of wires and rods (BARRATT and WINTER), ii, 756.
expansion of fused salts (LORENZ and HERZ), ii, 950.
of alkali halides (HENGLEIN), ii, 950.
reactions, temperature-coefficients of (DHAR), ii, 135.
and photochemical reactions (DHAR and MUKERJI), ii, 809.
Thermochemical data (SWIENTOSLAWSKI), ii, 540, 1139; (SWIENTOSLAWSKI and POPOV; SWIENTOSLAWSKI and STARCZEVSKA), ii, 1139.
Thermochemistry of diazo compounds (SWIENTOSLAWSKI; SWIENTOSLAWSKI and BLASZKOVSKA), ii, 1044.
of organic compounds (PARKS and KELLEY), ii, 949.
Thermodynamics, laws of, and the equation of state (KOLTSCHIN), ii, 1061.
third law of (WEBB), ii, 867.
Willard Gibbs' work on (MILLER), ii, 399.
of solutions of electrolytes (HARNED), ii, 977.
potentials in (FREUNDLICH and ETTISCH), ii, 873.
of surface action (GAY), ii, 539.
Thermo-electric power and the Hall coefficient (HEAPS), ii, 1135.
Thermo-electricity of electrolytes (THIELE), ii, 545.
Thermo-element, vacuum (MOLL and BURGER), ii, 613.
Thermometer, air differential (NOYES), ii, 896.
platinum-resistance (VAN DUSEN), ii, 590.
Thiazine red, preparation of (PROESCHER and KELLNER), i, 597.
Thiazine series, preparation of keto derivatives of (AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION), i, 596.
Thiazoles (BOGERT and CHERTCOFF), i, 315.
Thiazole colouring matters (BOGERT and CHERTCOFF), i, 80.
Thiazole-purple (KÖNIG and MEIER), i, 705.
α-Thienylmethyl bromide (V. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
α-Thienylmethylallylaniline, and its salts (V. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
α-Thienylmethylbenzylmethylamine, and its salts (V. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
α-Thienylmethylfurfurylmethylamine, and its salts (V. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
α-Thienylmethylthiocarbimide (V. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
α-Thienylmethyltrimethylammonium salts (V. BRAUN, FUSSGÄNGER, and KUHN), i, 1403.
Thioamides, action of sulphur chloride on (ISHIKAWA), i, 1149.
condensation of nitriles with (ISHIKAWA), i, 917, 1149.
Thiobacillus thio-oxidans, nutrition and physiology of (STARKEY), i, 1015.
Thiocarbamide (*thiourea*), constitution of (LECHER), i, 1390; (LECHER and HEYDWEILLER), i, 1392.
oxidation of, by charcoal (FREUNDLICH and FISCHER), ii, 307.
condensation of, with dihydroxyacetone and with methylglyoxal (SJOLLEMA and SEEKLES), i, 1175.
Thiocarbamides, substituted (DAINS, BREWSTER, MALM, MILLER, MANEVAL, and SULTZABERGER), i, 1063.
aryl derivatives, reactions of, with sulphur and amines (LEVI), i, 445.
Thiocarbamide-diacetic acid, ethyl esters (JOHNSON and RENFREW), i, 583.
Thiocarbanilide, formation of (SNEDKER), i, 385.
Thiocarbimides (*isothiocyanates*), formation of, from thiocyanates (BILLETER), i, 1051.
aromatic substituted, addition of ethyl sodioacetoacetate to (WORRALL), i, 244.
Thiocarbohydrazide, derivatives of (GUHA and DE), i, 599.
Thiocarbonic acid, *di*-β-naphthyl and pyrocatechyl esters (AUTENRIETH and HEFNER), i, 1376.

Thiocarbonyl chloride, preparation of, and its derivatives (AUTENRIETH and HEFNER), i, 1376.
Thiocyanates, conversion of, into thiocarbimides (BILLETER), i, 1051.
detection of, in organic matter (DANCKWORTT and PFAU), i, 196.
detection and determination of, in presence of cyanides (SCHULEK), ii, 432, 712.
determination of, bromometrically (OBERHAUSER), ii, 828.
determination of, colorimetrically (K. C. and D. F. H. BAILEY), ii, 447.
Thiocyanic acid, potassium salt, reaction of ferric chloride with (BAILEY; BAILEY and KIDD), ii, 422.
Thiocyanines (KÖNIG and MEIER), i, 705.
Thiocyanogen, preparation of (KAUFMANN and KÖGLER), i, 1252.
action of, on unsaturated compounds (SÖDERBÄCK), i, 899; (CHALLENGER and BOTT), i, 936.
reaction of azoimide with (WILCOXON, MCKINNEY, and BROWNE), i, 1051.
Thiodiazines (BOSE), i, 167, 1465.
Thiohydrates (BILTZ and KEUNECKE), ii, 986.
Thioindican. See 3-Oxy(1)thionaphthen glucoside.
Thioketones (SCHÖNBERG, ROSENBACH, KRÜLL, and OSTWALD), i, 1300.
Thionacetanilide, *m*-bromo- and *p*-iodo- (WORRALL), i, 244.
Thionacetoanisidides (WORRALL), i, 244.
Thionaceto-*m*-toluidide (WORRALL), i, 244.
Thionaphthen, hydrogenation of (FRICKE and SPILKER), i, 249, 1311.
2-Thionaphthen-9′-anthraceneindolignone (SANDER), i, 982.
3-Thionbenzoyldiphenyl-2:3-dihydro-1:2:4-triazoles (FROMM and TRUKA), i, 704.
Thionic acids. See under Sulphur.
Thionium compounds, heats of formation of (TSCHELINCEV), ii, 480.
Thionmalono-*p*-anisidic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
Thionmalono-*m*-bromoanilic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
Thionmalono-*p*-chloroanilic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
Thionmalono-*p*-iodoanilic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
Thionmalono-α-naphthylamic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
Thionmalono-*p*-phenetidic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
Thionmalono-*m*-toluidic acid, and its acetyl derivative, ethyl ester (WORRALL), i, 244.
3-Thion-1:2:3:4-tetrahydro-1:2 4-benztriazine, and its derivatives (GUHA and RAY), i, 1462.
Thiophen, and its derivatives, spectrochemistry of (V. AUWERS and KOHLHAAS), i, 150.
poisoning of catalysts by (KUBOTA and YOSHIKAWA), ii, 805.
derivatives, synthesis of (CHRZASZCZEWSKA), i, 956.
Thiuronium salts, constitution of (LECHER), i, 1390; (LECHER and HEYDWEILLER), i, 1392.
Thorium, preparation of (VAN ARKEL and DE BOER), ii, 1193.
β-ray spectra of the disintegration products of (BLACK), ii, 922.
velocity of α-particles from (ROSENBLUM), ii, 463.
emanation (BATSCHA), ii, 177.
Thorium hydroxide, precipitation of, electrometrically (BRITTON), ii, 1203.
oxide (*thoria*), catalytic activity of (KOMATSU and TANAKA), i, 905.
catalytic activity of reduced copper and nickel and (KOMATSU and MASUMOTO), ii, 1071.
promoter action of, on catalytic nickel (RUSSELL and TAYLOR), ii, 1071.
Thorium separation:—
separation of, from zirconium and rare earth metals (FERNANDES), ii, 426.
Thorium-*B*+*C*, magnetic spectrum of β-rays of (YOVANOVITCH and D'ESPINE), ii, 176; (POHLMEYER), ii, 347.
Thorium-*B*, -*C*, and **-*D***, spectra of (BLACK), ii, 177.
Thorium-*X*, production of, by recoil (BRIGGS), ii, 922.
determination of (GAZZONI), ii, 441.
Thoron. See Thorium emanation.
Thrombin (WÖHLISCH), i, 1486.
theory of the action of (WÖHLISCH), i, 452.
detection of, in blood (STUBER and KUHN), i, 452.
detection of, in oxalate plasma (STUBER and LEE), i, 94.
Thymine, 4:5-*di*hydroxy- (BAUDISCH and DAVIDSON), i, 1100.

Thymol, surface tension of aqueous solutions of (EDWARDS), ii, 387.
catalytic reduction of (DOMINIKIEWICZ), i, 146.
Thymol-blue, dissociation constant of (HOLMES and SNYDER), ii, 325.
Thymus, histones of the (FELIX), i, 1203.
Thyroglobulin, precipitation reaction of (HEKTOEN and SCHULHOF), i, 1345.
Thyroid, pharmacology of preparations of (HAFFNER and KOMIYAMA), i, 1119.
absorption, distribution and determination of iodine in the (RABINOVITSCH and FRITH), i, 1488; (ABELLES and POPPER; PICKWORTH), i, 1489.
iodine in the blood of (GLEY and CHEYMOL), i, 456.
lipases from (HERZFELD and ENGEL), i, 201.
goat's, iodine in (ARNOLD and GLEY), i, 325.
normal and diseased, constituents of (WEIR), i, 1491.
Thyroidectomy, fat and cholesterol in blood after (HECKSCHER), i, 999.
Thyroxin, ultra-violet absorption spectrum of, and its constitution (HICKS), ii, 473.
Tiglic aldehyde phenylhydrazone (v. AUWERS and KREUDER), i, 1454.
Tin, molecular weight of (JOUNIAUX), ii, 489.
absorption spectrum of the vapour of (NARAYAN and RAO), ii, 927.
absorption and arc spectra of (MCLENNAN, YOUNG, and MCLAY), ii, 454.
arc spectrum of (SPONER), ii, 454.
X-ray absorption coefficient of (WARBURTON and RICHTMYER), ii, 1103.
passivity of (ROTHMUND, EISENKOLB, and STEINHERZ), ii, 131.
electro-deposition of (SMRZ), ii, 677.
single crystal rods of, thermo-electric force of (BRIDGMAN), ii, 1136.
crystals, tensile strength of (POLANYI and SCHMID), ii, 752.
grey and white, specific heats of (COHEN and MOESVELD), ii, 950.
Tin alloys, electrolysis of (KREMANN and v. REHENBURG), ii, 313.
heat of formation of (BILTZ and HOLVERSCHEIT), ii, 268.
with aluminium, electrolysis of (KREMANN and DELLACHER), ii, 679.
with bismuth and lead, hardness of (DE CAPUA), ii, 1051.
with copper (ISHIHARA), ii, 122.
Tin alloys with copper, α-phase boundary in (STOCKDALE), ii, 973.
hardness of (BAUER and VOLLENBRUCK), ii, 104.
with mercury, electrolysis of (KREMANN, KAPAUN, and BUDAN), ii, 313.
with mercury and silver (TAMMANN and DAHL), ii, 502.
with molybdenum and nickel (PFAUTSCH), ii, 536.
with zinc, electrolysis of (KREMANN and BAUKOVAC), ii, 679.
Tin hydride, preparation and properties of (PANETH and RABINOVITSCH), ii, 59; (PANETH, HAKEN, and RABINOVITSCH), ii, 60.
pharmacology of (PANETH and JOACHIMOGLU), i, 197.
hydroxide, precipitation of, electrometrically (BRITTON), ii, 1203.
selenides (MOSER and ATYNSKI), ii, 584.
tellurides (BRUKL), ii, 895.
Stannous chloride, effect of neutral salts on the reaction of ferric chloride with (TIMOFEEV, MUCHIN, and GUREVITSCH), ii, 586.
iodide, properties of (FREUNDLER and LAURENT), ii, 1085.
photochemical properties of (FREUNDLER and LAURENT), ii, 22.
compounds of, with caesium and rubidium iodides (AUGER and KARANTASSIS), ii, 1182.
Stannic chloride, distillation of (RÖHRE), ii, 157.
weighting of silk with and its compounds with ethyl aminoacetate and acetic acid (FICHTER and REICHART), ii, 193.
compounds of, with β-diketones (DILTHEY), i, 1473.
iodide, complex compounds of (AUGER and KARANTASSIS), ii, 814.
additive compounds of hexamethylenetetramine and (SCAGLIARINI), i, 890.
Tin organic compounds (DRUCE), i, 798.
Tin dimethyl, derivatives of (KRAUS and GREER), i, 1394.
trimethyl, and its hydroxide and derivatives (KRAUS and SESSIONS), i, 1253; (KRAUS and HARADA), i, 1254.
tetra-*p*-nitrophenyl (VORLÄNDER), i, 1256.
Stannic halides, compounds of, with diamines and polycarboxylic esters (HIEBER, BECKER, and WAGNER), i, 1325.

Tin organic compounds:—
Chloro-stannates and -stannites (DRUCE), i, 1096.
Tin determination and separation:—
determination of, electrometrically (FLEYSHER), ii, 243.
determination and separation of, in alloys (EVANS), ii, 826.
separation of antimony and (SACCARDI), ii, 159.
separation of antimony, copper, lead, and (LASSIEUR), ii, 328.
separation of, from tungsten (JILEK and LUKAS), ii, 242.
Tissues, hydrogen-ion concentration in (SCHMIDTMANN), i, 99.
colloidal processes in stimulation of (LASAREV), i, 1499.
effect of salts on the adsorption of colouring matters by (MANN), ii, 35.
absorption of salts by (STILES), ii, 31.
respiration of (TERROINE and ROCHE), i, 709.
animal. See Animal tissues.
normal, and cancer, reducing power of (VOEGTLIN, JOHNSON, and DYER), i, 99.
vegetable. See Plant tissues.
determination of chlorine in (URBACH and FANTL), i, 1203.
determination of cholesterol and its esters in (GARDNER and FOX), i, 182.
determination of copper in (CURRIE), i, 183.
determination of iron in (YABUSOE), i, 724.
Titanium, preparation of (VAN ARKEL and DE BOER), ii, 1193.
arc spectrum of (BEHNER), ii, 1100.
vacuum-arc spectrum of (CREW), ii, 385.
crystal structure of (PATTERSON), ii, 345.
Titanium alloys with carbon and iron (TAMARU), ii, 787.
Titanium carbide and nitride (FRIEDERICH), ii, 374.
*di*oxide (*titania*), catalytic action of and adsorption of gases by (BISCHOFF and ADKINS), ii, 568.
jellies of (KLOSKY and MARZANO), ii, 1057.
Titanous chloride, reduction of nitric acid by (COBLENS and BERNSTEIN), ii, 804.
standardisation of solutions of (ZINTL and RAUCH), ii, 1003.
use of, in electrovolumetric analysis (TOMIČEK), ii, 243.
Titanic chloride, reduction of (SCHMIDT), ii, 315.

Toluene compounds Me = 1.
Titanium:—
Titanic chloride, compound of acetic acid with (FICHTER and REICHART), ii, 194.
Titanic organic compounds (GIUA and MONATH), i, 581.
Titanium ores, fusion of (SEARS and QUILL), ii, 580.
Tobacco, dried, fermentation of (FODOR and REIFENBERG), i, 1519.
o-**Tolidine**, preparation of solutions of (ROAKE), ii, 432.
p-**Tolualdehyde**, condensation of, with menthone (SAMDAHL), i, 414.
o- and *p*-**Tolualdehydes** *p*-nitrophenylhydrazines (STEPHEN), i, 1131.
Toluamides, hydroxy-, acetyl, and benzoyl derivatives (ANSCHÜTZ, ASCHENBERG, KUCKERTZ, KRONE, RIEPENKRÖGER, and ZERBE), i, 666.
Toluene, sorption of the vapour of, by sugar charcoal (BAKR and MCBAIN), ii, 193.
catalytic chlorination of (O. and C. A. SILBERRAD and PARKE), i, 1137.
chlorination of, with selenium (O. and C. A. SILBERRAD), ii, 1191.
mercuration of (COPLEY), i, 844.
oxidation of (KNOOP and GEHRKE), i, 1131.
electrochemical oxidation of (MANN and PAULSON), i, 556.
action of benzoyl peroxide on (GELISSEN and HERMANS), i, 545.
Toluene, 3:5-*di*amino-2:4-*di*hydroxy-, and its tetra-acetyl derivate (HENRICH and GÖTZ), i, 913.
p-chloro-, photochemical action of iodine on (SILBERRAD), i, 16.
nitration of (HODGSON), i, 1397.
p-chlorothiol- (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.
p-nitro-, melting point of (PUSHIN), ii, 277.
*tri*nitro-, heat of fusion of (RINKENBACH and HALL), ii, 207.
2:4:6-*tri*nitro-, decomposition of, by sunlight (KRAUZ and TUREK), i, 646; (WICHERT and DONAT), i, 803.
halogenation of (GANGULY), i, 647.
Toluenes, iodo-, isomeric, polarity effects in (SHOESMITH and SLATER), i, 16.
electrolytic oxidation of (FICHTER and LOTTER), i, 1055.
nitro-, action of light on (SCHULTZ and GANGULY), i, 647.
o- and *p*-nitro-, separation of (MOLINARI), i, 380.

Toluene compounds, Me = 1.

Toluenes, *as-tri*nitro-, reactions of (BRADY, HEWETSON, and KLEIN), i, 16.

***o*-Tolueneazoacetylacetone**, and its derivatives, and 3-nitro- (BÜLOW and SPENGLER), i, 1102.

***p*-Tolueneazoallylformaldoxime** (WALKER), i, 1193.

***p*-Tolueneazobenzylformaldoxime**, and its phenylcarbamate (WALKER), i, 1193.

4-*p*-Tolueneazo-3:5-dimethyl*iso*oxazole, and 4-*m*-nitro- (BÜLOW and SPENGLER), i, 1102.

4-*p*-Tolueneazo-3:5-dimethylpyrazole, and its salts, and 4-*m*-nitro- (BÜLOW and SPENGLER), i, 1102.

Toluene-3-azo-oximinoacetotoluidides (KARRER, DIECHMANN, and HAEBLER), i, 243.

4-*p*-Tolueneazo-1-phenyl-3:5-dimethylpyrazole, and 4-*m*-nitro- (BÜLOW and SPENGLER), i, 1102.

1-*p*-Tolueneazoxy-2-aminonaphthalene (CHARRIER, CRIPPA, TOIA, and BIANCHESSI), i, 591.

***p*-Toluenesulphenanilide** (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.

***p*-Toluenesulphobenzylamide** (HOLMES and INGOLD), i, 1143.

***p*-Toluenesulphobenzylmethylamide**, and its hydrochloride (HOLMES and INGOLD), i, 1143.

***o'*-Toluenesulphonamidobenzaldoximes**, and the corresponding acetates (V. AUWERS), i, 1461.

***o*-2-Toluenesulphonamidobenzonitrile** (V. AUWERS), i, 1460.

1-*p*-Toluenesulphonamidonaphthalene-8-sulphonic acid, and its sodium salt (FINZI), i, 654.

Toluene-*o*-sulphonic acid, electrochemical oxidation of (FICHTER and STOCKER), i, 239.

indazole ester (V. AUWERS), i, 1461.

Toluene-*p*-sulphonic acid, esters, alkylation by (FINZI), i, 648.

action of magnesium organic halides with (GILMAN and BEABER), i, 802.

substituted phenyl and tolyl esters (SANÉ and JOSHI), i, 134.

Toluenesulphonic acids, *di*nitro-, sodium salts (BRADY, HEWETSON, and KLEIN), i, 16.

***d*-α-*p*-Toluenesulphonoxypropionic acid**, and its ethyl ester and amide (KENYON, PHILLIPS, and TURLEY), i, 507.

***p*-Toluenesulphonyl chloride**, action of on nitrophenols (SANÉ and JOSHI) i, 134.

Toluene compounds, Me = 1.

***p*-Toluenesulphonylhydrazine**, and its derivatives (FREUDENBERG and BLÜMMEL), i, 52.

***o*-Toluenesulphonylindazoles** (V. AUWERS), i, 1461.

Toluene-*p'*-sulpho-*p*-phenetidide, nitroderivatives, and their derivatives (REVERDIN), i, 1409.

***p*-Toluenethiolsulphonic acid**, *o*-nitrophenyl ester (MILLER and SMILES), i, 392.

***m*-Toluic acid**, 6-thiol- (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306; (ARNDT), i, 1311.

***p*-Toluic acid**, 2-amino- and 2-nitro-, diethylaminoethyl esters, and their hydrochlorides (SODERMAN and JOHNSON), i, 814.

ω-trichloro-, synthesis of (BÖESEKEN and GELISSEN), i, 30.

Toluic acids, hydroxylamine salts (OESPER and BALLARD), i, 1233.

Toluic acids, amino-, separation of (MAYER and SCHULZE), i, 1315.

***o*-Toluidine**, 3:5-*di*bromo-, additive compounds of, with metallic salts (HANN and SPENCER), i, 653.

5-iodo-, preparation of, and its salts and derivatives (HANN and BERLINER), i, 908.

***m*-Toluidine**, bromo-4:6-*di*hydroxy-, hydrobromide, and its derivatives (HENRICH and GÖTZ), i, 913.

***p*-Toluidine**, surface tension of aqueous solutions of (EDWARDS), ii, 387.

Toluidines hydroferricyanides of (CUMMING), i, 122.

detection of, colorimetrically (MURRAY), ii, 163.

ω-*o*- and -*p*-Toluidineacetophenones, hydrazones of (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.

***p*-Toluidino-*p*-anisidino-1:4-naphthaquinone** (FRIES and BILLIG), i, 940.

β-Toluidinobenzylmalonic acids, esters of (WAYNE and COHEN), i, 550.

3-Toluidino-5-keto*iso*oxazoles (WORRALL), i, 308.

3-Toluidino-5-ketopyrazoles (WORRALL), i, 308.

1-Toluidinomethylbenzthiazoles, and their derivatives (HUNTER), i, 1336.

2-*p*-Toluidino-1:4-naphthaquinone, 3-chloro-2-*N*-nitroso- (FRIES and BILLIG), i, 939.

1-*p*-Toluidino-β-naphthol-4-sulphonic acid (LANTZ and WAHL), i, 910.

Toluidino-oximinopinacolin (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.

Toluene compounds, Me = 1.

Toluidino-5-phenyl-1:3:4-thiodiazines, and their hydrobromides and derivatives (BOSE), i, 1465.

m-**Toluidino-***m*-**toluthiazole**, and its derivatives (LEVI), i, 445.

5-Toluidino-4-*o*-**tolyl-1:2:4-triazole**, 3-thiol-, derivatives of (FROMM and SZENDRŐ), i, 985.

p-**Toluidino-3:4:5-trimethoxyphenylcarbinol**, and its hydrochloride (SONN and MEYER), i, 932.

p-**Toluimino***iso***thio-***p*-**toluamide**, and its hydrochloride (ISHIKAWA), i, 1149.

p-**Toluoyl** chloride, 2-nitro- (SODERMAN and JOHNSON), i, 814.

Toluoylacetamides, hydroxy-(ANSCHUTZ, ASCHENBERG, KUCKERTZ, KRONE, RIEPENKRÖGER, and ZERBE), i, 667.

o-**Toluoylbenzoic acid**, methyl ester (WEISS and KOREZYN), i, 560.

o-**Toluoylbenzoic acids** (BRAND, LUDWIG, and BERLIN), i, 904.

m-**Toluoylbenzoic acid**, *o*-4-bromo- (HELLER and MÜLLER-BARDORFF), i, 546.

m-**Toluoyl-3:4:5:6-***tetra***chloro-2-benzoic acid**, 2′-hydroxy- (ORNDORFF and PATEL), i, 672.

8-Toluoyl-α-naphthoic acid (MASON), i, 33.

β-Toluoyloxypropionic acids, and their amides (POWELL and JOHNSON), i, 278.

γ-*m*- and **-***p*-**Toluoyloxypropyl alcohols** (POWELL and JOHNSON), i, 278.

2-*o*-**Toluoylphenyldi-***o*-**tolylcarbinol** (WEISS and KOREZYN), i, 560.

Toluquinone, action of azides with (CHATTAWAY and PARKES), i, 985.

Toluyleneamidine-2-phenyl-*o*-**carboxylic acid.** See 4-Methylbenziminazole-2-benzoic acid.

m-**Tolyl** hydroxyethyl ether (CASSELLA & Co.), i, 397.

p-**Tolyl** *p*-acetoxybenzyl ether (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1263.

*iso*amyl sulphide (GILMAN, BEABER, and MYERS), i, 1057.

benzyl ether (v. BRAUN and REICH), i, 1405.

β-chloroethyl sulphide (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.

cinnamyl ether (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.

methyl ether, 2-amino-, and 5-bromo-2-amino-, 2-acetyl derivatives (GRIFFITH and HOPE), i, 827.

o- and *p*-**Tolyl** acetates, action of sodium on (HALL), i, 23.

p-**Tolylacetaldehyde** *p*-nitrophenylhydrazone (STEPHEN), i, 1131.

Toluene compounds, Me = 1.

o-**Tolylacetic acid**, ω-amino- and its derivatives (v. BRAUN and REICH), i, 1407.

p-**Tolyl***iso***amylsulphone** (GILMAN, BEABER, and MYERS), i, 1057.

o-**Tolyl anisyl ketone** (DE DIESBACH and STREBEL), i, 1435.

o-**Tolylarsinic acid** (BURTON and GIBSON), i, 84.

Tolyl-5-arsinic acids, *di*amino-, and nitroamino-, benzoyl derivatives (HAMILTON and MAJOR), i, 990.

N-*p*-**Tolylbenzimido-***p*-**tolyl ether** (CHAPMAN), i, 1401.

o-**Tolylbenzylketimine**, and its hydrochloride (JASPERS), i, 936.

p-**Tolylborneol** (LEDUC), i, 821.

p-**Tolylcamphene** (LEDUC), i, 821.

o- and *p*-**Tolylcarbamic acids**, *di*nitro-, esters of (KNIPHORST), i, 906.

o-**Tolylcarbamide**, 5-iodo-, and its hydrochloride (HANN and BERLINER), i, 908.

m-**Tolylcarbamide**, 2:4- and 4:6-*di*nitro- (GIUA and PETRONIO), i, 1397.

o- and *p*-**Tolylcarbamides**, *di*nitro- (KNIPHORST), i, 906.

o-**Tolylcarbylamine**, 5-iodo- (HANN and BERLINER), i, 908.

p-**Tolylcitronellylamine**, and its derivatives (RUPE and RINDERKNECHT), i, 658.

m-**Tolylcyanamide**, 4:6-*di*nitro- (GIUA and PETRONIO), i, 1397.

1-Tolyl-3:5-diketopyrazolidines, tolylhydrazine derivatives of (VAN ALPHEN), i, 83.

p-**Tolyldimethylaminomethyl-***p*-**tolylmethane**, and its hydrochloride (SOMMELET), i, 803.

p-**Tolyldiphenylyl-α-naphthylmethyl** chloride and methyl ether (DILTHEY), i, 653.

p-**Tolyl diphenylyl ketone**, and its oxime (DILTHEY), i, 653.

β-**Tolylethylamines**, ω-chloro-, salts and derivatives of (v. BRAUN and REICH), i, 1406.

α-*o*-**Tolyl-β-ethylcarbamide** (KNIPHORST), i, 906.

o-**Tolylethylketimine**, and its hydrochloride (JASPERS), i, 936.

α-**Tolyl-ββ-ethylnitrocarbamides**, *di*nitro- (KNIPHORST), i, 906.

p-**Tolylidenemalonic acid**, and its ethyl ester (CHRZASZCZEWSKA), i, 956.

p-**Tolylidenementhone**, and its hydrochloride (SAMDAHL), i, 415.

5-Tolylimino-4-acetyl-2-methylthiol-4:5-dihydrothiodiazole (GUHA and RÂY), i, 703.

Toluene compounds, Me = 1.

1-Tolylimino-β-naphthaquinone (Société Anonyme des Matières Colorantes), i, 413.

5-Tolylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, and its derivatives (Guha and Rây), i, 703.

***o*-Tolylcycloiminotoluquinone** (Chattaway and Parkes), i, 985.

2-*p*-Tolylindazole, 3-cyano-, and its oxide (Helle and Spielmeyer), i, 838.

1-Tolylindazoles, 4-nitro- (v. Auwers and Frese), i, 1102.

2-*p*-Tolylindazole-3-carboxylic acid (Heller and Spielmeyer), i, 838.

***p*-Tolylmercuric** hydrogen carbonate and mercaptan (Koten and Adams), i, 236.

***p*-Tolylmercuri-2:4:6-trinitrophenyl** (Koten and Adams), i, 237.

***o*-Tolylmethylketimine**, and its hydrochloride (Jaspers), i, 936.

α-*p*-Tolyl-ββ-methylnitrocarbamide, 2:6-*di*nitro- (Kniphorst), i, 907.

3-*m*′-Tolyl-5-methylpyrazole, 3:2′-hydroxy- (Wittig), i, 279.

4-*p*-Tolylmorpholine (Cretcher and Pittenger), i, 228.

Tolylnaphthalimide, *o*-amino- (Chakravarti), i, 162.

2-Tolyl-αβ-naphthatriazoles, and their oxides, and 4-hydroxy- (Charrier, Crippa, Toia, and Bianchessi), i, 591.

1-*p*-Tolyl-*lin*-naphthatriazole-4:9-quinone (Fries and Billig), i, 940.

***m*-Tolyl-α-** and **-β-naphthylamines**, *di*nitro- (Brady, Hewetson, and Klein), i, 16.

***s-o*-Tolyl-α-naphthylcarbamide**, 5-iodo- (Hann and Berliner), i, 908.

α-*m*-Tolyl-β-nitrocarbamide, α-4:6-*di*nitro- (Giua and Petronio), i, 1397.

α-*m*-Tolyloxy-αβ-dibenzoylethane (Conant and Lutz), i, 682.

α-Tolyloxy-αβ-dibenzoylethylenes (Conant and Lutz), i, 682.

2-*p*-Tolyloxy-2:3-dihydro-*p*-benzoquinonemethane, and its derivatives (Pummerer, Puttfarcken, and Schopflocher), i, 1262.

***p*-Tolyloxy-*P*-oxodihydrobenzodiazphospholium** (Autenrieth and Bölli), i, 1469.

***p*-Tolyloxy-*P*-oxotetrahydrodiazphospholium** (Autenrieth and Bölli), i, 1469.

***p*-Tolyloxy-*p*-thiodihydrobenzodiazphospholium** (Autenrieth and Meyer), i, 990.

***p*-Tolyloxythiophosphoryl *di*chloride** (Autenrieth and Meyer), i, 807.

***o*-Tolylphenylketimine**, and its derivatives (Jaspers), i, 936.

Toluene compounds, Me = 1.

γ-*o*- and -*p*-Tolylpropinenes (Bert, Dorier, and Lamy), i, 1373.

β-*m*-Tolylpropionic acid, α-cyano- (Baker and Lapworth), i, 30.

1-*p*-Tolyl-2-pyrrolidone, and its picrate (Lipp and Caspers), i, 963.

3-Tolylrhodanylidene-Δ$^{5:3}$-oxindoles (Hann), i, 987.

***p*-Tolylselenoglycollic acid**, and its salts (Morgan and Porritt), i, 1197.

***p*-Tolylselenoxyglycollic acid** (Morgan and Porritt), i, 1197.

4-*p*-Tolylsemicarbazide, and its derivatives (Wheeler and Bost), i, 317.

***p*-Tolylsuccinic acid** (Chrzaszczewska), i, 956.

***p*-Tolylsulphonyl-β-phenylpropionic acid** (Arndt), i, 1310.

β-*p*-Tolylsulphonylpropionic acid (Arndt), i, 1310.

β-*p*-Tolylsulphoxypropionic acid (Arndt), i, 1310.

Tolyl-2-thio-4-ketothiazolidines, condensation of, with substituted vanillins (Hann), i, 1105.

β-*p*-Tolylthiol-*n*-butyric acid (Kroll-pfeiffer, Schultze, Schlumbohm, and Sommermeyer), i, 1305.

α-*p*-Tolylthioldiphenylacetic acid (Bistrzycki and Risi), i, 1426.

2-*p*-Tolylthiophen (Chrzaszczewska), i, 956.

***o*-Tolyl *p*-tolyl ketone** (de Diesbach and Strebel), i, 1435.

4-*o*-Tolyl-1-*o*-tolylthiocarbamidophenylthiosemicarbazide (Guha and Ray), i, 1462.

Tomato plants, nutrition and growth of (Kraybill and Smith), i, 1122.
effect of sodium nitrate on growth of (Work), i, 1366.

Torulin (Kinnersley and Peters), i, 1516.

Tourmaline in Dartmoor granite (Brammall and Harwood), ii, 819.

Toxicological analysis. See Analysis.

Toxicology, chemical (Kohn-Abrest), i, 1116.

Toxins (Karrer, Weber, and van Slooten), i, 1226.
conversion of, into anatoxins (Berthelot and Ramon), i, 481.

Train oil, separation of unsaturated fatty acids in (Toyama and Tsuchiya), i, 1129.

Transfer resistance (Ferguson and van Zyl), ii, 547.

Transport numbers, apparatus for determination of (MacInnes and Brighton; Smith and MacInnes), ii, 542.

Trees, descent of nitrogenous substances in leaves of, in autumn fading (COMBES), i, 1023.
deciduous, constituents of leaves of (FRICKE), i, 764.
Trehalose in yeast (E. M. and F. C. KOCH), i, 1508.
*iso***Trehalose**, and its octamethyl ether (SCHLUBACH and MAURER), i, 888.
Triacetonamine, nitroso-, catalysis of decomposition of, by hydroxyl ions (BRÖNSTED and KING), ii, 1171.
ω-2:4-Triacetoxyacetophenone (NIERENSTEIN, WANG, and WARR), i, 34.
2:4:6-Triacetoxybenzaldehyde (PRATT and ROBINSON), i, 826.
Triacetoxy*di*hydroxychlorodititanium chloride (GIUA and MONATH), i, 531.
Triallylacetophenone (HALLER, BAUER, and RAMART), i, 261.
Triallylsulphonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 496.
β-Triamylose nitrates (PRINGSHEIM, LEIBOWITZ, and SILMANN), i, 1244.
Trianhydrostrophanthidin (JACOBS and COLLINS), i, 566.
Trianhydrotetrakisdiphenylgermanediol (MORGAN and DREW), i, 1197.
4:4′:4″-Trianilinotri-*m*-tolylcarbinol (GOMBERG and ANDERSON), i, 1065.
4:4′:4″-Trianilinotri-*m*-tolylmethane (GOMBERG and ANDERSON), i, 1065.
Triaquotriamminecobaltictriaquotrisulphatocobaltiate. See under Cobalt.
Triarsenatomanganic acid (DEISS), ii, 893.
Triarylcarbinols, *o*-hydroxy-, tautomerism of (GOMBERG and MCGILL), i, 1269.
Triazine derivatives, thermal properties of binary mixtures of (PASCAL), ii, 953.
Triazines, preparation of (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 441.
Triazinetricarboxylic acid, complex iron derivatives of (PASCAL), i, 984.
1:2:3-Triazole, 4:5-*di*cyano-, and its derivatives (GRISCHKEVITSCH-TROCHIMOVSKI; GRISCHKEVITSCH-TROCHIMOVSKI and KOTKO), i, 1104.
1:2:3-Triazolecarboxylic acid, cyano-, and its ethyl ester (GRISCHKEVITSCH-TROCHIMOVSKI; GRISCHKEVITSCH-TROCHIMOVSKI and KOTKO), i, 1104.
Triazoledicarboxylic acid, *N*-hydroxy-, and its potassium hydrogen salt (WIELAND), i, 1050.
1:2:3-Triazole-4:5-dicarboxylic acid, monoamide of (GRISCHKEVITSCH-TROCHIMOVSKI), i, 1104.
3:4:5-Tribenzoyloxybenzaldehyde (SONN and MEYER), i, 932.
3:4:5-Tribenzoyloxybenzanilide (SONN and MEYER), i, 932.
Tribenzylammonium iodide, compound of iodoform with (STEINKOPF and BESSARITSCH), i, 495.
*tri*iodide (STEINKOPF and BESSARITSCH), i, 497.
Tribenzylmethylammonium iodide, compound of iodine with (STEINKOPF and BESSARITSCH), i, 495.
3:4:5-Tribenzyloxybenzanilide (SONN and MEYER), i, 932.
Tributylcarbinol (IVANOV), i, 503.
Tributylmethane. See ε-Butylnonane.
Tricarbethoxyglycerol (ALLPRESS and MAW), i, 4.
Tricarbomethoxyglycerol (ALLPRESS and MAW), i, 4.
Tri-*p*-carboxyphenylbismuthine *di*chloride (SUPNIEWSKI), i, 1473.
Tricyclene, nitration of (NAMETKIN and ZABRODIN), i, 416.
*di*chloride. See Camphane, *di*chloro-.
Tricyclo-(2,2,1,1,1,1,)-dodecane-5:10:11:12-tetraone, and its derivatives (WEDEKIND, MILLER, and WEINAND), i, 510.
Triethylamine, action of, on adipyl and β-methyladipyl chlorides (WEDEKIND, MILLER, and WEINAND), i, 510.
compound of iodoform with (STEINKOPF and BESSARITSCH), i, 496.
Triethylcarbinyl iodide (MORGAN, CARTER, and DUCK), i, 877.
Triethylene *tri*sulphide, supposed (BENNETT and BERRY), i, 695.
*tetra*sulphide, oxidation of, with potassium permanganate, and metallic salts derived therefrom (RÂY), i, 352.
Triethylphosphine, salts and derivatives from (COLLIE), i, 797.
additive compound of carbon disulphide and (WIBAUT), i, 527.
compounds of, with iodoform (STEINKOPF and BESSARITSCH), i, 496.
Triethylpropylphosphonium iodide (STEINKOPF and BESSARITSCH), i, 496.
Triethyltrimethylenetriamine, salts of (GRAYMORE), i, 76.
Trimercuriaceto-*o*-toluidide acetate (ROSSI and BOCCHI), i, 601.
3:4:5-Trimethoxyacetophenone, oxime of, and ω-amino-, hydrochloride and ω-oximo-, and its sodium salt (SONN, MÜLLER, BÜLOW, and MEYER), i, 932.
3:4:5-Trimethoxy-1-γ-aminopropylbenzene (MERCK, WOLFES, and DÜTZMANN), i, 393.
1:2:6-Trimethoxyanthraquinone, 7-hydroxy- (JACOBSON and ADAMS), i, 1077.

1:2:6-Trimethoxy-9-anthrone, 7-hydroxy- (JACOBSON and ADAMS), i, 1077.
3:4:5-Trimethoxybenzaldehyde, formation of, from trimethylgallic acid (SONN and MEYER), i, 931.
3:4:5-Trimethoxybenz-*p*-anisidide, and its derivatives (SONN and MEYER), i, 932.
3:4:5-Trimethoxybenzbenzylamide, and its derivatives (SONN and MEYER), i, 932.
3′:4′:5-Trimethoxybenzil, 2:4-*di*- and 2:4:6-*tri*-hydroxy-, and their acetyl derivatives (MARSH and STEPHEN), i, 1158.
3:4:5-Trimethoxybenzmethylamide, and its derivatives (SONN and MEYER), i, 932.
3:4:5-Trimethoxybenz-*p*-toluidide (SONN and MEYER), i, 931.
5:3′:4′-Trimethoxy-4-benzyl-1:2-dihydrocoumarone, α:3:6-*tri*hydroxy- (DEAN and NIERENSTEIN), i, 282.
5:3′:4′-Trimethoxy-4-benzyl-1:2-dihydro-3:6-quinocoumarone, α-hydroxy-, and its acetyl derivative (DEAN and NIERENSTEIN), i, 282.
3:4:5-Trimethoxybenzylidenemethylamine (SONN, MÜLLER, BÜLOW, and MEYER), i, 932.
4(3′:4′:5′-Trimethoxybenzylidene)-2-phenyl-5-oxazolone (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
3:4:5-Trimethoxybenzylmethylamine, and its derivatives (SONN, MÜLLER, BÜLOW, and MEYER), i, 932.
3:4:5-Trimethoxy-1-γ-bromopropylbenzene (MERCK, WOLFES, and DÜTZMANN), i, 393.
3:5.7-Trimethoxy-2-(2′:4′-dimethoxyphenyl) benzopyrylium chloride (WILLSTÄTTER and SCHMIDT), i, 54.
3 5:7-Trimethoxy-2-3′:4′-dimethoxyphenylbenzopyrylium chloride (WILLSTÄTTER, ZECHMEISTER, and KINDLER), i, 54.
3:7:2′-Trimethoxyflavone, 5-hydroxy- (KALFF and ROBINSON), i, 1303.
Trimethoxyglutaric acid, methyl ester and diamide of (HIRST and ROBERTSON), i, 365.
3:4:5-Trimethoxy-1-γ-methylaminopropylbenzene (MERCK, WOLFES, and DÜTZMANN), i, 393.
β-3:4:5-Trimethoxyphenylacrylic acid, α-amino-, benzoyl derivative (SONN, MÜLLER, BÜLOW, and MEYER), i, 933.
2:4:6-Trimethoxyphenyl α-bromo-β-phenylethyl ketone (FREUDENBERG, FIKENTSCHER, and HARDER), i, 420.
α-3:4:5-Trimethoxyphenylethylamine, and its derivatives (SONN, MÜLLER, BÜLOW, and MEYER), i, 932.
3′:5:7-Trimethoxy-2-phenyl-4-styrylbenzopyrylium chloride, 4′-hydroxy- (WALKER and HEILBRON), i, 693.
Trimethoxy-2-styrylchromones, *mono*- and *di*-hydroxy- (ROBINSON and SHINODA), i, 1302.
2:4′:4″-Trimethoxytriphenylmethane (GOMBERG and SNOW), i, 660.
4 4′:4″-Trimethoxytri-*m*-tolylmethyl chloride (GOMBERG and ANDERSON), i, 1065.
Trimethylalkoxyammonium hydroxides, strength of, as bases (STEWART and MAESER), i, 12.
ααβ-Trimethylallyl alcohol. See βγ-Dimethyl-Δ^α^-buten-γ-ol.
Trimethylamine, action of acid chlorides on (JONES and WHALEN), i, 801.
action of, on halogenated allyl halides (v. BRAUN and KÜHN), i, 1374.
Trimethylamine, chloro-, and its chloroplatinate (JONES and WHALEN), i, 802.
Trimethylamine oxide, strength of, as a base (STEWART and MASER), i, 12.
Trimethylammonium chloroferrates (REMY and ROTHE), ii, 1089.
Trimethylammoniumacetal, salts of (GUTH), i, 1248.
Trimethyl γ-arabinose (BAKER and HAWORTH), i, 365.
Trimethylarabonolactones (PRYDE, HIRST, and HUMPHREYS), i, 365.
3:3′:3″-Trimethylaurin (*o-cresaurin*), and its derivatives (GOMBERG and ANDERSON), i, 1064.
Trimethylbenzenesulphonic acids, and their amides (KRUBER), i, 1138.
2:2:6-Trimethylbenzopyran (CLAISEN), i, 277.
Trimethylcellulose-*A* (HESS and WELTZIEN), i, 517.
Trimethyldextrose (SCHLUBACH and RAUCHENBERGER), i, 889.
δε-Trimethyldextrose, and its phenylosazone (PACSU), i, 1243.
Trimethyldiethylguanidines (LECHER, GRAF, and GNÄDINGER), i, 1393.
Trimethyl-*N*:*N*′-diethylthiuronium salts (LECHER), i, 1391.
Trimethylemetine *di*iodide (KELLER and BERNHARD), i, 1086.
Trimethylene, chlorination of polymerides of (PUXEDDU), i, 1266.
Trimethylenedisulphonyl chloride, and its derivatives (AUTENRIETH and BÖLLI), i, 1469.
αα′-Trimethylene*di*iminodioctoic acid, and its derivatives (SCHLESINGER), i, 1250.

Trimethylene*di*thiolacetic acid, and its salts and derivatives (ROTHSTEIN), i, 231.

Trimethylene*di*thioglycollic acid. See Trimethylenedithiolacetic acid.

Trimethylenetriphenylmethane triketone (WEISS and KOREZYN), i, 560.

1:2:6-Trimethyl-4-ethyl-2:3-dihydropyridine-3:5-dicarboxylic acid, ethyl ester (MUMM), i, 966.

α-Trimethylethylene oxide, heat of combustion of (ZUBOV and SWIENTOSLAWSKI), ii, 364.

***N*:*N'*:*S*-Trimethyl-*N*-ethyl-ψ-thiocarbamide** (LECHER, GRAF, and GNÄDINGER), i, 1392.

ω-2:4 Trimethylfisetol (NIERENSTEIN, WANG, and WARR), i, 34.

Trimethyl galactonolactones (PRYDE, HIRST, and HUMPHREYS), i, 365.

αββ-Trimethylglutaro-γ-lactones, α- and α'-hydroxy- (ROTHSTEIN, STEVENSON, and THORPE), i, 884.

Trimethylglyoxalinium iodides, 4(5)-nitro- (BHAGWAT and PYMAN), i, 1175.

***trans*-*d*-2:2:4-Trimethyl*cyclo*hexane-1-carboxylic acid**, 3-hydroxy-, and its methyl ester (GIBSON and SIMONSEN), i, 920.

***d*-2:2:4-Trimethyl*cyclo*hexan-3-one-1-carboxylic acid**, and its derivatives (GIBSON and SIMONSEN), i, 919.

***l*-2:2:4-Trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid**, and its salts and methyl ester (GIBSON and SIMONSEN), i, 920.

1:2:5-Trimethylindazolium iodide, 3-bromo- (v. AUWERS and LOHR), i, 75.

Trimethyl β-methylarabinoside (HIRST and ROBERTSON), i, 365.

Trimethyl γ-methylarabinoside (BAKER and HAWORTH), i, 365.

Trimethylnaphthalene, amino-, and nitro- (PLÜSS), i, 1410.

2:3:3-Trimethyl-β-naphthindolenine (PLAUCHER, COLACICCHI, and BARBIERI), i, 379.

β-2:2:3-Trimethyl*cyclo*pentyl*iso*propyl alcohol, 3-cyano-, and its derivatives (HALLER and LEGAGNEUR), i, 924.

3:5:5'-Trimethylpyrazolidine cuprochloride (DIELS and KOLL), i, 988.

3:5:5-Trimethylpyrazoline-1-carbamide (LOCQUIN and HEILMANN), i, 837.

2:4:5-Trimethylpyrrole-3-aldehyde (FISCHER and NENITZESCU), i, 835.

2:3:4-Trimethylpyrryl-bis-(3-acetyl-2:4-dimethylpyrryl)methane (FISCHER and HEYSE), i, 78.

2:3:4-Trimethylpyrryl-bis-(3-carbethoxy-2:4-dimethylpyrryl)methane (FISCHER and HEYSE), i, 78.

Trimethylstibine, reactions of, with platinic and palladous chlorides (MORGAN and YARSLEY), i, 378.

Trimethylstibine *di*chloropalladium hydrochloride (MORGAN and YARSLEY), i, 378.

2:4:6-Trimethyl*cyclo*telluripentane-3:5-dione 1:1-*di*chloride (MORGAN and TAYLOR), i, 634.

2:4:6-Trimethyl*cyclo*telluropentane-3:5-dione, and its dioxime (MORGAN and TAYLOR), i, 634.

Trimethyltetrahydroindazoles, and their picrates (v. AUWERS, v. SASS, and WITTEKINDT), i, 1183.

3:3:5-Trimethyl-Δ^4-tetrahydro-1:2-pyridazine-1:2-dicarboxylic acid, ethyl ester (DIELS, BLOM, and KOLL), i, 976.

4:6:8-Trimethylthiochroman-4-ol (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

4:6:8-Trimethyl-Δ^3-thiochromene (KROLLPFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1307.

***N*:*N*:*N'*-Trimethyl-*N'*:*N''*:*N''*-triethylguanidinium salts** (LECHER, GRAF, and GNÄDINGER), i, 1393.

Trimethyltrimethylenetriamine, salts of (GRAYMORE), i, 76.

Trimethyltriphenylmethyl-α-methyl-*d*-glucoside, and its triacetyl derivative (HELFERICH and BECKER), i, 10.

3:3':3''-Trimethyl-*N*:*N'*:*N''*-triphenylpararosaniline (*triphenylros*-o-*toluidine*) (GOMBERG and ANDERSON), i, 1064.

1:4:5-Trimethyluracil, dimeride of, and its derivatives (SCHMEDES), i, 435.

1:3:9-Trimethyluric acid, action of alkalis on (GATEWOOD), i, 1189.

Trinaphthylenebenzene. See Decacyclene.

Tri-α-naphthylstibine, and its derivatives (MATSUMIYA), i, 1472.

2:4:6-Trinaphthyl-1:3:5-triazine, 2:4:6-*tri*-*p*-hydroxy- (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 441.

Trioxymethylene, and its diacetate (STAUDINGER and LÜTHY), i, 361.

Triphendioxazine, methylammonium base from, and its salts (KEHRMANN and WILD), i, 444.

Triphenylacetonitrile, *tri*-*p*-amino-, and its derivatives and *tri*-*o*-nitro- (VORLÄNDER), i, 1256.

Triphenylallene, dimerisation of (ZIEGLER, GRABBE, and ULRICH), i, 131; (STRAUS and EHRENSTEIN), i, 584.

aaγ-Triphenylallyl alcohol and its methyl ether (ZIEGLER, GRABBE, and ULRICH), i, 132.

Triphenylbenzylarsonium iodides (STEINKOPF and BESSARITSCH), i, 496.

Triphenylbismuthine, *tri*nitro-, and its derivatives (SUPNIEWSKI), i, 1473.

Triphenylcarbinol hydrochloride (HELFERICH and DEHE), i, 1269.

Triphenylcarbinol, 4:4′:4″-*tri*hydroxy-, hydrate (GOMBERG and SNOW), i, 661.

***d*- and *l*-Triphenylethanols, β-amino-**, camphosulphonates of (MCKENZIE and WILLS), i, 396.

***d*- and *l*- aaβ-Triphenylethyl alcohols, β-amino-** (MCKENZIE and WILLS), i, 396.

β-Triphenylethylamine hydrochloride (RUPE and GISIGER), i, 1095.

Triphenylgermanium bromide and oxide (MORGAN and DREW), i, 1197.

2:4:5-Triphenylglyoxaline, 2:4:5-*tri*-*p*-nitro- (TRÖGER and THOMAS), i, 979.

2:4:5-Triphenylglyoxaline-*m*-sulphonic acid (TRÖGER and THOMAS), i, 980.

Triphenylmethane (STRAUS and HEYN), i, 1430.
preparation of (NORRIS and YOUNG), i, 20.
constitution of coloured derivatives of (KEHRMANN), i, 435.
derivatives, halochromism of (BRAND, STALLMANN, GROEBE and STEIN), i, 397.

Triphenylmethane, *o*-hydroxy-. See *o*-Benzhydrylphenol.

Triphenylmethane colouring matters (DILTHEY), i, 650.
metallic lakes of (HALLER), ii, 287.
violet, detection of (HOLMES), ii, 1212.

Triphenylmethane series, coloured salts of (MADELUNG), i, 1459.

Triphenylmethanecarboxylic acid, *p*-hydroxy- (ORNDORFF and BARRETT), i, 36.

Triphenylmethanetricarboxylic acid, trimethyl ester (WEISS and KOREZYN), i, 560.

β-Triphenylmethoxypropionic acid and its sodium salt and ethyl ester (HELFERICH, MOOG, and JÜNGER), i, 791.

Triphenylmethyl (GOMBERG and FORRESTER), i, 1266.
chloride and peroxide, *tri*-*p*-hydroxy-acetyl and benzoyl derivatives (GOMBERG and SNOW), i, 661.

Triphenylmethylaminoacetic acid, and its salts and ethyl ester (HELFERICH, MOOG, and JÜNGER), i, 791.

***dl*-α-Triphenylmethylaminopropionic acid**, and its sodium salt and ethyl ester (HELFERICH, MOOG, and JÜNGER), i, 792.

Triphenylmethyldibenzoyldextrose *iso*-propylidene ether (HELFERICH, MOOG, and JÜNGER), i, 791.

α-Triphenylmethylethylene glycol, and its *di*-*p*-nitrobenzoate (LEWIS, NIERENSTEIN, and RICH), i, 936.

Triphenylmethyl-*d*-galactose (HELFERICH, MOOG, and JÜNGER), i, 790.

Triphenylmethyl-*d*-gluconic acid, potassium salt (HELFERICH, MOOG, and JÜNGER), i, 791.

Triphenylmethyl-*d*-gluconphenylhydrazide (HELFERICH, MOOG, and JÜNGER), i, 791.

Triphenylmethyl-*d*-glucoses, and their tetra-acetates (HELFERICH, MOOG, and JÜNGER), i, 790.

Triphenylmethyl-α- and -β-methyl-*d*-glucosides, and their derivatives (HELFERICH and BECKER), i, 10.

Triphenylmethylthiocarbamide (HELFERICH, MOOG, and JÜNGER), i, 791.

2:4:5-Triphenyloxazole, and amino-, and hydroxy-, and their derivatives (TRÖGER and PHILIPPSON), i, 986.

aaε-Triphenyl-Δ$^{\beta\delta}$-pentadiene γ-chloro- (STRAUS and EHRENSTEIN), i, 535.

Triphenylphosphine oxide, *tri*-, *m*-, and *p*-chloro- (CHALLENGER and WILKINSON), i, 172.

aaγ-Triphenylpropane (ZIEGLER, GRABBE, and ULRICH), i, 132.

aaγ-Triphenylpropane, **αβ-*di*bromo-** (ZIEGLER, RICHTER, and SCHNELL), i, 915.

aaγ-Triphenylpropan-α-ol, β-amino-, hydrochloride (THOMAS and BETTZIECHE), i, 250.

Triphenylpropargyl alcohol, and its ethers (MOUREU, DUFRAISSE and BLATT), i, 136.
thermochemistry of, and its derivatives (LANDRIEU and BLATT), i, 137.

aaγ-Triphenyl-Δ$^{\alpha}$-propene (ZIEGLER, GRABBE, and ULRICH), i, 132.

aγγ-Triphenylpropenyl methyl ether (STRAUS and EHRENSTEIN), i, 534.

aaβ-Triphenylpropyl alcohol, β-amino- (MCKENZIE and WILLS), i, 396.

aaγ-Triphenylpropyl alcohol (ZIEGLER, GRABBE, and ULRICH), i, 132.

ββγ-Triphenylpropyl alcohol (RAMART and AMAGAT), i, 659.

aaγ-Triphenylpropyl methyl ether (STRAUS and EHRENSTEIN), i, 535.

aaγ-Triphenylpropyl methyl ether β-bromo- (ZIEGLER, RICHTER, and SCHNELL), i, 915.

ααγ-Triphenyl-Δβ-propylene, γ-chloro- (STRAUS and EHRENSTEIN), i, 534.
ααβ-Triphenylpropylene αβ-glycol (ROGER), i, 660.
Triphenylpyrylium compounds, *m*-substituted (DILTHEY and RADMACHER), i, 1441.
Triphenylros-*o*-toluidine. See 3:3′:3″-Trimethyl-*N*:*N*′:*N*″-triphenylpararosaniline.
Triphenyltetrazolium *d*-camphorsulphonates (WEDEKIND), i, 678.
Tripyrocatechylarsinic acids, optically active, and their salts (ROSENHEIM and PLATO), i, 1412.
Tripyrocatechylantimonic acid, formula of (REIHLEN, SAPPER, and KALL), i, 912.
Tripyrrylmethanes (FISCHER and HEYSE), i, 76.
Triterpene from *l*-pinene (KONDAKOV and SAPRIKIN), i, 1293.
Trithiocarbonic acid, *di*-*p*-tolyl ester (AUTENRIETH and HEFNER), i, 1376.
Tri-*p*-tolyl thiophosphate (AUTENRIETH and MEYER), i, 807.
Tri-*p*-tolylbismuthine, *tri*-2-nitro-, and its derivatives (SUPNIEWSKI), i, 1473.
Tri-*m*-tolylcarbinol, 4:4′:4″-*tri*hydroxy-, triacetyl derivative (GOMBERG and ANDERSON), i, 1065.
Triton tæniatus, skin secretion of (MAKI), i, 327.
Tritopine, constitution of (SPÄTH and SEKA), i, 1093.
Trivinylarsine, βββ-*tri*chloro-, silver nitrate compound of (LEWIS and STIEGLER), i, 1470.
Trivinylmethylarsonium salts, βββ-*tri*chloro- (LEWIS and STIEGLER), i, 1470.
Trixanthylhydrazine (FOSSE and HIEULLE), i, 1130.
Trocstite (WHEATLEY), ii, 488.
l-**Tropamide** (MCKENZIE and STRATHERN), i, 401.
Tropic acid, β-dimethylaminoethyl and β-piperidinoethyl esters (CHEMISCHE WERKE GRENZACH), i, 31.
Tropic acid group, displacement reactions in (MCKENZIE and STRATHERN), i, 401.
Tropine *N*-oxide, and its derivatives (POLONOVSKI and POLONOVSKI), i, 829.
Trouton's rule, at absolute zero (PERRAKIS), ii, 492.
revised (BYK), ii, 97.
for associated liquids (WAGNER), ii, 762.
Truxenequinone (RADULESCU and GEORGESCU), i, 1286.
ζ-Truxinamic acids, and their methyl esters (STOERMER and KLOCKMANN), i, 928.
ζ-Truxinanilic acids, methyl esters and nitroso derivative (STOERMER and KLOCKMANN), i, 927.
ζ-Truxinic acid, and its derivatives (STOERMER and KLOCKMANN), i, 927.
Truxones, constitution and synthesis of (DE FAZI), i, 269.
Trypaflavine, sensitivity to light of (JOHN), i, 465.
Trypanocidal action and chemical constitution (KING and MURCH), i, 319.
Trypanocidal compounds (ADAMS and JOHNSON), i, 319.
Trypsin, activity of (EHRENBERG), i, 103.
effect of reagents on the activity of (HUGOUNENQ and LOISELEUR), i, 1198.
inactivation of, by Röntgen rays (CLARK and NORTHROP), i, 1361.
digestion with low concentrations of (EHRENBERG), i, 202.
production of ammonia in digestion by (HUNTER and SMITH), i, 473.
action of, on insulin (SCOTT), i, 870.
effect of lecithin and cholesterol on digestion by (STANDENATH), i, 473.
synthesis of proteins by (WASTENEYS and BORSOOK), i, 865.
pancreatic (WALDSCHMIDT-LEITZ and HARTENECK), i, 1360.
determination of (WILLSTÄTTER and PERSIEL), i, 741.
determination of, colorimetrically (SMORODINCEV and ADOVA), i, 473.
Tryptophan from silk fibroin (HIRATSUKA), i, 836.
content of, in proteins (JONES, GERSDORFF, and MOELLER), i, 98.
metabolism of. See **Metabolism.**
colour reactions of aldehydes with (BLANCHETIÈRE), i, 963; (KOMM), ii, 164.
detection of, by means of *Bacillus coli* (MME. E. and E. WOLLMAN), i, 205.
determination of, colorimetrically, and its separation from indole and skatole (KRAUS), ii, 448.
Tuberculin (MUELLER), i, 616.
Tuberculosis, lipase in (CAPPELLI), i, 725.
basic constituents of urine in (REINWEIN), i, 189.
Tumours, carbohydrate metabolism of (C. F. and G. T. CORI), i, 999, 1492.
formation of lactic acid in (WARBURG), i, 1492.

Tumours, urea in blood after inoculation with, and exposure to *X*-rays (DODDS, LAWSON, and MOTTRAM), i, 1492.
Tungsten, physical properties of (ZWIKKER), ii, 1041.
line spectrum of (WORTHING and RUDY), ii, 1102.
Röntgen ray absorption and emission spectra of (ZUMSTEIN) ii, 725.
K-series spectrum of (ALLISON and DUANE), ii, 250.
M-series spectrum of (THORAEUS), ii, 5.
spark spectrum of (BAYEN), ii, 168; (L. and E. BLOCH), ii, 168, 727; (LEMON), ii, 454.
X-ray absorption coefficient of (WARBURTON and RICHTMYER), ii, 1103.
electron emission from (DUSHMAN, ROWE, EWALD, and KIDNER), ii, 345.
emission of electrons from films on (KINGDON), ii, 9.
secondary electrons from (STUHLMAN), ii, 1104.
pure, electrical properties of (GEISS and VAN LIEMPT), ii, 638.
electrical properties of, after cold working (GEISS and VAN LIEMPT), ii, 372.
electro-deposition of (VAN LIEMPT), ii, 694.
incandescent, specific heat of (BOCKSTAHLER), ii, 643.
diffusion of carbon through (ANDREWS and DUSHMAN), ii, 500,
effect of cold working on density of (GEISS and VAN LIEMPT), ii, 762.
movement of a crystal of, under loads (GEISS), ii, 96.
macro-crystal formation in (ALTERTHUM), ii, 136.
equilibria of, with oxygen and with water vapour (ALTERTHUM and KOREF), ii, 1159.
Tungsten halides, action of, with ammonia and with potassamide in liquid ammonia (BERGSTROM), ii, 1083.
trioxide, equilibria of, with alkali tungstates (VAN LIEMPT), ii, 421.
selenide (MOSER and ATYNSKI), ii, 583.
Tungstic acid, electrolytic reduction of, in hydrochloric acid (COLLENBERG and BACKER), ii, 571.
electrolytic reduction of, in presence of oxalic acid (COLLENBERG and WILSON), ii, 1166.
alkyl and aryl ammonium salts (KRAUSE and KRAUSKOPF), i, 908.
Tungsten:—
Tungstic acid, complex compounds of, with pyrocatechol and pyrogallol (FERNANDES), i, 912, 1061.
Tungstates, reduction of (SPITZIN), ii, 1191.
Tungsten determination and separation:—
determination of, by means of bismuth and lead amalgams (SOMEYA), ii, 904.
determination of boron in (BROPHY), ii, 901.
determination of carbon in (KING), ii, 435.
separation of, from tin (JILEK and LUKAS), ii, 242.
Tungsten arc, measurements of (DE GROOT), ii, 1137.
Tungsten filaments, hafnium oxide in (VAN LIEMPT), ii, 233.
Tungsten wire, electrical explosion of (BRISCOE, ROBINSON, and STEPHENSON), ii, 348.
hard-drawn, softening of (KOREF), ii, 846.
Tunicin, Röntgen spectra of cellulose and (HERZOG and GONELL), i, 871.
Turbidimeter, micro- (CONKLIN), ii, 708.
Turgoelectricity (KOPACZEWSKI), ii, 978.
Turmeric paper, double-reacting (BRINSMAID), ii, 435.
Turpentine, oxidation of organic compounds in (WALKER), i, 990.
spruce, *l*-borneol from (WHEELER and HARRIS), i, 1437.
Tutocaine, experiments with (WAGNER), i, 1503.
Tyramine, preparation of (JOHNSON and DASCHAVSKY), i, 540.
influence of, on nitrogen metabolism (IWATSURU), i, 1502.
detection of, microchemically (VAN ITALLIE and STEENHAUER), ii, 608.
Tyrosinase in plants (BOAS and MERKENSCHLAGER), i, 474.
oxidative deamination by (ROBINSON and MCCANCE), i, 745.
deamination of tyrosine by (RAPER and WORMALL), i, 473; (HAPPOLD and RAPER; GORTNER), i, 474.
Tyrosine, deamination of, by tyrosinase (RAPER and WORMALL), i, 473; (HAPPOLD and RAPER; GORTNER), i, 474.
methylation of (ABDERHALDEN and SCHWAB), i, 1423.
determination of, in proteins (FÜRTH and FISCHER), ii, 448.
Tyrosine, bromo-, bromonitro-, chloro-, chlorobromo-, and chloronitro-, and their derivatives (ZEYNEK), i, 920.

Tyrosylalaninecarboxylic acid (HAVESTADT and FRICKE), i, 163.
Tyrosylaspartic acid (HAVESTADT and FRICKE), i, 163.
Tyrosylhistidinecarboxylic acid (HAVESTADT and FRICKE), i, 163.
Tyuyamunite (TSCHIRVINSKI), ii, 430.

U.

Ulmins, coal (FRANCIS and WHEELER), i, 1389.
Ultrabalance (HOLTZ and KUHLMANN), ii, 319; (KUHLMANN), ii, 706; (HOLTZ), ii, 1091.
Ultracentrifuge (SVEDBERG and RINDE), ii, 233.
Ultrafilters (MÜLLER), ii, 1061.
Ultrafiltration, mechanism of (DUCLAUX and ERRERA), ii, 530.
under pressure (BRUCKNER and OVERBECK), ii, 529.
of non-aqueous solutions (BECHHOLD and SZIDON), ii, 529.
electro- (BECHHOLD), ii, 1158.
Ultramarine, structure of (DOMINIKIEWICZ), ii, 1131.
Ultramicrons (SIEDENTOPF), ii, 637.
Ultramicroscope, kino- (KRAEMER), ii, 1156.
Umbilicus pendulinus, maltose in tubers of (BRIDEL), i, 620.
n-**Undecane-***a*-*ι*-**diol** (HELFERICH and SCHÄFER), i, 7.
n-**Undecan-ζ-ol** (HESS and BAPPERT), i, 849.
Undecaoxymethylene diacetate (STAUDINGER and LÜTHY), i, 361.
Unsaturated compounds, formation of, from halogenated open-chain derivatives (INGOLD), i, 357; (HAERDI and THORPE), i, 923.
polar and non-polar valencies in (SUGDEN, REED, and WILKINS), ii, 936.
catalytic hydrogenation of (LEBEDEV, KOBLIANSKY, and YAKUBCHIK), i, 350.
addition of iodine bromide and hypoiodous acid to (HOLDE and GORGAS), i, 882.
oxidation of, with permanganate (NAMETKIN), i, 1146.
action of silicates on (LEBEDEV and FILONENKO), i, 225.
action of thiocyanogen on (SÖDERBÄCK), i, 899; (CHALLENGER and BOTT), i, 936.
cyclic, theory of (PETRENKO-KRITSCHENKO), ii, 1122.
Unsaturation of organic ring systems (MEREJKOVSKI), i, 1291.
Unstable substances, attempts to isolate (STAUDINGER and KREIS), ii, 316.
Uracil xylosides, substituted (LEVENE and SOBOTKA), i, 1463.
Uracylic acid, brucine salt (PEISER), i, 1477.
Uræmia, diazo reactions of serum in (HEWITT), i, 726.
Uragoga ipecacuanha, alkaloids of (KELLER and BERNHARD), i, 1086.
Uranic hydroxide. See under Uranium.
Uranic acid. See under Uranium.
Uranium, isotopes of (HAHN), ii, 921.
change of, into uranium-*X* (GASCHLER), ii, 925.
Uranium compounds, isomorphism of zirconium and (FERNANDES), ii, 1133.
isomorphism of, with those of metals of the magnesium group (CAROBBI), ii, 892.
reactions of, with organic compounds in presence of sunlight (ALOY and VALDIGUIÉ), ii, 1081.
Uranium sulphates (MEYER and NACHOD), ii, 230.
Uranic hydroxide, precipitation of, electrometrically (BRITTON), ii, 1204.
Uranic acid, complex compounds of, with pyrocatechol and pyrogallol (FERNANDES), i, 912, 1061.
Uranyl salts, reduction of, with the dropping mercury cathode (HERASYMENKO), ii, 695.
Uranyl barium and silver carbonates (HEDVALL), ii, 990.
Uranylsulphites of the rare earths (CANNERI and FERNANDES), ii, 888.
Uranium determination and separation:—
determination of, oxidimetrically (KOBLIC), ii, 831.
determination of, in carnotite (BRINTON and ELLESTAD), ii, 72.
separation of, from rare earths (CANNERI and FERNANDES), ii, 71.
Uranylsalicylic acid, alkali salts (CANNERI and FERNANDES), ii, 71.
Urazole, *di*thio-, structure of (GUHA and RÂY), i, 702.
Urea (*carbamide*), formation of, in autolysis of liver and spleen (MCCANCE), i, 472.
metabolism of. See Metabolism.
as a source of nitrogen in ruminants (LAVROV, MOLTSCHANOVA, and OCHOTNIKOVA), i, 464.
influence of adrenaline on concentration of, in blood (DUBOIS and POLONOVSKI), i, 481.

Urea (*carbamide*), in fungi (IVANOV), i, 344, 746.
effect of, and its derivatives, on higher plants (E. and G. NICOLAS), i, 757.
in soils (COUTURIER and PERRAUD), i, 765.
decomposition of, in soils (LITTAUER), i, 218.
replacement of proteins by, in diet of milch animals (MORGEN, WINDHEUSER, and OHLMER), i, 217.
new form of, in urine (MOOR), i, 460.
determination of (HUNTER and DAUPHINEE), ii, 247.
apparatus for determination of (HORVATH), ii, 237.
determination of, colorimetrically (HUNTER and DAUPHINEE), i, 104.
determination of, in blood (KARR), i, 323; (PATTERSON), i, 1200.
determination of, in blood and urine (MURRAY), i, 710.
determination of, in physiological fluids (REHBERG; ROIG and HELMHOLTZ), i, 853.
determination of, in urine (KIKUCHI; GOLSE), i, 609.
See also Carbamide.
Urease, effect of alcohol on (ROSENFELD), i, 336.
gastric (KORTSCHAGIN), i, 200.
physiology of (LUCK and SETH), i, 1010.
soja bean, hydrolysis by (TAUBMANN), i, 744.
Urethane, density and compressibility of solutions of (RICHARDS and CHADWELL), ii, 1049.
Urethane, hydroxy-, alkyl derivatives of (NEUFFER and HOFFMAN), i, 891.
Urethanes, hydroxy- (OESPER and BROKER), i, 1407.
Urginea Burkei (African squill), active principles of (GEORGE), i, 823.
Uric acid, first synthesis of (BEHREND), i, 441.
supersaturated solutions of (STERN), ii, 196, 504, 1152.
solvent action of trimethylenetriamines on, and its trimethyl- and triethyl-trimethylenetriamine salts (GRAYMORE), i, 76.
catalytic oxidation of, and its copper salts (PIAUX), i, 592.
oxidation of, with iodine (FÜRTH), i, 1462.
decomposition of, by bacteria and moulds (MORRIS and ECKER), i, 478.
excretion of, in bile and urine (BRUGSCH and ROTHER), i, 860.
Uric acid, in blood (HARDING, ALLIN, and VAN WYCK), i, 94; (LENNOX and O'CONNOR), i, 711.
effect of fat diet on (HARDING, ALLIN, EAGLES, and VAN WYCK), i, 604.
in cerebrospinal fluid (BERNHARD), i, 326.
accumulation of, after liver removal (BOLLMANN, MANN, and MAGATH), i, 1496.
excretion of, in urine (RANGIER), i, 186; (CHELLE and RANGIER), i, 187.
sodium salt, transformation of, on keeping (STERN), ii, 34.
determination of, by Benedict's method (COHEN), i, 184.
determination of, in blood (BULMER, EAGLES, and HUNTER; GARRY), i 605; (BENEDICT), i, 995; (DELAVILLE and JONES), i, 1344.
determination of, in blood plasma (DELAVILLE and JONES), i, 1201.
determination of, in urine (AUFRECHT), i, 187.
Uric acids, methylated, synthesis of (PRÜSSE), i, 441.
substituted, action of alkalis on (GATEWOOD), i, 1188, 1189.
Uric acid glycols, oxidation of (SLOTTA), i, 1189.
Uricolytic index in diabetes (LANGFELDT and HOLMSEN), i, 1207.
Urindigo. See Diuracil-4:4′-indigotin.
Urine, effect of muscular exercise on composition of (LILJESTRAND and WILSON; WILSON, LONG, THOMPSON, and THURLOW), i, 1115.
effect of neutral salts on the acidity of (GYÖRGY), i, 459.
effect of calcium and potassium salts on acidity of (BENATT and HÄNDEL), i, 722.
secretion of (STARLING and VERNEY), i, 458.
effect of pituitary extracts on (SMITH and MCCLOSKY), i, 207.
acetone substances in (HUBBARD and NOBACK), i, 712.
acetone and β-hydroxybutyric acid in (LUBLIN), i, 459.
arsenic in (COX), ii, 157.
basic constituents of, in tuberculosis (REINWEIN), i, 189.
calculi in (RANDALL), i 1491.
capillary active substance of (KIESEL), i, 98.
excretion of carbon and nitrogen in (SCHIMIZU), i, 185.
excretion and detection of chlorophyll degradation products in (HOFSTETTER; KITAHARA), i, 460.

Urine, cholesterol in (GARDNER and GAINSBOROUGH), i, 1204.
red colouring matter in, after administration of chlorophyll (GODINHO), i, 460.
red pigment from *p*-dimethylaminobenzaldehyde and (SCHEFF), i, 855.
dextrose in (LUND and WOLF), i, 1205.
diastase in, in pancreatic diseases (HANSEN), i, 856.
nitrogen distribution in hydroxyproteic acids of (BRINGS), i, 328; (FREUND and SITTENBERGER-KRAFT), i, 723; (EDLBACHER), i, 855.
excretion of iminazole in, after disappearance of carnosine (HUNTER), i, 459.
nitrogen and chloride excretion in (TAKANOSU), i, 185.
organic bases in (HEFTER), i, 1350.
oxalate from (MOOR), i, 1490.
organic phosphorus of (YOUNGBURG and PUCHER), i, 98.
propepsin in (GOTTLIEB), i, 742.
salicyluric acid in (DRZIMAL), i, 99.
sugars in (GREENWALD, GROSS, and SAMET), i, 185.
urochrome and new form of urea in (MOOR), i, 460.
excretion of uric acid in (RANGIER), i, 186; (CHELLE and RANGIER), i, 186.
volatile substance of (PITTARELLI), i, 98.
of various animals, comparative biochemistry of (ROTHWELL), i, 1350.
camel's, constituents of (READ), i, 1204.
dog's, excretion of purine derivatives in (LANGFELDT and HOLMSEN), i, 1205.
of ruminants, distribution of nitrogen in, and its alkalinity after administration of sodium nitrate (ROGOZINSKI and STARZEVSKA; STARZEVSKA), i, 1355.
whale's (MORIMURA), i, 1348.
Urine, analytical methods relating to:—
analysis of (RAQUET and PAGET), i, 1350.
diazo reaction in (HUNTER), i, 459.
clinical detection of dextrose in (RUOSS), i, 185.
detection of hæmatoporphyrin and urobilin in (POLICARD and LEULIER), i, 1351.
detection and determination of indican in (GORE), i, 186.
detection of nitroaminophenols in (DESVERGNES), i, 328.
Urine, analytical methods relating to:—
detection of urobilin in (RODILLON), i, 722.
detection of urobilin and urobilinogen in (BENGUEREL), i, 460.
detection and determination of acetone in (ENGFELDT), i, 1490.
determination of, in urine and fæces (VAN SPENGLER; TERWEN), i, 1351.
determination of acetoacetic acid and β-hydroxybutyric acid in (GOLDBLATT), i, 1204.
determination of acetone in, colorimetrically (SITSEN), i, 855.
determination of ammonia in (YOVANOVITCH), i, 1114.
determination of ammonia in, colorimetrically (ORR), i, 184.
determination of ammonia and ammonium salts in (YOVANOVITCH), i, 1204.
determination of ammonia and urea in (MURRAY), i, 710.
determination of bismuth in (KÜRTHY and MÜLLER), i, 100.
determination of cystine in (MAGNUS-LEVY), i, 610.
determination of formic acid in (DE EDS), i, 713.
determination of guanidines in (SHARPE), i, 722.
hydrogen-ion determination in (HASTINGS, SENDROY, and ROBSON), i, 1490.
determination of iodides in (v. BODÓ), i, 1490.
determination of organic acids in (GOIFFON), i, 459.
determination of phenolsulphonephthalein in, in jaundice (ABRAMSON), i, 329.
determination of potassium and sodium in (v. DEHN), i, 855.
determination of reducing sugars in (WOKES), i, 1205.
diabetic, determination of sugar in (SUMNER), i, 186, 1491; (WILLIAMS and CASEY), i, 998.
determination of sugar, after santonin treatment (PÉGURIER), i, 609.
determination of urea in (KIKUCHI; GOLSE), i, 609; (ROIG and HELMHOLTZ), i, 853; (ADDIS), i, 1113.
determination of uric acid in (AUFRECHT), i, 187.
determination of urobilin in (VAN SPENGLER; TERWEN), i, 1351.
determination of urobilinogen in (TERWEN), i, 1351.

Urobilin, detection of (ADLER), i, 328.
detection of, in urine (BENGUEREL), i, 460.
detection of, in fæces (ADLERSBERG and PORGES), i, 98.
detection of, in urine (RODILLON), i, 720; (POLICARD and LEULIER), i, 1351.
determination of, in human excreta (OPITZ and BREHME), i, 187.
Urobilinogen, detection of, in urine (BENGUEREL), i, 460.
determination of, in urine and fæces (TERWEN), i, 1351.
Urocanic acid, formation and fate of, in the animal body (KONISHI), i, 731.
Urochrome, glycuronic acid as a constituent of (POLLECOFF), i, 186.
in urine (MOOR), i, 460.
Urochromogen (MOOR), i, 328.
Uroflavine (REINWEIN), i, 725.
Ursolic acid (VAN DER HAAR), i, 50.
Utricularia vulgaris, enzymes of (ADOVA), i, 202.

V.

Vaccines, bacterial, nitrogen content of (KAUTSKY, LEINEWEBER, and FAMULENER), i, 1511.
Vacuum apparatus, trap for mercury vapour in (HUGHES and POINDEXTER), ii, 818.
Vacuum door (MEHL and SMITH), ii, 707.
Vacuum gauge, laboratory (HAMLIN), ii, 431.
Valency (SCHÖNBERG), i, 557; (LORING), ii, 841.
problems of (MÜLLER), ii, 863.
electron theory of (LOWRY), ii, 15; (ODDO), ii, 623.
in relation to heat of combustion (KHARASCH and SHER), ii, 636.
magnetic theory of (LAURIE), ii, 16.
higher, in relation to assimilation and catalysis (TSCHELINCEV), ii, 481.
polar and non-polar, theories of (BURKHARDT and LAPWORTH), ii, 937.
in unsaturated compounds (SUGDEN, REED, and WILKINS), ii, 936.
Valeraldehyde, γ-hydroxy-, and its dimethylacetal, and their benzoyl derivatives (HELFERICH and FRIES), i, 1039.
Valerian root, Indian, oleo-resin from (BULLOCK), i, 1294.
n-Valeric acid, preparation of (GILMAN and PARKER), i, 228.
n-**Valeric acid**, hydroxylamine salt (OESPER and BALLARD), i, 1233.
furfuryl ester (ZANETTI), i, 567.
*iso***Valerylglycine**, ethyl ester (KARRER, MIYAMICHI, STORM, and WIDMER), i, 594.
Valonia, cell sap of, with reference to flotation (OSTERHOUT and DORCAS), i, 868.
Valonia macrophysa, permeability of, by arsenic (BROOKS), i, 1004.
Valve, fat-free, with porous glass plates (STOCK), ii, 1195.
Vanadic acid. See under Vanadium.
Vanadisalicylic acid (SCAGLIARINI and AIROLDI), i, 920.
Vanadium, ultra-violet spark spectrum of (KING), ii, 453.
ionised, spectrum of (MEGGERS), ii, 913.
Vanadium alloys with iron, temper colours of (TAMMANN and SIEBEL), ii, 1169.
Vanadium carbide and nitride (FRIEDERICH), ii, 375.
*pent*oxide sols (FREUNDLICH, STAPELFELDT, and ZOCHER), ii, 199, 200; (FREUNDLICH), ii, 1153.
alkali sulphates (ROSENHEIM and MONG), i, 1411.
Vanadic acid, determination of (FURMAN), ii, 442.
Vanadium organic compounds (SCAGLIARINI and AIROLDI), i, 920.
salts of organic acids (ROSENHEIM and MONG), i, 1411.
pyridine sulphate (SCAGLIARINI and AIROLDI), i, 920.
Vanadium determination and separation:—
determination of (HARTMANN), ii, 604.
determination of, iodometrically (STOPPEL, SIDENER, and BRINTON), ii, 73.
determination of, in presence of iron (SOMEYA), ii, 161.
determination of, in presence of iron and chromium (KOLTHOFF and TOMIČEK), ii, 72.
separation of, from molybdenum (STOPPEL, SIDENER, and BRINTON), ii, 718.
Vanillin, solubility of (MANGE and EHLER), ii, 119.
ferrous salt (ZETZSCHE, SILBERMANN, and VIELI), i, 1411.
condensation of, with methyl ethyl ketone (ICHIKAWA), i, 1156.
determination of (RADCLIFFE and SHARPLES), ii, 1210.
Vanillin, 5-chloro- (HANN), i, 1105.

Vanillinoxime *N*-phenyl ether (BAMBERGER), i, 142.
Vanillylidenenitromethane as an indicator (RAO, SRIKANTIA, and IYENGAR), i, 676.
5-Vanillylidene-2-thio-3-tolyl-4-ketothiazolidines, and 5-bromo-, 5-chloro-, 5-iodo-, and 5-nitro- (HANN), i, 1105.
Vanillylsuccinic acid, and its derivatives (BAKER and LAPWORTH), i, 670.
Vaporisation, kinetic theory of (BRADFORD), ii, 1142.
Vapour pressure (BERLINER and MAY), ii, 1045.
application of kinetic theory to (BRADFORD), ii, 26.
thermodynamic equation for (EUCKEN, KARWAT, and FRIED), ii, 98.
and ionisation of gases (BECKER), ii, 342.
of binary mixtures (BROWN), ii, 377.
and miscibility of binary mixed liquids (HERZFELD), ii, 1143.
of organic mixed liquids (LESLIE and CARE), ii, 1050.
of metallic chlorides (MAIER), ii, 850.
of monatomic substances (EGERTON), ii, 25.
of molecular compounds of phenols (WEISSENBERGER and SCHUSTER), 766.
of salts (LORENZ and HERZ), ii, 493.
of salt solutions, measurement of (SIDGWICK and EWBANK), ii, 38.
of solutions of non-volatile solvents (MALI), ii, 850.
charts for organic vapours (DAVIS), i, 1033.
Vasicine, and its salts (SEN and GHOSE), i, 958.
Vaterite (GIBSON, WYCKOFF, and MERWIN), ii, 1183.
Vegetables, cobalt and nickel in (BERTRAND and MOKRAGNATZ), i, 873.
effect of storage on the anti-scurvy value of (DELF), i, 484.
green, action of ultra-violet light on (HESS and WEINSTOCK), i, 212.
Velocity of absorption, effect of gas velocity and temperature (HASLAM, HERSHEY, and KEEN), ii, 106.
Velocity of chemical change, effect of diffusion on (SANO), ii, 681.
Velocity of coagulation of colloids (JABŁCZYŃSKI), ii, 34, 35.
Velocity of crystallisation (JENKINS), ii, 559.
Velocity of decomposition of esters (KARLSSON), ii, 877.
Velocity of diffusion, relation of, to viscosity and pressure (COHEN and BRUINS), ii, 280.
Velocity of diffusion of metals in mercury (COHEN and BRUINS), ii, 648.
Velocity of dissociation of solids (CENTNERSZWER and BRUŽS), ii, 685.
Velocity of esterification (PETRENKO-KRITSCHENKO, BOGATSKY, and LUBMAN), ii, 556.
Velocity of gas reactions, apparatus for measuring (LATSHAW and PATRICK), ii, 681.
Velocity of photochemical reaction (PERRIN and CHOUCROUN), ii, 55.
Velocity of reaction, theory of (BRÖNSTED), ii, 681; (LEWIS and SMITH), ii, 799.
coefficients of (WAGNER), ii, 406, 407.
and distribution of energy (HINSHELWOOD and THORNTON), ii, 1167.
ions influencing (v. EULER and RUDBERG), i, 135.
between two liquid phases (JABŁCZYŃSKI, WIECKOWSKI, and KLEIN), ii, 410.
in mixed solvents (JONES, MCCOMBIE, and SCARBOROUGH), ii, 137; (MCCOMBIE, ROBERTS, and SCARBOROUGH), ii, 554.
in heterogeneous systems in relation to rate of stirring (KLEIN), ii, 802.
bimolecular, in solutions (CHRISTIANSEN), ii, 47.
coupled (WEGSCHEIDER), ii, 47.
rapid, measurement of (HARTRIDGE and ROUGHTON), ii, 47.
Velocity of saponification of ionic esters (BRÖNSTED and DELBANCO), ii, 684.
Velocity of swelling of gels (LIEPATOV), ii, 685.
Velocity of transformation of metastable systems (STEPANOV), ii, 645.
β-Veratrylacrylic acid, α-cyano- (BAKER and ROBINSON), i, 926.
Veratrylaminoacetyl (FORSYTH, KELLY, and PYMAN), i, 1167.
1-Veratrylhydrohydrastinine, and 6′-amino-, 6′-nitro-, and their derivatives (HAWORTH, PERKIN, and RANKIN), i, 1314.
Veratrylideneaminoacetal (FORSYTH, KELLY, and PYMAN), i, 1167.
Veratrylnorhydrohydrastinine, 6′-bromo-, and its salts and formyl derivative and 6′-nitro- (HAWORTH and PERKIN), i, 970.
β-Veratrylpropionic acid, α-cyano- (BAKER and ROBINSON), i, 926.
β-Veratrylpropionitrile (BAKER and ROBINSON), i, 926.
Veronal, compound of pyramidone with (PFEIFFER), i, 1318.
Vesuvius, radioactivity of gases from (STOKLASA and PENKAVA), ii, 235.

Vibrio choleræ, biochemistry of (HIRSCH), i, 479.
Vicia faba, proteolytic enzymes in pods of (DANCKWORTH and PFAU), i, 202.
effect of boron compounds on the growth of (BRENCHLEY and THORNTON), i, 1368.
Vicianose, preparation of, from gein (HÉRISSEY and CHEYMOL), i, 1383.
Vine, alkaline chlorosis of (PRATOLONGO), i, 623.
phosphoric acid and nitrogen in leaves of (LAGATU and MAUME), i, 756.
tannins in shoots of ripening (PICARD), i, 346.
See also *Vitis vinifera*.
Vinegar, acetylmethylcarbinol in (VAN'T HOOFT), i, 772.
Vinylalkylcarbinols, conversion of, into ethyl alkyl ketones (DELABY and DUMOULIN), i, 632.
Vinylarsenious oxide, β-chloro- (LEWIS and STIEGLER), i, 1470.
Vinylarsines, bromo-, chloro-, and chloroiodo-derivatives (LEWIS and STIEGLER), i, 1470.
chloro- (HUNT and TURNER), i, 843.
Vinylarsinic acid, β-bromo-, and β-chloro-, silver salt (LEWIS and STIEGLER), i, 1470.
Vinylcarbinols, aryl-substituted, and their derivatives (ZIEGLER, RICHTER, and SOHNELL), i, 915.
poly-arylated, and their derivatives (ZIEGLER, GRABBE, and ULRICH), i, 131; (ZIEGLER), i, 395.
Vinyldiacetonamine, benzoyl derivatives of (KIPPING and GREASLEY), i, 144.
7-Vinyl-7:12-dihydro-7-benzophenarsazine, 7-β-chloro- (LEWIS and STIEGLER), i, 1470.
2:2′-*streptomono*Vinylene-4:4′-dicarbethoxy-3:3:5:5′-tetramethylpyrroflavinium salts (KÖNIG), i, 1184.
3:3′-*streptomono*Vinylene-2:2′-dimethylindorhodinium hydroxide, and its salts (KÖNIG), i, 1184.
3:3′-*streptomono*Vinylene-2:2′:5:5′-tetramethylindorhodinium salts (KÖNIG), i, 1184.
Vinylhydroxythiocyanoarsine, β-chloro- (LEWIS and STIEGLER), i, 1470.
Vinylindole, 3-ω-nitro-, 1-acetyl derivative (MAJIMA and KOTAKE), i, 1450.
3-Vinyl-2-methylindole, ω-nitro- (SEKA), i, 67.
1-Vinylphenanthrene (GADAMER, OBERLIN, and SCHOEBLER), i, 577.
6-Vinylphenarsazine, 6-β-chloro- (LEWIS and STIEGLER), i, 1470.
*iso*Violanthrone, *di*bromo-, and 4′:4″-*di*chloro- (ZINKE, FUNKE, and PONGRATZ), i, 819.
*di*hydroxy- (ZINKE, FUNKE, MATSCHER, WOLFBAUER, and LORBER), i, 1436.
Viscose, plasticity of (VENABLE), ii, 1058.
Viscosimeter, new (AUERBACH), ii, 589.
Ostwald (MARTIN), ii, 499.
Viscosity, measurement of (MARTIN), ii, 499; (DUCLAUX and ERRERA), ii, 1048.
and its relation to diffusion velocity (COHEN and BRUINS), ii, 280.
temperatures of equal (HERZ), ii, 1049.
as a function of volume (DUBIEF), ii, 498.
during esterification (CAUQUIL), ii, 964.
of colloidal solutions (SZEGVARI), ii, 111; (FREUNDLICH and SCHALEK), ii, 112; (MATTHÄUS; OSTWALD), ii, 663; (DE WAELE), ii, 777.
of disperse systems (OSTWALD), ii, 291, 392.
of reversible emulsions (JOSHI), ii, 776.
of gases at low temperatures (GÜNTHER), ii, 100.
and molecular weight of liquids (MACLEOD), ii, 498.
of liquids at the boiling point (MACLEOD), ii, 1049.
under pressure (BRIDGMAN), ii, 1143.
containing dissolved gases (LEWIS), ii, 377.
of binary mixed liquids (MACLEOD), ii, 280.
of organic liquids (WÖHLISCH), ii, 277.
of solutions (DE KOLOSOVSKI), ii, 765.
effect of, on specific heat of solutions (DE KOLOSOVSKI), ii, 653.
Vital-red. See Brilliant Congo R.
Vitamins (SCHEUNERT and HERMERSDÖRFER), i, 617; (GROEBBELS and SPERFELD), i, 1514; (SCHEUNERT and CANDELIN), i, 1515.
action of ultra-violet light on (SPINKA), i, 212; (ZILVA), i, 485.
colloid chemistry of (v. HAHN), ii, 664.
promoting bacterial growth (DAVIDSOHN), i, 108.
parasympathetic stimulants in extracts of (MORI), i, 1021.
deficiency of, in pernicious anæmia (DHAR), i, 1221.

Vitamins, influence of, on phosphates in blood (v. EULER and MYRBÄCK), i, 1515.
in milk (PRINGLE), i, 1018.
antineuritic, effect of ultra-violet light on (WILLIAMS), i, 751.
fat-soluble (NELSON and STEENBOCK), i, 484, 1020; (STEENBOCK and BLACK), i, 1020.
plant, formation of, by micro-organisms (MOCKERIDGE), i, 106.
water-soluble, of beer wort (SOUTHGATE), i, 209.
determination of, biochemically (SAGASTUME and SPEGAZZINI), i, 209.
Vitamin-*A* (STEENBOCK, NELSON, and BLACK; BEZSSONOFF; STEENBOCK and NELSON), i, 107.
formation of, in germination of (STEPP), i, 1220.
occurrence and distribution of, in the body according to age, diet, etc. (SHERMAN and BOYNTON), i, 1018; (SHERMAN and STORMS; SHERMAN and MACLEOD), i, 1019.
synthesis of, by *Chlorella* (COWARD), i, 750.
physical and chemical properties and derivatives of (TAKAHASHI, MAKAMIYA, KAWAKAMI, and KITASATO), i, 1365.
occurrence of copper compounds with (MCHARGUE), i, 1515.
persistence of, in plant tissues (COWARD), i, 1017.
in yeast fat (LUCE and MACLEAN), i, 483.
identity of (JAVILLIER, BAUDE, and LEVY-LAJEUNESSE), i, 617.
detection of, colorimetrically (ROSENHEIM and DRUMMOND), i, 1515.
determination of (SHERMAN and MUNSELL), i, 1018.
determination of, physiologically (JAVILLIER, BAUDE, and LEVY-LAJEUNESSE), i, 1364.
Vitamins-*A* and -*B*, influence of, on diet (EDERER), i, 869.
Vitamin-*B*, effect of phosphate manuring on production of, in plants (HORNEMANN), i, 623.
concentration of (LEVENE and VAN DER HOEVEN; KINNERSLEY and PETERS), i, 1516.
basal diet free from (BACHARACH), i, 1220.
in dried and evaporated milks (HARTWELL), i, 751.
effect of deficiency in, on blood sugar and liver glycogen (RANDOIN and LELESZ), i, 751.
Vitamin-*B*, effect of absence of, on fats and lipoids in blood (IWATSURU), i, 1515.
effect of deficiency of, on blood sugar (EGGLETON and GROSS), i, 1220.
in excreta of rats (SALMON), i, 1516.
effect of, on reproduction (PARKES and DRUMMOND), i, 1021.
reaction for (BEZSSONOFF; LEVINE), i, 1220.
Jendrassik reaction for (LEVINE), i, 108.
effect of bacterial flora on biological detection of (HELLER, MCELROY, and GARLOCK), i, 1365.
Vitamin-*C*, synthesis of, in germination (HONEYWELL and STEENBOCK), i, 751.
possible isolation of, from cabbage (BEZSSONOFF), i, 751.
effect of deficiency in, on urea in blood (RANDOIN and MICHAUX), i, 751.
in chicken liver (CARRICK and HAUGE), i, 617.
Vitamin-*D*, formation of, in germinating seeds (STEPP), i, 1221.
diets deficient in (MCCOLLUM, SIMMONDS, BECKER, and SHIPLEY), i, 1366.
Vitamin-*E* (EVANS and BURR), i, 1022.
in maize, wheat, and hemp-seed (SURE), i, 212.
solubility of, in organic solvents (SURE), i, 752.
Vitis vinifera (vine), constituents of the sap of (WORMALL), i, 215.
Vivianite, synthetic formation of (KURNAKOV), ii, 767.
Volatility, law of (MATIGNON), ii, 670.
Volcanoes, radioactivity of gases from (STOKLASA and PENKAVA), ii, 235.
rare gases from (PIUTTI and BOGGIO-LERA), ii, 1092.
Volume, contraction of, on solution (RAKSHIT), ii, 288.
of liquid mixtures (LORENZ and HERZ), ii, 101.
molecular, and molecular refraction (LORENZ and HERZ), ii, 356.
and molecular field (BATSCHINSKI), ii, 932.
relation between critical temperature and (LORENZ and HERZ), ii, 25, 183.
and internal pressure (SCHUSTER), ii, 1142.
changes of, in formation of solid compounds (SASLAVSKY), ii, 933.
of crystals (HENGLEIN), ii, 477.
of isomerides (WÖHLISCH), ii, 269.
of organic liquids (WÖHLISCH), ii, 277.

Volume, molecular, of salts at the melting point (LORENZ and HERZ), ii, 840.

W.

Walden inversion (LEVENE and MIKESKA), i, 5; (SENTER and WARD), i, 31, 1128; (MCKENZIE and TUDHOPE), i, 226; (KENYON, PHILLIPS, and TURLEY), i, 507; (TERRY and EICHELBERGER), i, 631.
Walnut. See *Juglans regia*.
Water, formation of, from its elements in presence of chlorine (NORRISH and RIDEAL), ii, 572.
catalytic synthesis of (LARSON and SMITH; REMY and SCHAEFFER), ii, 563.
physical properties of (MACLEOD), ii, 498.
absorption spectrum of (WITT), ii, 352; (REMY and GÖNNINGEN), ii, 1176.
infra-red absorption spectra of (DREISCH), ii, 627.
vapour, infra-red absorption spectrum of (DESLANDRES), ii, 736.
ultra-violet absorption spectrum of (DIEKE), ii, 180, 927.
emission spectrum of (WATSON), ii, 349.
thermal variation of magnetism of (CABRERA and DUPERIER), ii, 754.
conductivity of (BORDAS and TOUPLAIN), ii, 155.
activity coefficients and ionisation of, in solutions of potassium and sodium chlorides (HARNED), ii, 538.
distilled, hydrogen-ion concentration of (DAWSON), ii, 680.
effect of strong electrolytes on the dielectric constant of (ZAHN), ii, 263.
vapour, heat of adsorption of, by silica gels (PATRICK and GREIDER), ii, 870.
expansion of, on freezing (LAURIE), ii, 762.
vapour, temperature of, from a boiling aqueous solution (REISSMANN), ii, 105.
effect of salts on the vapour pressure of (SIDGWICK and EWBANK), ii, 38.
surface tension of (ALI), ii, 763.
effect of organic vapours on the surface tension of (KORÁN), ii, 659.
effect of electrolytes on the diffusion of, through collodion membranes (ADOLPH), ii, 859.
viscosity of (LEROUX), ii, 1048.
adsorption of, on glass and platinum (MCHAFFIE and LENHER), ii, 854.
Water, adsorption of, by silica gels (PATRICK and EBERMAN), ii, 284.
effect of curvature of surface on solubility of air in (BAYLIS), ii, 980.
structure of films on (ADAM), ii, 195.
influence of surface films on evaporation of (HEDESTRAND), ii, 102; (ADAM), ii, 658.
films on salt solutions, structure of (HARKINS and MCLAUGHLIN), ii, 959.
movement of bubbles of gas in (MCTAGGART), ii, 509.
capillary rise of, in various metallic tubes (CARVER and HOVORKA), ii, 647.
partial pressure of, in mixtures with sulphuric acid (GREENEWALT), ii, 493.
rôle of, in solids (BALAREFF), ii, 409.
effect of, on chemical reactions (PARSONS), ii, 880.
combination of, in colloids (HÜTTIG), ii, 516.
decomposition of, by metallic couples (HEDGES and MYERS), ii, 306.
fixation and metabolism of, in the organism (FISCHER; SCHADE; HANDOVSKY), ii, 36.
toxic effects of (UNDERHILL and SALLICK), i, 613.
distilled, use of, in biological work (CANALS and GENEVET), ii, 847.
Conductivity water, preparation of (BENCOWITZ and HOTCHKISS), ii, 317.
NATURAL WATER:—
action of, on copper (HENSTOCK), ii, 696.
presence of iodates in (HICKETHIER and JACOBUCCI), ii, 1197.
Lake water, nitrogen in (DOMOGALLA, JUDAY, and PETERSON; PETERSON, FRED, and DOMOGALLA), i, 765.
River water of the Rhine, gold and silver in (HABER and JAENICKE), ii, 997.
River and lake water of the United States (CLARKE), ii, 323.
Sea water, hydrogen-ion concentration of (ATKINS), i, 199.
equilibrium of carbonates and other weak acids in (IRVING), i, 1022.
evolution of iodine from (v. FELLENBERG), ii, 306.
corrosion of metals in (BENGOUGH and MAY), ii, 218.
oxidation in (HARVEY), ii, 1171.
Spring and mineral waters, ageing of (BAUDISCH and WELO), ii, 992.

NATURAL WATER:—
Spring and mineral waters, effect of, on colloids (HENRIJEAN and KOPACZEWSKI; D'ARSONVAL and BORDAS), ii, 291.
diuretic action of (STARKENSTEIN), i, 327.
Swiss, iodine in (v. FELLENBERG), i, 347.
Water analysis:—
distilled, detection of copper in (POIROT), ii, 242.
determination of, in mixtures of ether, alcohol, and water (NEWMAN), ii, 156.
determination of iron in (HOPKINS), ii, 1096.
Water bath, constant-level (WING), ii, 707.
Weights, molecular, determination of (BERL and RAU), ii, 24; (SADIKOV and MICHAILOV), ii, 32; (RASTELLI), ii, 1040.
by isothermal distillation (HRYWAKOWSKI), ii, 187.
with liquid ammonia as solvent (SCHMID and BECKER), i, 1386; (STOCK and POHLAND), ii, 489.
and viscosity of liquids (MACLEOD), ii, 498.
Weiss-Curie law, value of A in the (CABRERA; DUPERIER), ii, 173.
Wetting and capillarity (SCHULTZE), ii, 856.
Whale, biological relations of types of (FUSE), i, 1348.
cartilage and tendon of (OIKAWA), i, 1349.
genital cysts of (OKAZAKI), i, 1348.
flesh of (SUZUKI), i, 1349.
peritoneal fluid of (FUSE), i, 1349.
enzymes of the pancreas of (TAKATA), i, 1349.
nature of the stomachs of (TAKATA), i, 1348.
synovial fluid of (FUSE), i, 1348.
urine of. See Urine.
fin-back, blood of. See Blood.
sperm, amniotic fluid of (SUZUKI), i, 1350.
Whale oil, South Georgia, fatty acids in (ARMSTRONG and HILDITCH), i, 778.
Wheat, nutrients for culture of (JONES and PEMBER), i, 1030.
influence of a mineral fertiliser on development of (CHAUSSIN), i, 623.
culture of, with nitrogen, phosphorus, and potassium (PEMBER and McLEAN), i, 1121.
influence of soil temperature and moisture on (ECKERSON and DICKSON), i, 217.
Wheat, development of grains of (WOODMAN and ENGLEDOW), i, 217.
amino-nitrogen and protein in grains of (SHARP), i, 622.
nucleic acid from embryos of, and its sodium salts (THOMAS and DOX), i, 873.
vitamin-*E* in embryos of (SURE), i, 212.
Wheat bran, proteins of (JONES and GERSDORFF), i, 1027.
Wheat flour, gluten proteins from (BLISH and PINCKNEY), i, 176.
Whelk. See *Buccinum undatum*.
Wires, thermal conductivity of (BARRATT and WINTER), ii 736.
Wood from deciduous trees, chemistry of (HEUSER and BROTZ), i, 889.
degradation of, by fungi (WEHMER), i, 521.
determination of pentosans in (GIERISCH), i, 1122.
Woodruff. See *Asperula odorata*.
Wool, adsorption of dyes by (SPEAKMAN and BATTYE), ii 284.
absorption of water by (SHORTER and HALL), ii, 782.
dyeing of (SPEAKMAN), ii, 515.
mordanting of (ELÖD), ii, 531.
Wool fat (LIFSCHÜTZ), i, 327.
Wurtzite, crystal structure of graphite and (BECKENKAMP), ii, 271.

X.

Xanthates. See under Xanthic acid.
Xanthen, 3-hydroxy-, and its *di*bromo-derivative (SEN and SARKAR), i, 813.
Xanthic acid, salts, analysis of (CALCOTT, ENGLISH, and DOWNING), ii 606; (HIRSCHKIND), ii, 1212.
cadmium and molybdenum salts (CECCHETTI), i, 503.
alkylmercuric derivatives of (KOTEN and ADAMS), i, 236.
Xanthine oxydase (DIXON), i, 1010; (DIXON and THURLOW), i, 1213.
Xanthione (SCHÖNBERG, ROSENBACH, KRÜLL, and OSTWALD), i, 1300.
Xanthone, 1-hydroxy-, magnesium salt (ZETZSCHE, SILBERMANN and VIELI), i, 1411.
Xanthonecarboxylic acids, and their salts and derivatives (ANSCHÜTZ, STOLTENHOFF, and VOELLER), i, 1274.
Xanthophyll, preparation and properties of (SCHERTZ), i, 1024.
determination of (SCHERTZ), i, 871.
Xanthopropionic acid, and its sodium salt (LEVENE and MIKESKA), i, 512.

(o-*Xylene*, *Me* : *Me* = 1:2 ; m-*xylene*, *Me* : *Me* = 1:3 ; p-*xylene*, *Me* : *Me* = 1:4.)

Xanthopterin, and its barium salt, from *Gonypteryx rhamni* (WIELAND and SCHÖPF), i, 1465.

Xanthopyrrolecarboxylic acid, synthesis of (FISCHER and KLARER), i, 577.

d-**Xanthosuccinamic acid** (LEVENE and MIKESKA), i, 6.

Xanthosuccinic acid, and its sodium salts (LEVENE and MIKESKA), i, 6, 512.

Xenon hydrate (DE FORCRAND), ii, 812.

Ximenia americana (wild plum), constituents of (ANON.), i, 764.

m-**Xylene**, electrochemical oxidation of (FICHTER and MEYER), i, 381.

action of aluminium chloride on a mixture of phenanthrene and (SCHAARSCHMIDT, MAYER-BUGSTRÖM, and SEVON), i, 241.

Xylenes, extraction of, from crude xylol (PATTERSON, MCMILLAN, and SOMERVILLE), i, 124.

Xylenes, ω-bromo-, isomeric, polarity effects in (SHOESMITH and SLATER), i, 16.

p-**Xylene-2:6-disulphonyl** chloride (CHOUFOER), i, 896.

p-**Xylene-5-sulphonyl** chloride, 2-nitro- (CHOUFOER), i, 896.

as-m-**Xylidine**, oxidation of, and its methyl derivatives (FICHTER and MÜLLER), i, 805.

p-**Xylidine** hydroferricyanide (CUMMING), i, 122.

p-**2-Xylidine**, 5-chloro- hydrochloride (WHEELER and MORSE), i, 22.

ω-*as-m*-**Xylidinoacetophenone-***o*-**tolylhydrazone** (BUSCH, FRIEDENBERGER, and TISCHBEIN), i, 41.

Xylidino-*m*-**xylothiazole**, and its derivatives (LEVI), i, 445.

Xylindein, and its derivatives (KÖGL and v. TAEUFFENBACH), i, 1441.

Xylol, extraction of xylenes from (PATTERSON, MCMILLAN, and SOMERVILLE), i, 124.

3-Xyloyl-α-naphthoic acids (MASON), i, 33.

4-*m*-**Xylyl** benzyl ether (SCHORIGIN), i, 1404.

β-*p*-**Xylylaminoethyl alcohol**. See Ethyl-*p*-xylidine, *N*-hydroxy-.

p-**Xylylchrysofluorene** (DILTHEY), i, 652.

o-**Xylylene** sulphide (v. BRAUN, BAYER, and KAISER), i, 1445.

5-Xylylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, and its derivatives (GUHA and RÂY), i, 703.

1-*as-m*-Xylylindazole, 4-nitro- (v. AUWERS and FRESE), i, 1102.

s-m-**Xylylmethylcarbinol** (v. AUWERS, LECHNER, and BUNDESMANN), i, 266.

4-*m*-Xylyl methyl ketoximes, 5-hydroxy-, and their derivatives (v. AUWERS and JORDAN), i, 264.

3-Xylylrhodanylidene-Δ$^{5:3'}$-oxindoles (HANN), i, 987.

4-*m*-Xylylthiosemicarbazide (GUHA and RÂY), i, 703.

Y.

Yajeine (BARRIGA VILLALBA), i, 828.

Yajenine (BARRIGA VILLALBA), i, 828.

Yamamomo, fruit of (KOMATSU and NODZU), i, 1025.

Yeast, growth of (PESKETT), i, 1011, 1012.

effect of ammonium salts on (FULMER), i, 1508.

effect of calcium sulphate on the growth and fermentation of (RICHARDS), i, 1011.

non-homogeneity of (VAN NIEL and HOOFT), i, 1286.

acceleration of the activity of, by a biocatalyst (v. EULER and MYRBÄCK), i, 745.

effects of marmite and of, on calcification (KORENCHEVSKY and CARR), i, 211.

antineuritic concentrates of (KINNERSLEY and PETERS), i, 1516.

formation of acetylmethylcarbinol and 2:3-butyleneglycol in fermentation by (KLUYVER and DONKER), i, 1215.

toxicity of acids towards (TAYLOR), i, 1011.

reserve carbohydrates in (WARKANY), i, 105.

carbohydrate and fat metabolism in growth of (MACLEAN and HOFFERT), i, 204.

synthesis of coproporphyrin by (FISCHER and FINK), i, 105.

extracts, action of, on dextrose (KUHN and v. GRUNDHERR) i, 203.

enzymes of (NEUBERG), i, 336.

fermentation of galactose by (v. EULER and LÖVGREN), i, 1214; (ABDERHALDEN), i, 1362.

glycogen from (LING, NANJI, and PATON), i, 1011.

increase in invertase content of (WILLSTÄTTER, LOWRY, and SCHNEIDER), i, 1214.

fate of invertase of, in the animal organism (NOGAKI) i 745.

action of, on lactic acid (MYRBÄCK and EVERITT), i, 105.

Yeast, fermentation of mannitol by (Lvov), i, 1509.
metabolism of (Balls and Brown), i, 476.
effect of nitrates on (Fernbach and Nicolau), i, 477.
cells, nitrogenous equilibrium of (v. Euler and Sandberg), i, 1213.
changes in phosphates and glycogen by means of (v. Euler, Myrbäck, and Karlsson), i, 744.
adsorption of phosphoproteins of, by various adsorbents (Fodor and Schönfeld), ii, 857.
cleavage of polypeptides by (Fodor and Epstein), i, 1214; (Fodor, Bernfeld, and Schönfeld), i, 1215.
porphyrins in (Fischer and Fink), i, 866.
action of reductase of (Lvov), i, 1508.
sulphur-containing constituent of (Suzuki, Odake, and Mori), i, 338.
presence of trehalose in (E. M. and F. C. Koch), i, 1508.
crystalline bios-like substance from (Eddy, Kerr, and Williams), i, 342.
relations between the water-soluble growth factors in (v. Euler and Swartz), i, 209.
vitamin-*A* in the fat of (Luce and Maclean), i, 483.
co-zymase of (v. Euler and Myrbäck), i, 105.
zymocasein from (Lüers and Nowak) i, 338.
dried (v. Euler and Westling), i, 203; (Sobotka), i, 865.
fermentation by (Harden), i, 1010.
oxygenated, action of, on glycerol and on β-hydroxybutyric acid (Marian), i, 105.
effect of insulin on the functions of (Fürth), i, 107.
Yeast-nucleic acid, hydrolysis of (Jones and Perkins), i, 487.
Yttrium, arc spectrum of (Meggers and Moore), ii, 612.
arc and spark spectra of (Meggers), ii, 77.
Yttrium salts, solubility of (Crew, Steinert, and Hopkins), ii, 190.
Yttrium oxide, preparation of (Prandtl), ii, 489.

Z.

Zanthoxylum ovalifolium, constituents of oil from (Simonsen), i, 565.
Zea mays, proteins from the leaves of (Chibnall and Nolan), i, 215.
Zeeman effect (Heisenberg), ii, 8, 729; (Pauli), ii, 251; (Ornstein and Burger; Landé), ii, 340; (Back), ii, 341, 917; (Zeeman), ii, 614; (Hicks; Ornstein, Burger, and van Geel), ii, 729; (Mosharrafa; Conway; Gianfrancheschi), ii, 830; (Kronig), ii, 917; (Kapitza and Skinner), ii, 918; (van Geel; Tartakovski), ii, 1016.
Zeolites, properties and occurrence of (Weigel), ii, 709.
combination of water in (Rothmund), ii, 710.
Zinc, occurrence of, in soils, plants, and animals (McHargue), i, 1023.
structure of (Collins), ii, 926.
shifting of lines in spectrum of (Fukuda), ii, 1101.
K-absorption spectrum of (Walter), ii, 611.
atomic and band spectra of (Hulthèn), ii, 1113.
infra-red line spectrum of (Randall and St. Peter) ii, 1101.
spark spectrum of (v. Salis), ii, 334.
vacuum spark spectrum of (Sawyer and Martin), ii, 1100.
optical constants of crystals of (Graber), ii, 1041.
conductivities of (Schofield), ii, 273.
potentials of, in cyanide solutions (Walker, Sorrels, and Breckenridge), ii, 1066.
polarisation of, in alkaline solution (Jirsa and Loris), ii, 45.
electro-deposition of (Marshall), ii, 808.
absorption coefficient of electrons in vapour of (Brode), ii, 1020.
expansion coefficient of (Borelius and Johansson), ii, 27.
thermal expansion of (Grüneisen and Goens), ii, 488.
vapour pressure and entropy of (Rodebush and Dixon), ii, 492.
physical properties of crystals of (Grüneisen and Goens) ii, 22.
tensile strength of (Masing and Pólányi), ii, 370; (Schmid), ii, 752.
effect of colloids on the displacement of lead and copper by (Gray), ii, 578.
effect of impurities on the solubility of, in acids (Vondrаček and Izak-Križko) ii, 686.
solubility of, in hydrochloric acid (Ipatiev and Verchovski), ii, 1069.

Zinc, effect of emulsoids on the solution of, in solutions of copper, lead, and nickel salts (FRIEND and TIDMUS), ii, 306.
corrosion of, in sea-water (BENGOUGH and MAY), ii, 218.
physiological effects of iron and (BERTRAND and NAKAMURA), i, 1114.
Zinc alloys with aluminium (TANABE), ii, 204; (ISIHARA), ii, 298, 786.
tensile strength of (ELAM), ii, 954.
decomposition of (FRAENKEL and GOEZ), ii, 314.
with aluminium and copper (HANSON and GAYLER), ii, 974.
with antimony and lead (TAMMANN and DAHL), ii, 535.
with copper (GENDERS and BAILEY), ii, 297.
β-transformations in (HAUGHTON and GRIFFITHS), ii, 973.
equilibrium in (IITSUKA), ii, 651.
with copper, gold, and silver, Röntgen ray analysis of (WESTGREN and PHRAGMÉN), ii, 746.
with copper and magnesium, determination of magnesium in (SCHÜRMANN and SCHOB), ii, 902.
with gold (SALDAU), ii, 205.
with mercury and sodium, velocity of reaction of, with aqueous solutions (KLEIN), ii, 802.
with tin, electrolysis of (KREMANN and BAUKOVAC), ii, 679.
Zinc chloride, equilibrium of pyridine with (MASON and MATHEWS), ii, 1063.
compounds of proteins with (PAULI and SCHÖN), ii, 198.
additive compound of 3:5-dibromo-*o*-toluidine and (HANN and SPENCER), i, 653.
hydroxide, two crystal forms of (FRICKE), ii, 484.
precipitation of, electrometrically (BRITTON), ii, 1203.
oxide, solubility of, in water (REMY and KUHLMANN), ii, 119.
selenide (MOSER and ATYNSKI), ii, 583.
sulphate, specific heat of aqueous solutions of (COHEN, HELDERMAN, and MOESVELD), ii, 126.
solubility of hydrates of (BURY), ii, 119.
solubility of, in water (COHEN and MOESVELD; COHEN and HETTERSCHIJ), ii, 652.
action of lead iodide with (STOFFELLA), ii, 1064.
Zinc sulphide, scintillations in (STALONY-DABROVSKI), ii, 1027.
Hall effect with crystals of (LENZ), ii, 920.
Zinc organic compounds:—
Zinc diethyl, preparation of (MEYER), i, 893.
preparation and purification of (DENNIS and HANCE), i, 798.
diphenylcarbazides (FEIGL and LEDERER), i, 171.
phenylarsine iodide (JOB, REICH, and VERGNAUD), i, 173.
Zinc determination and separation:—
determination of (JÄRVINEN), ii, 602; (CONGDON, GUSS and WINTER), ii, 1002.
determination of, electrolytically, in presence of copper (SPRINGER), ii, 241.
determination of, gravimetrically (MARCKWALD and GEBHARDT), ii, 1002
determination of, in organic matter (LUTZ), ii, 825.
determination of, volumetrically (BEYNE), ii, 69, 438; (KIEPER), ii, 70.
recovery of, and its determination in biological material (THOMPSON), i, 1489.
separation of cadmium and (LUFF), ii, 159.
separation of cobalt, manganese, nickel, and (LEMARCHANDS), ii, 242.
separation of nickel and (KLING and LASSIEUR), ii 439.
Zinc wire, single crystal, thermo-electric effect of (LINDER; BRIDGMAN) ii, 1136.
Zincite, experiments on (DITTLER), ii, 1184.
Zingerone, preparation of (NOMURA), i, 1157.
homologues of (NOMURA and HOTTA), i, 1156.
*iso***Zingerone**. See 4-Methoxyphenylethyl methyl ketone, β-3-hydroxy-.
Zirconium, atomic weight of (HÖNIGSCHMID, ZINTL, and GONZÁLEZ), ii, 174; (HEVESY), ii, 255.
preparation of (VAN ARKEL and DE BOER), ii, 1193.
Zirconium compounds, isomorphism of uranium and (FERNANDES), ii 1133.
Zirconium carbide and nitride (FRIEDERICH), ii, 374.
*tetra*chloride compounds of, with β-diketones (DILTHEY), i, 1473.
double fluorides, solubility of (HEVESY, CHRISTIANSEN, and BERGLUND), ii, 505.

Zirconium hydroxide precipitation of, electrometrically (BRITTON), ii, 1203.
nitride (FRIEDERICH and SITTIG), ii, 420.
oxide, density of (HEVESY and BERGLUND), ii, 25.
phosphate (HEVESY and KIMURA), ii, 1085.
solubility of hafnium phosphate and (HEVESY and KIMURA), ii, 1147.
action of acids and bases on (DE BOER and VAN ARKEL), ii, 1185.
sulphate, isomorphism of cerium sulphate and (FERNANDES), ii, 748.
Zirconium separation:—
separation of, from its ores (DE BOER and VAN ARKEL), ii, 705.
Zirconium separation:—
separation of, from cerium, thorium, and titanium (MOSER and LESSING), ii, 718.
separation of hafnium and (NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN), ii, 62, 63; (DE BOER and VAN ARKEL), ii, 243; (MARQUIS, P. and G. URBAIN), ii, 699.
separation of, from iron (WENGER and MÜLLER), ii, 1207.
Zirconium ores, hafnium content of HEVESY and JANTZEN), ii, 430.
Zymase, formation of, in plants (PALLADIN and ILLJUVIEV), i, 1519.
activity of (PARIS), i, 475.
fermentation with (JENSEN), i, 337.
Zymocasein from yeast (LÜERS and NOWAK), i, 338.

ERRATA.

VOL. 126 (ABSTRACTS, 1924).

Page	Line	
i, 273	26	*for* "KERNER" read "KIRNER."

VOL. 128 (ABSTRACTS, 1925).

i, 30	9*	,,	"*α-cyano-β-salicylylpropionic acid*" read "*α-cyano-β-salicylpropionic acid*," and for "*α-cyano-β-*m*-tolylpropionic acid*" read "*α-cyano-β-*m*-hydroxyphenylpropionic acid.*"
i, 298	14—15	,,	"*ethyl 3-aldehydo-5-methylindole-2-carboxylate*" read "*3-aldehydo-5-methylindole-2-carboxylic acid.*"
i, 495	26	,,	"*dipropylallylammonium iodide*" read "*dipropyldiallylammonium iodide.*"
i, 510	26*	,,	"MÜLLER" *read* "MILLER."
i, 743	6*		Insert author's name, "S. THURLOW."
i, 759	7, 9, 18 and 20		for "*Mercuralis*" read "*Mercurialis.*"
i, 830	16 and 18		*for* "Columba" *read* "Calumba."
i, 881	23		*for* "Glattfield" *read* "Glattfeld."
i, 890	7*	,,	"N. EUSSLIN" *read* "H. ENSSLIN."
i, 943	26	,,	"hexahydrocadaline" *read* "hexahydrocadalene."
i, 954	15*	,,	"Nöhreu" *read* "Nöhren."
i, 971	2*	,,	"*Ketonor-7-demethylo-ψ-corydaline*" read "*Keto-7-demethylo-ψ-corydaline.*"
i, 1010	33	,,	"*Biochem. J.*" read "*Biochem. Z.*"
ii, 23	7*	,,	"JOUNEAUX" *read* "JOUNIAUX."
ii, 59	3	,,	"GETMAN" *read* "GERMANN."
ii, 65	18*	,,	"C. MÜLLER" *read* "E. MÜLLER."
ii, 195	4	,,	"ADAMS" *read* "ADAM."
ii, 257	5	,,	"SKOBELZYN" *read* "SKOBELTZYN."
ii, 279	17	,,	"SCHENK" *read* "SCHENCK."
ii, 382	1*		*for* "Maximum . . . 18 hours," *read* "The lowering of the adsorptive power of silica by decreasing the water content, noted by other observers, was confirmed."
ii, 383	1, 2		
ii, 763	10*		*for* "I. MASSOW" *read* "I. MASSON."
ii, 888	22	,,	"Thiosulphites" *read* "Thiosulphates."
ii, 936	18*	,,	"READ" *read* "REED."
ii, 942	6	,,	"WEISENBERG" *read* "WEISSENBERG."
ii, 1166	14	,,	"PUTTEN" *read* "PATTEN."

* From bottom.

INDEX TO PATENTS.

Austrian Patents.
99641, i, 1511
99642, i, 1511
99680, i, 1419

British Patents.
199091, i, 447
199092, i, 447
199093, i, 448
199870, i, 429
206150, i, 413
206152, i, 122
208151, i, 844
208721, i, 21
209767, i, 844
212569, i, 558
214628, i, 172
219922, i, 541
220302, i, 441
221976, i, 66
222136, i, 393
223190, i, 541
223221, i, 1453
223596, i, 955
224363, i, 145
224913, i, 809
230116, i, 685
230487, i, 1470
230607, i, 697
232740, i, 839
234677, i, 991
237735, i, 1154
239951, i, 1471
239985, i, 1446
240051, i, 1452
241109, i, 1448

German Patents (D.R.-P.).
382137, i, 31
387762, i, 133
387963, i, 13
388185, i, 132
388534, i, 136
389151, i, 86
389405, i, 402
389816, i, 425
389851, i, 407
389948, i, 376
390333, i, 431
390658, i, 380
392067, i, 440
392456, i, 427
392459, i, 427
393411, i, 429
393633, i, 374
393722, i, 989
394195, i, 804

German Patents (D.R.-P.).
394794, i, 406
394795, i, 86
394797, i, 277
394850, i, 148
395092, i, 297
395435, i, 408
395683, i, 429
395704, i, 544
395917, i, 587
396453, i, 387
396507, i, 301
396508, i, 294
396509, i, 414
396512, i, 599
396697, i, 85
396864, i, 87
397079, i, 87
397150, i, 407
397151, i, 86
397275, i, 86
397312, i, 406
397458, i, 86
397750, i, 400
397813, i, 397
398010, i, 374
398011, i, 393
398204, i, 301
398851, i, 300
399148, i, 824
399902, i, 589
399903, i, 828
400391, i, 572
402642, i, 596
402868, i, 598
402869, i, 598
403552, i, 988
410969, i, 1197
411050, i, 1170
411051, i, 1170
411052, i, 1145
411217, i, 1277
411519, i, 1233
411530, i, 1315
411955, i, 1418
412120, i, 1290
412122, i, 1334
412168, i, 1329
412169, i, 1410
412699, i, 1423
413835, i, 1473
413836, i, 1426
414142, i, 1431
414261, i, 1407
414262, i, 1437
414798, i, 1423

French Patents.
541612, i, 990
543112, i, 601
553300, i, 447
553301, i, 447
553302, i, 448
567181, i, 406
568978, ii, 62
569016, ii, 63
573368, i, 591
573603, i, 598
584401, i, 1330

Swiss Patents.
98917, i, 31
99208, i, 31
99209, i, 31
101817, i, 1377
103431, i, 406
103553, i, 447
103647, i, 1150
103774, i, 447
103980, i, 448
104479, i, 447
104480, i, 447
104481, i, 447
104482, i, 447
104483, i, 447
104484, i, 447
104720, i, 448
104721, i, 448
104946, i, 448
104947, i, 447
105164, i, 448
105845, i, 1377
105846, i, 1377
105847, i, 1377
107383, i, 1312
107349, i, 1249
107617, i, 1413
107776, i, 1133
107777, i, 1133
107778, i, 1133
107779, i, 1133
107780, i, 1133
107781, i, 1133
107782, i, 1133

United States Patents.
1501894, i, 319
1511919, i, 435
1518730, i, 399
1526627, i, 1889
1527868, i, 1045

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS

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8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

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14. The following abbreviations are permitted:—

melting point	m. p.
freezing point	f. p.
boiling point at 240° under 35 mm. pressure	b. p. 240°/35 mm.
density 1·462 at 20° compared with water at 4°	d_4^{20} 1·462
observed rotation at 17°	α_D^{17}
specific rotation at 17°	$[\alpha]_D^{17}$
specific refraction for D line at 10°	n_D^{10}
atomic weight	at. wt.
molecular weight	mol. wt.
molecule	mol.
gram-molecule	g.-mol.
atmospheres	atm.
with decomposition (in connexion with m. p.)	decomp.
absolute (temperature)	Abs.
corrected (do.)	corr.
gram-calories	cal.
kilogram-calories	Cal
British thermal units	B.Th.U.
grams	g.
kilograms	kg.
milligrams	mg.
centimetres	cm.
decimetres	dm.
cubic centimetres	c.c.
metres	m.
millimetres	mm.
normal (for solutions)	*N*
electromotive force	*E.M.F.*
potential difference	*P.D.*
for example	*e.g.*
that is	*i.e.*
namely	viz.
per cent.	%

Nomenclature.

15. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radical; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

16. Term compounds of metallic radicals with the OH group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

17. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen

phosphate, etc., to the acid salts. Basic salts as a rule are best designated merely by their *formulae*.

18. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

19. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$ α-iodobutane, $CH_3 \cdot CH_2 \cdot CHCl \cdot CN$, α-chlorobutyronitrile.

20. Isomeric open chain compounds must be represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$CH_3 \cdot CH_2 \diagup \!\!\!\diagdown CH \cdot CH \diagup \!\!\!\diagdown \begin{matrix} CH_3 \\ CH_3 \end{matrix} \text{ or } CH_3 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot CH_3$$

should be termed $\beta\gamma$-dimethylpentane, not methylethyl*iso*propylmethane, and

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \diagup \!\!\!\diagdown CH \cdot CH \diagup \!\!\!\diagdown \begin{matrix} CH_3 \\ CO_2H \end{matrix} \text{ or } CH_3 \cdot CHMe \cdot CHMe \cdot CO_2H$$

should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

21. Use names such as methane, ethane, etc., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3 \cdot [CH_2]_5 \cdot CH_3$, etc. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2 \cdot C \cdot CH_2$.

22. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, PhONa, etc., should be termed sodium methoxide, sodium phenoxide, etc.

23. The radicals indicated in the name of a compound are to be given in the order chloro-, bromo-, iodo-, fluoro-, nitro-, nitroso-, amino-, imino-, hydroxy-, aldehydo-, keto-, thiocyano-, acyloxy-,* alkyloxy-,* acyl-,* alkyl-.*

24. Compounds analogous to the acids of the lactic series containing the OH group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, etc., should in like manner be termed ethoxy-, phenoxy-, acetoxy-derivatives. Thus α-ethoxypropionic acid, $OEt \cdot CHMe \cdot CO_2H$, instead of ethyl-lactic acid;

* In these groups, closed chain radicals precede open chain radicals (*e.g.*, benzoyl, acetyl, or phenyl, methyl); within the same section, more saturated precede less saturated (*e.g.*, *cyclo*hexyl, phenyl, styryl) or less complex, more complex (*e.g.*, phenyl, naphthyl), univalent radicals precede bivalent, and so on.

3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3\cdot CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc\cdot CHMe\cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radical of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2\cdot CO_2H$, and not $C_6H_3(OEt)_2\cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot CO_2H$.

25. The term *ether* should be restricted to the oxides of hydrocarbon radicals and their derivatives, and the esters should be represented by names similar to those given to metallic salts.

26. When a substituent is one of the groups NH_2, NHR, NR_2, NH, or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, β-anilinoacrylic acid, $NHPh\cdot CH{:}CH\cdot CO_2H$, α-iminopropionic acid, $NH{:}CMe\cdot CO_2H$. When, however, the NH_2 group is substituted with an acid residue such as acetyl it becomes acetamido, etc.

27. Compounds of the radical SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

28. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

29. The Chemical Society's Collective Index (1913–1922) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

30. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

31. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

32. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicals, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^α for $CH_2\cdot CH_2\cdot CH_3$, Pr^β for $CH(CH_3)_2$, Bu for $CH_2\cdot[CH_3]_3$, Ph for C_6H_5, Ac for $CO\cdot CH_3$, and Bz for $CO\cdot C_6H_5$.

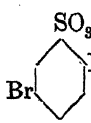
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

33. In representing the constitution of benzene derivatives, the relative positions of the radicals in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

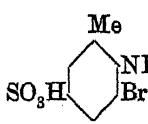
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radical of each of these parent substances is to be regarded as in position 1 (compare Chemical Society's Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—



Br is 2 : 5-dibromobenzenesulphonic acid;



is 3-bromo-*o*-toluidine-5-sulphonic acid.

34. In representing the constitution of derivatives of other cyclic hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, pending the adoption of a scheme by the International Committee.

35. Attention is directed to the list of physico-chemical symbols on pp. 10–13, which should be used whenever possible, and also to the list of radicals which appears at the end of the Chemical Society's Collective Index.

Manuscript.

36. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts must be written on quarto paper (8×10 in.).

37. Each abstract, however short, should be written on a separate sheet.

38. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

39. The name of the abstractor must be written at the end of the abstract.

40. Abstracts, whether in typescript or MS., should have a wide margin at the left side and sufficient space between the lines for insertion of corrections.

Proofs.

41. Abstractors are expected to read and correct proofs carefully, and to check all names, formulæ, and figures against MSS.

42. All proofs, however small, must be returned to the Editor not later than 24 hours after receipt from the printers.

*** The Editor's decision, in all matters connected with the Abstracts, must be considered final.

List of Physico-chemical Symbols adopted by the Chemical Society.

[See J.C.S., 1921, **119**, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation.....	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity.....	g	
Mechanical equivalent of heat	J	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height.....	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c t_c, T_c d_c	
Reduced quantities: pressure, volume, temperature, density	p_r, v_r t_r, T_r, d_r	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	σ
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	K, (K_c, K_p)	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal, etc.)	α	

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

Wave-length of light	λ	
Refractive index	n	n_r
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]^t_\lambda$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]^t_\lambda$	
Molecular refractive power	R_G, R_L $[R_G]^t_\lambda$, $[R_L]^t_\lambda$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10^3}, Λ_v, Λ_∞	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions	Λ_K, $\Lambda_{Cl'}$	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
δ	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h$, ${}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	Gas constant per mole; electrical resistance.
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_{cs}	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_{cs}	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_c, v_r	Critical volume : reduced volume.
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
${}_0\epsilon_h, {}_0\epsilon$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
$\Lambda_{10}, \Lambda_v, \Lambda_\infty$	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Bureau of Chemical Abstracts.

Abbreviated Title.	Journal.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Abh. Deut. Naturwiss. Med. Ver. Böhmen	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
Acta Phytochim.	Acta Phytochimica.
Acta. Sci. Fennicae	Acta Societatis Scientiarum Fennicae.
Agric. Bull. F. M. S.	Agricultural Bulletin of the Federated Malay States.
Agric. J. India	Agricultural Journal of India.
Agric. Res. Inst., Pusa, Rep. (Bull.)	Agricultural Research Institute, Pusa, Report and Bulletins.
Allgem. Z. Bierbrau.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Española de Física y Química.
Analyst	Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. di Bot.	Annali di Botanica.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique et de Chimie Appliquée.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Falsif.	Annales des Falsifications.
Ann. hyg. pub. méd. légale	Annales d'hygiène publique et de médicine légale.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Geol. Congo	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
Apoth.-Ztg.	Apotheker-Zeitung.
Arb. Gebiet. Physik, Math., Chem.	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
Arch. Entw.-mech. Org.	Archiv für Entwicklungsmechanik der Organismen.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim. Sci. aff.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Fisiol.	Archivio di Fisiologia.
Arch. Int. Med.	The Archives of Internal Medicine.
Arch. ital. Biol.	Archives italiennes de Biologie.

Abbreviated Title.	Journal.
Arch. Med. Pharm. milit.	Archives de Médicine et de Pharmacie militaires.
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Ist. Veneto Sci.	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti.
Beitr. Min. Japan	Beiträge zur Mineralogie von Japan.
Berg-Hüttenm. Rundsch.	Berg- und Hüttenmannisches Rundschau.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Oberhess. Ges. Natur. Heilkunde	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Berlin. Klin. Woch.	Berliner Klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt.
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacíonal des Ciencias, Cordoba.
Boll. Chim. farm.	Bolletino Chimico farmaceutico.
Boll. Soc. Geol. Ital.	Bolletino della Società Geologica Italiana.
Boll. Soc. Med.-Chirurg.	Bolletino della Società Medico-Chirurgica, Pavia.
Bot. Centr.	Botanisches Centralblatt.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. J. Phot.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Buletinul Chim.	Buletinul Chimie.
Bul. Soc. Chim. România	Buletinul Societătei de Chimie din România.
Bul. Soc. Romane Stiin.	Buletinul Societatii Romane de Stiinte.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Bureau of Standards	Bulletin of the Bureau of Standards (U.S.A.).
Bull. Com. Géol. Finlande	Bulletin de la Commission Géologique de Finlande.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. gén. Thérap.	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.

Abbreviated Title.	Journal.
Bull. Geol. d'Alsace . .	Bulletin du Service de la Carte Geologique d'Alsace et de Lorraine.
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institution of the University of Upsala.
Bull. Geol. Soc. Amer. .	Bulletin of the Geological Society of America.
Bull. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
Bull. Geol. Survey, West Australia	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Inst. . .	Bulletin of the Imperial Institute.
Bull. Indian Ind. Lab. .	Bulletin of Indian Industries and Labour.
Bull. Inst. Phys. Chem. Res., Japan.	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikwagaku Kerkyujo Ihō).
Bull. Johns Hopkins Hospital	Bulletin of the Johns Hopkins Hospital.
Bull. School Mines and Met., Univ. Missouri .	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol. .	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim. . .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg. .	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol. .	Bulletin de la Société de Chimie biologique.
Bull. Soc. d'Encour. . .	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franç. Phot. .	Bulletin de la Société Française de Photographie.
Bull. Soc. Géol. Belg. .	Bulletin de la Societie Géologique de Belgique.
Bull. Soc. Ind. Mulhouse .	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord. .	Bulletin de la Société Industrielle du Nord de la France.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull.WellcomeTrop.Res.Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J. . . .	Cairo Scientific Journal.
Canada Dept. Mines Publ. .	Canada Department of Mines Publications.
Canadian Chem. Met. .	Canadian Chemistry and Metallurgy.
Canadian Med. Assoc. J. .	Canadian Medical Association Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Casopis Math. Fysiky .	Časopis pro pěstování Mathematiky a Fysiky.
Cellulosechem. . . .	Cellulosechemie.
Centr. Min. . . .	Centralblatt für Mineralogie, Geologie und Paläontologie.
Chem. App. . . .	Chemische Apparatur.
Chem. Erde . . .	Chemie der Erde.
Chem. and Ind. . . .	Chemistry and Industry.
Chem. Ind. . . .	Chemische Industrie.
Chem. Listy . . .	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. and Met. Eng. .	Chemical and Metallurgical Engineering.
Chem. News . . .	Chemical News.
Chem. Trade J. . . .	Chemical Trade Journal.
Chem. Umschau . .	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad. . .	Chemisch Weekblad.
Chem.-Ztg.	Chemiker-Zeitung.
Chem. Zentr. . . .	Chemisches Zentralblatt.
Chim. et Ind. . . .	Chimie et Industrie.
Collegium	Collegium.

Abbreviated Title.	Journal.
Compt. rend. . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol. .	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch. . .	Deutsche medizinische Wochenschrift.
E.P.	English Patent.
Econ. Geol. . . .	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Engineering . . .	Engineering.
Eng. and Min. J. . .	Engineering and Mining Journal.
Exper. Stat. Rec. . .	Experiment Station Record.
F.P.	French Patent.
Farben-Ztg. . . .	Farben-Zeitung.
Fermentforsch. . . .	Fermentforschung.
Feuerungstechnik . .	Feuerungstechnik.
Flora	Flora.
Földtani Közlöny . .	Földtani Közlöny.
G.P.	German Patent.
Gas J.	Gas Journal.
Gas- u. Wasserfach . .	Gas- und Wasserfach.
Gas World	Gas World.
Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh. . .	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag.	Geological Magazine.
Gerber	Gerber.
Giorn. Chim. Ind. Appl. .	Giornale di Chimica Industriale ed Applicata.
Gummi-Ztg. . . .	Gummi-Zeitung.
Handl. Vijft. Nat. . .	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Heart	Heart.
Helv. Chim. Acta . .	Helvetica Chimica Acta.
Indian J. Med. Res. . .	Indian Journal of Medical Research.
India-rubber J. . . .	India-rubber Journal.
Ind. Eng. Chem. . .	Industrial and Engineering Chemistry.
Int. Rev. Sci. Pract. Agric.	International Review of the Science and Practice of Agriculture.
Int. Sugar J. . . .	International Sugar Journal.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.C.S.	Journal of the Chemical Society.
Jahrb. geol. Reichsanst. .	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min. . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.
Jahrb. Min. Beil.-Bd. .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv. . .	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot. . .	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Japan. J. Med. Sci. . .	Japanese Journal of Medical Sciences.
Japan. J. Phys. . . .	Japanese Journal of Physics.
Jernk. Ann. . . .	Jern-kontorets Annaler.
J. Agric. Res. . . .	Journal of Agricultural Research.
J. Agric. Sci. . . .	Journal of Agricultural Science.
J. Amer. Ceram. Soc. . .	Journal of the American Ceramic Society.

Abbreviated Title.	Journal.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo	*See* Kōgyō-Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Soc. Japan.	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Agric. Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Genetics.	Journal of Genetics.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene.	Journal of Hygiene.
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Indian Ind. Lab.	Journal of Indian Industries and Labour.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Ind. Hygiene.	Journal of Industrial Hygiene.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc.	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
J. Phys. Radium	Journal de Physique et le Radium.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal.	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.

Abbreviated Title.	Journal.
J. Roy. Agric. Soc. . .	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps .	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc. . .	Journal of the Royal Horticultural Society.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Scot. Met. Soc. . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts . . .	Journal of the Royal Society of Arts.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col. .	Journal of the Society of Dyers and Colourists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
J. Soc. Glass Tech. . .	Journal of the Society of Glass Technology.
J. S. African Chem. Inst. .	Journal of the South African Chemical Institute.
J. Textile Inst.	Journal of the Textile Institute.
J. Usines Gaz . . .	Journal des Usines à Gaz.
J. Washington Acad. Sci. .	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
K. Svenska Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch. . .	Keramisch Rundschau.
Kew Bull. . . .	Kew Bulletin.
Kōgyō-Kwagaku-Zasshi .	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
Kolloid Z. . . .	Kolloid Zeitschrift.
Koll.-Chem. Beih. . .	Kolloid-chemische Beihefte.
Kosmos	Kosmos (Lemberg).
Kühn-Archiv . . .	Kühn-Archiv.
Kunststoffe . . .	Kunststoffe.
Lancet	The Lancet.
Landw. Jahrb. . . .	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat. .	Die landwirtschaftlichen Versuchs-Stationen.
Louisiana Bull. . . .	Louisiana Bulletin.
Louisiana Planter . .	Louisiana Planter.
Lunds Univ. Arsskr. . .	Lunds Universitets Års-skrift.
Math. és Termés. Ert. .	Mathematikai és Természettudományi Ertesítö, Budapost.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Medd. on Grönland . .	Meddelser on Grönland.
Med. Genees. Lab. Weltevreden	Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden.
Med. Chron. . . .	Medical Chronicle.
Med. Klinik . . .	Medizinische Klinik.
Mem. Accad. Lincei . .	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō .	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mem. Soc. Ing. Civ. . .	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Mém. Poudres . . .	Mémorial des Poudres.
Metall u. Erz . . .	Metall und Erz.
Metallurgie . . .	Metallurgie.

Abbreviated Title.	Journal.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Materialprüf.	Mittheilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Mitt. Path. Inst. K. Univ. Japan	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik	Monatshefte für Mathematik und Physik.
Mon. Sci.	Moniteur Scientifique.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Naturw. Rdsch.	Naturwissenschaftliche Rundschau.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nippon Kwagaku Kwai Shi (J. Chem. Soc. Japan).	Nippon Kwagaku Kwa Shi (Journal of the Chemical Society of Japan).
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societétens Förhandlingar, Helsingfors.
Oesterr. Chem.-Ztg.	Oesterreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Paper	Paper.
Papierfabr.	Papier-Fabrikant.
Perf. and Essent. Oil Rec.	Perfumery and Essential Oil Record.
Per. spis. Sofia	Periodicesko spisanie Sofia.
Petroleum	Petroleum (German).
Pflüger's Archiv.	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Physica	Physica.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.

Abbreviated Title.	Journal.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc.	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania	Proceedings of the Royal Society of Tasmania.
Proc. Sci. Assoc., Vizianagram	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat.	Processi verbali Società Toscana di Scienze Naturali.
Pub. Fac. Sci. Univ. Masaryk.	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Prírodovèdeckou Facoultou Masarykovy University).
Pulp and Paper Mag.	Pulp and Paper Magazine of Canada.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Radium in Biol. Heilkunde	Radium in Biologie und Heilkunde.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rep. Aust. Assoc. Sci.	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Rev. chim.	Revue chimique . . . Oficijelni organ udruženja Jugoslavenskih Kemičara.
Rev. gén. Bot.	Revue générale de Botanique.
Rev. gén. Colloïd.	Revue générale des Colloïdes.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.

Abbreviated Title.	Journal.
Rev. Mét.	Revue de Métallurgie.
Rev. Real Acad. Ciencias exact. Madrid	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
Riv. Min. Crist. Ital. .	Rivista di Mineralogia e Cristallografia Italiana.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sbornik Klubu Pri. .	Sbornik Klubu Přírodovědeckého (Prague).
Schweiz. Apoth. Ztg.	Schweizerische Apotheker Zeitung.
Schweiz. Chem.-Ztg.	Schweizerische Chemiker Zeitung.
Science . . .	Science.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Seifensied. Ztg. . .	Seifensieder Zeitung.
Sitzungsber. Akad. München	Sitzungsberichte der bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Ges. Naturwiss. Marburg	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
Sitzungsber. Heidelberger Akad. Wis.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Med. Naturwiss. Münster	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
Sitzungsber. Naturforsch. Ges. Rostock	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
Sitzungsber. phys. med. Ges. Erlangen	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol. .	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll. .	Smithsonian Miscellaneous Collections.
Soil Sci.	Soil Science.
South African J. Ind. .	South African Journal of Industries.
South African J. Sci. .	South African Journal of Science.
Sprechsaal	Sprechsaal.
Stahl u. Eisen . . .	Stahl und Eisen.
Staz. sper. agr. ital. . .	Stazioni sperimentali agrarie italiane.
Strahlenther . . .	Strahlentherapie.
Suom. Tied. Toim. . .	Suomalaisen Tiedeakatemian Toimituskia.
Svensk Kem. Tidskr. .	Svensk Kemisk Tidskrift.
Tech. Rep. Tôhoku Imp. Univ.	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Tekn. Tidsk. . . .	Teknisk Tidskrift.
Textilber.	Melliand's Textilberichte über Wissenschaft, Industrie und Handel.
Ther. Gegenw. . .	Die Therapie der Gegenwart.
Ther. Monatsh. . . .	Therapeutische Half-Monatshefte.
Tonind.-Ztg. . . .	Tonindustrie-Zeitung.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals .	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.

Abbreviated Title.	Journal.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. Sth. Africa	Transactions of the Royal Society of South Africa.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind.	United States Bureau of Plant Industry.
U.S. Comm. Rept.	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull.	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
U.S.P.	United States Patent.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verh. Geol. Reichsanst. Wien	Verhandlungen der geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl.	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Vict. Mem. Mus. Geol. Survey, Canada	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
Videnskab. Skrifter	Skrifter udgivne af Videnskabsselskabet i Kristiania.
Wiener Klin. Woch.	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal.-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Wochbl. Papierfabr.	Wochenblatt für Papierfabrikation.
Woch. Brau.	Wochenschrift für Brauerei.
Yakugakuzasshi (J. Pharm. Soc. Japan).	Yakugakuzasshi (Journal of the Pharmaceutical Society of Japan).
Z. allg. Physiol.	Zeitschrift für allgemeine Physiologie.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. deut. Oel-Fett Ind.	Zeitschrift der deutschen Oel- und Fett-Industrie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. exp. Path. Ther.	Zeitschrift für experimentelle Pathologie und Therapie.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.

Abbreviated Title.	Journal.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Immunit.	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Z. Instrument.	Zeitschrift für Instrumentenkunde.
Z. Kryst.	Zeitschrift für Krystallographie.
Z. Leder-Gerb.-Chem.	Zeitschrift für Leder-und Gerberei-Chemie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. prakt. Geol.	Zeitschrift für praktische Geologie.
Z. Sauerstoff Stickstoff Ind.	Zeitschrift für Sauerstoff und Stickstoff Industrie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuckerind. Cechoslov.	Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.
Zellstoff u. Papier	Zellstoff und Papier.
Zentr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, January 15th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Robert P. Douglas	May 2nd, 1912.	Nov. 24th, 1924.
Khasberao B. Jadhava	June 16th, 1887.	Oct. 6th, 1924.
Edmund G. Lamb	May 4th, 1893.	Jan. 3rd, 1925.
George Downing Liveing	Nov. 21st, 1853.	Dec. 26th, 1924.
James McAlley	June 15th, 1899.	Feb. 1924.
William Sharman	June 4th, 1874.	Dec. 21st, 1924.

The PRESIDENT announced:

(1) That the names of the Members of Council who retire at the Annual General Meeting on the 26th March, 1925, and who are ineligible for re-election to the same office until the lapse of one year, are as follows:

President:
Prof. W. P. Wynne.

Foreign Secretary:
Dr. A. W. Crossley.

Vice-Presidents who have filled the office of President:
Prof. H. B. Dixon, Prof. P. F. Frankland.

Vice-Presidents who have not filled the office of President:
Prof. E. C. C. Baly, Dr. J. T. Hewitt.

Ordinary Members of Council:

(*a*) Town Members:
Dr. C. Dorée, Dr. J. J. Fox, Prof. J. R. Partington.

(*b*) Country Members:
Prof. I. M. Heilbron, Prof. J. W. McBain, Dr. W. H. Mills.

The following vacant places fall due to be filled at the Annual General Meeting on March 26th, 1925, in accordance with the Bye-Laws :

President	One vacancy.
Secretaries	One vacancy.
Foreign Secretary	One vacancy.
Vice-Presidents who have filled the office of President	Three vacancies.

(Note : the vacancy additional to the two prescribed by the Bye-Laws is caused by the death of Sir James Dobbie.)

Vice-Presidents who have not filled the office of President	Two vacancies.

Ordinary Members of Council :

(*a*) Town Members (*i.e.*, those living within a radius of 50 miles from Charing Cross)	Five vacancies.
(*b*) Country Members (*i.e.*, those living beyond a radius of 50 miles from Charing Cross)	Two vacancies.

(Note : In accordance with the Bye-Laws, the number of vacancies in each of the categories (*a*) and (*b*) is three. But this year the vacancies among Town Members are increased by two and among Country Members reduced by two, owing to Prof. C. K. Ingold and Prof. J. Reilly, who are no longer resident in the London area, being transferred from Town to Country Members; while the resignation of a Country Member increases the number of vacancies among Country Members from one to two.

The Council has nominated :

Dr. A. W. Crossley to the office of President.
Dr. T. Slater Price to the office of Secretary.
Prof. F. G. Donnan to the office of Foreign Secretary.

(2) That the following address of congratulation was presented by Sir William Pope, F.R.S., to the Société Chimique de France on December 22nd, 1924, on the occasion of the celebrations of the 50th Anniversary of the foundation of Stereochemistry by van't Hoff and Le Bel in 1874 :

" To the Société Chimique de France.

" The President, Council and Fellows of the Chemical Society rejoice to learn that the Société Chimique de France is meeting on December 22nd on the occasion of the 50th anniversary of the foundation of Stereochemistry by Joseph Achille Le Bel and Jacobus Henricus van't Hoff.

"These two savants will ever be remembered for one of the most important advances in modern chemical thought and practice. The masterly conception which they gave to the chemical world has proved a fruitful incentive to brilliant researches, which have not only confirmed their theoretical reasoning, but have also immeasurably widened our knowledge of chemical structure.

"The Chemical Society, which is proud to have the name of Joseph Achille Le Bel on its list of Foreign Fellows, welcomes the opportunity of joining with its sister Society in doing honour to Le Bel and van't Hoff and in paying homage to their genius.

"Signed on behalf of the Chemical Society,
W. P. WYNNE, *President.*
JOCELYN THORPE, *Treasurer.*
(L.S.)
T. SLATER PRICE, } *Secretaries.*
C. S. GIBSON, }
ARTHUR W. CROSSLEY, *Foreign Secretary.*

"Sealed in Council this Eighteenth day of December, One Thousand Nine Hundred and Twenty-four."

The following were formally admitted Fellows of the Chemical Society: H. J. George, E. Rothstein, R. F. Goldstein, S. Barratt, E. Roberts, J. A. Aeschlimann, J. Ross, and C. I. Kelly.

Certificates were read for the first time in favour of:

Claud McClellan Bottomley, B.Sc., 43, Manor Road, Blackburn.
Frederick Stanley Brown, B.Sc., A.I.C., Rosebank, Tile Hill Lane, Coventry.
Herbert Isaac Coombs, B.Sc., B.A., Trinity College, Cambridge.
Ernest James Davis, 45, McClure Street, Ormeon Road, Belfast.
Henry Bell Footner, B.Sc., Great Dean, nr. Christchurch, Hants.
Robert Owen Griffith, M.Sc., A.I.C., Muspratt Laboratory of Physical Chemistry, The University, Liverpool.
Herbert Henry Hodgson, M.A., Ph.D., B.Sc., F.I.C., 136, Paley Road, Bradford.
Wilford Jordayne Johnson, Devanha, South Road, Brighton Beach, Victoria, Australia.
William Wenallt Jones, M.Sc., 19, White Hart Lane, Wood Green, N. 22.
Jacob Kracovski, B.Sc., 11, Ernest Street, E. 1.
John Joseph Laws, 45, Fulham Road, South Kensington, S.W. 7.
Alexander John Simpson Leiper, 74, Whitworth Road, South Norwood, S.E. 25.
William Hamilton McVicker, M.Sc., 45, Wellington Park, Belfast.
Frank Douglas Miles, Caldwell Road, West Kilbride, Ayrshire.
William Bayley Parker, F.I.C., 3, Murray Road, Rugby.
Isaac Vogel, B.Sc., 16, Wellclose Square, E. 1.
Nellie Walker, M.A., Ph.D., B.Sc., 15, Fintry Place, Broughty Ferry.
James Ewart Whipp, 15, St. John's Street, Longsight, Manchester.

The following papers were read:

"6-Chlorophenoxarsine." By E. E. TURNER and A. B. SHEPPARD.

"The chemistry of the three-carbon system. Part III. αβ-βγ-Change in unsaturated acids." By G. A. R. KON and R. P. LINSTEAD.

"The influence of valency direction on the dissociation constants of dibasic acids." By C. H. SPIERS and J. F. THORPE.

"The relation of pilocarpidine to pilocarpine. Synthesis of 1 : 4- and 1 : 5-dimethylglyoxalines." By R. BURTLES, F. L. PYMAN, and J. ROYLANCE.

LECTURE.

Sir William Hardy, Sec.R.S., will deliver his Lecture entitled "Problems presented by Films on Solid Surfaces," on Thursday, February 26th, 1925, at 8 p.m., in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1.

ANNIVERSARY DINNER.

The Anniversary Dinner will be held in the Grand Hall of the Hotel Victoria, Northumberland Avenue, W.C. 2, on Thursday, March 26th, 1925, the day of the Annual General Meeting. Further particulars will be issued shortly.

ORDINARY SCIENTIFIC MEETINGS IN FEBRUARY.

February 5th, at 8 p.m.

February 19th, at 8 p.m., when a ballot for the election of Fellows will be held.

List of Papers received between December 19th, 1924, and January 15th, 1925. (This List does not include the titles of papers, or abstracts thereof, which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"Note on a simple constant-level apparatus for thermostats and water-baths." By J. M. SMITH.

"Studies of equilibrium in systems of the type $Al_2(SO_4)_3$–$M''SO_4$–H_2O. Part I. $Al_2(SO_4)_3$–$CuSO_4$–H_2O. $Al_2(SO_4)_3$–$MnSO_4$–H_2O at 30°." By R. M. CAVEN and T. C. MITCHELL.

"The mercuration of aromatic substances. Part I. Toluene." By S. COFFEY.

"The chemistry of the three-carbon system. Part IV. A case of retarded mobility." By G. A. R. KON and R. P. LINSTEAD.

"The velocity of reaction in mixed solvents. Part VIII. The velocity of formation of certain quaternary ammonium salts." By H. McCombie, H. M. Roberts, and H. A. Scarborough.

"Crystalline cuprous bromide." By D. B. Briggs.

"Phenyl benzyl diketone and some derivatives." By T. Malkin and R. Robinson.

"Tautomerism of amidines. Part V. Methylation of glyoxalines by diazomethane. Bromination of 4(or 5)-phenylglyoxaline." By W. G. Forsyth and F. L. Pyman.

"The mass of the hydrogen atom computed." By E. F. Morris.

"The reduction of aromatic nitro-compounds." By R. W. West.

"A redetermination of the atomic weight of boron." By H. V. A. Briscoe and P. L. Robinson.

"The interaction of nitrogen sulphide and sulphur. Nitrogen persulphide." By F. L. Usher.

"The composition of the liquid and vapour phases in mixtures of glycerol and water." By M. P. I. V. Iyer and F. L. Usher.

"Note on some metallic couples decomposing water at the ordinary temperature." By E. S. Hedges and J. E. Myers.

"Styrylbenzopyrylium salts. Part IV. γ-Styryl derivatives of 5 : 7-dihydroxy- and 5 : 7-dimethoxy-2-phenyl-4-methylbenzopyrylium chloride." By G. H. Walker and I. M. Heilbron.

"Styrylbenzopyrylium salts. Part V. Distyryl derivatives of 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride." By I. M. Heilbron, G. H. Walker, and J. S. Buck.

"Interactions of tellurium tetrachloride and acetic anhydride." By G. T. Morgan and H. D. K. Drew.

"Quantitative reduction by hydriodic acid of halogenated malonyl derivatives. Part IV. The influence of substitution in the amide group on the reactivity of the halogen atom in bromomalonamide." By R. W. West.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, FEBRUARY 19TH, 1925.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Ashley, Julius Nicholson, 37, Scarsdale Road, Victoria Park, Manchester. British. Chemical Research student at the Victoria University of Manchester. B.Sc. Hons. (Birm.) 1923. A.I.C. 1923. (*Signed by*) Arthur Lapworth, R. Robinson, Frederick Challenger.

BARTRAM, GEORGE ALFRED, 19, Valley Rd., Spital, Chesterfield. British. Teacher of Chemistry. Student at University College, Nottingham, 1914–15, 1919 and 1920. B.Sc. (London Pass), 1920; B.Sc. (Lond., 2nd Class Hons. Chem.), 1922. Elected A.I.C. 1923. Teacher of Chemistry 1920 to present time. In charge of Chem. Advanced Course recognised by Board of Education 1922 to present time. (*Signed by*) F. Stanley Kipping, E. B. R. Prideaux, J. B. Firth, A. R. Blackburn.

BEEBY, GEORGE HARRY, 92, Ashby Rd., Loughborough. English. Chemistry Research Student. Training received at Loughborough College, under A. Bramley, Esq., D.Sc., F.I.C., etc. Hold degree of B.Sc. London. 2nd Hons. Chemistry. A.I.C. Diploma of Loughborough College (Hons.). Engaged on Metallurgical Research. (*Signed by*) Arthur Bramley, George Lawton, T. L. Garner, A. T. Eggington.

BISHOP, ARTHUR HENRY BURDICK, Westminster Training College, 130, Horseferry Rd., Westminster, S.W. 1. British. Assistant Lecturer in Chemistry. Research for one year at Jesus College, Oxford, on "Adsorption of Gases by Glass Wool." At present engaged in research on "Optical Rotatory Dispersion." (*Signed by*) P. C. Austin, E. E. Walker, Gerald Druce.

BLOOMER, VINCENT, B.Sc., 33, Balfour St., Oldham. British. Student. Have completed 3 years' Honours Chemistry Course at Victoria University, Manchester; am now doing one year's research course for the degree of M.Sc. (*Signed by*) Henry Stephen, F. P. Burt, D. H. Bangham.

BOTTOMLEY, CLAUD MCCLELLAN, 43, Manor Road, Blackburn. British. Brewer. B.Sc. (Lond.) [Chemistry taken at Final Exam.]. (*Signed by*) W. J. Stansfield, A. Bramley, G. W. F. Holroyd.

BROWN, FREDERICK STANLEY, "Rosebank," Tile Hill Lane, Coventry. British. Research Student (in receipt of a Scientific and Industrial Research Grant). Two years' works experience. Academic training at University College of Wales, Aberystwyth, from 1919 up to present time. 1st Hons. B.Sc. (Wales). A.I.C. Over two years' research experience. *J.C.S.* 1923, Vol. **123**, 2430. *J.C.S.* 1924, Vol. **125**, 2219. (*Signed by*) T. Campbell James, C. R. Bury, Albert Green.

CHORLEY, PERCY, 87, Hazelbottom Rd., Crumpsall, Manchester. British. Chemist. M.Sc. (Vict.). Beyer Fellow, Victoria University, Manchester, 1914. Published, with Professor A. Lapworth, a paper on "A new series of nitrogenous compounds derived from camphoroxalic acid" (*Trans.*, 1920, 728). Chemist, on the staff of British Dyestuffs Corporation, Ltd. (*Signed by*) E. H. Rodd, R. Brightman, H. Swann, Carlton Butler, Morvan Lapworth.

COOMBS, HERBERT ISAAC, Trinity College, Cambridge. British. Student. Bachelor of Science, First-class Bachelor of Arts of Oxford; Research work under Professor Perkin, F.R.S., and Professor Hopkins, F.R.S. (*Signed by*) W. H. Perkin, H. Raymond Ing, R. H. Griffith, N. V. Sidgwick.

CORBET, ALEXANDER STEVEN, "Abbey Stone House," Sidmouth St., Reading. British. Chemist. B.Sc., Ph.D. (London University). A.I.C. Papers published with Professor H. Bassett: "The Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid," *J.C.S.*, June 1924. "A Phase-rule Study of the Cupro-, Argento-, Auro-, and Thallo-cyanides of Potassium," August, 1924. (*Signed by*) H. Bassett, J. W. Dodgson, D. Roy Maxted.

CROWE, WILLIAM HAUGHTON, "Bettwsville," Cherry Valley Park, Belfast (N. Ireland). British. Assistant in Chemistry (Q.U.B.). Research in Chemistry, Queen's University, Belfast. 1922–23, subject, "Effect of Light

on Brominations." 1923–24, University College, London, "Pyridones." (*Signed by*) A. W. Stewart, J. K. Marsh, H. Graham.

DAVIDSON, ALFRED, 91, Hazelbottom Rd., Cheetham, Manchester. British. Research Chemist, British Dyestuffs Corporation. B.Sc. (Glasgow) with distinction in Chemistry. T. S. Patterson and A. Davidson, *J.C.S.* (1912), **101**, 374. (*Signed by*) E. J. Amies, C. Hollins, S. C. Bate.

DAVIS, ERNEST JAMES, 45, McClure Street, Ormeau Road, Belfast. British. Chief Assistant Chemist, Messrs. Harland and Wolff, Belfast. Ten years Industrial Chemist with Messrs. J. Stone & Co., Deptford; Martin's Heat Treating and Testing Works, Coventry; Harland and Wolff, Ltd., Belfast. (*Signed by*) Henry Wren, Theophilus Harper, James W. Porter.

DUFFIN, WALTER MARK, 35, Binfield Road, S.W. 4. English. Research Student. A.R.C.S. B.Sc., London. Engaged in Research. (*Signed by*) H. B. Baker, G. A. R. Kon, Arnold Stevenson, M. A. Whiteley.

DURRANT, ARTHUR HYNARD, 47, Cassiobury Rd., London, E. 17. British. Bacteriologist and Demonstrator in Chemistry, Guy's Hospital and The Technical Institute, E. 17. Inventor of a Constant Cell, see *Junior Mechanic*, May, 1921. (*Signed by*) W. H. Collier, H. L. Long, E. C. Edgar.

EATON, FREDERICK JOHN, Ph.D. (Edin.), B.Sc. (Edin.), A.I.C., Chemical Laboratory, Gas Light and Coke Coy., Horseferry Rd., Westminster. British. Research Chemist, Gas Light and Coke Coy. Formerly part time Assistant Dept. of Medical Chemistry, Univ. of Edinburgh, and Research Student under Prof. Barger, F.R.S., Univ. of Edinburgh. Paper on "Blue Adsorption Compounds of Iodine," accepted 9th Sept., 1924. (*Signed by*) George Barger, Ellen Field, John E. Mackenzie.

EDWARDS, GEORGE ALFRED, 21, Crystal Palace Rd., London, S.E. 22. British. Demonstrator in Chemistry, King's College, London University. B.A. Oxon., First Class Honours in Chemistry. B.Sc. Oxon. Demonstrator in Chemistry at King's College, London University. Joint author of "Amino-derivatives of Tetrahydrocarbazole." (*Signed by*) Samuel Smiles, A. J. Allmand, E. W. McClelland, Frank W. Stoyle.

EMELÉUS, HARRY JULIUS, Battle, Sussex. British. Student. Research Student at Imperial College of Science and Technology. Graduate of London University. Chemistry (1st Class Hons.). A.R.C.S. (1st Class Chemistry). (*Signed by*) H. B. Baker, M. A. Whiteley, M. Carlton.

ESDAILE, RALPH MARGRAVE, the Lytle Coal Co., Ltd., Minerville, Pa., U.S.A. British. Chemist to the Lytle Coal Co., Ltd., Minerville, Pa., U.S.A. Trained at Finsbury Technical College, 1919–1923. Desires to receive the publications of the Chemical Society. Awarded Diploma, July, 1922, A.C.G.F.C. (*Signed by*) A. J. Hale, H. M. Atkinson, R. J. Seal.

FLACK, EDWARD HUGH ST. CLAIR, 9, Bridge Street, Cambridge. British born subject. Research Student in Organic Chemistry, Univ. of Cambridge. M.Sc. (Univ. of S. Africa). (*Signed by*) W. J. Pope, W. H. Mills, R. C. Odams.

FOOTNER, HENRY BELL, Great Dean, nr. Christchurch, Hants. British. Chemist. B.Sc. (Lond.), 1st Hons. Chemistry. 1922–1924, Research work on reactions of Alkyl Thiosulphates and Allied Compounds—publication pending. (*Signed by*) Samuel Smiles, C. Montague Bere, Hubert Painter.

GEOGHEGAN, DESMOND, 13, Port View, Heavitree, Exeter. British. Analytical Chemist. Three years pupil-assistant to T. Tickle, Esq., Devon County Analyst; two and a half years' experience in Practical Organic Chemistry and General Chemical Analysis at University College, Exeter, under Prof. W. H. Lewis. Educated at Sherborne School, Dorset, and at Douai School, Berks. Desire Fellowship, to have use of the Library, and

to keep in touch with modern research through the publications of the Society. (*Signed by*) Thomas Tickle, S. Glasstone, F. Southerden, R. King, W. H. Lewis.

GIBBY, CLIFTON WILLIAM, "The Rise," Foxley Lane, Purley, Surrey. British. Research Worker in Chemistry. Three years' study of Chemistry at University College, London, including a year's research with Professor Irvine Masson. Honours B.Sc. in Chemistry. A.I.C. by Exam. Now appointed Research Assistant to Mr. A. C. Egerton, at the Clarendon Laboratory, Oxford. (*Signed by*) F. G. Donnan, Henry Terrey, L. F. Gilbert.

GIBSON, REGINALD OSWALD, 41, Peak Hill, Sydenham, S.E. 26. British. Research Chemist. Bachelor of Science (London), 1924. Associate of the Institute of Chemistry, 1924. (*Signed by*) F. G. Donnan, W. E. Garner, O. L. Brady, I. E. Weber, V. W. Slater.

GIMINGHAM, CONRAD THEODORE (F.I.C.), Haddon House, Aarenbury Lane, Harpenden, Herts. British. Research Chemist, Insecticides and Fungicides Dept., Rothamsted Experimental Station, Harpenden, Herts. Research and Advisory Work in Agric. Chemistry at University of Bristol, 1909–1919. Research Work, Chemical Warfare Dept., 1916–1919. Chemist, Research Dept., Olympia Agric. Co., 1920–1923. Since then at Rothamsted Experimental Station. Various papers on Agric. Chem. subjects in *Jour. Agric. Sci.*, *Ann. App. Biol.*, etc. (*Signed by*) E. J. Russell, H. J. Page, H. W. Dudley.

GOODSPEED, JONATHAN, 36, Vicarage Lane, East Ham, E. 6. Student. Chemistry Student at East London College. (*Signed by*) J. R. Partington, E. E. Turner, B. D. Shaw.

GREENHALGH, RICHARD, 139, Stuart Street, Clayton, Manchester. British. Research work at Manchester University for M.Sc. Degree. Degree of B.Sc. in Chemistry Honours at Manchester University, Class II, Division I. (*Signed by*) Arthur Lapworth, Henry Stephen, Frederick Challenger, Fred Fairbrother, Colin Campbell.

GRIFFITH, ROBERT OWEN, Muspratt Laboratory of Physical Chemistry, Liverpool University. British. Lecturer in Physical Chemistry, Liverpool University. B.Sc., 1st Class Hons. Chem. (Liverpool), 1914; M.Sc., 1915; A.I.C., 1915–1918. Chemist under D.I.H.E., Liverpool. 1919, Lecturer in Physical Chemistry, Liverpool University. *Publications :* "Einstein's Law of the Photochemical Equivalent," Appendix VII. Lewis's "System of Physical Chemistry," Vol. 3, 3rd edition. Sections "Chemical Equilibrium" and "Reaction Velocity" in "Tables Annuelles de Constanter," Vol. 5 (in print). Papers in *J.C.S.* : (1) 1916, **109**, 67; (2) 1917, **111**, 389; (3) 1921, **119**, 1948; (4) 1923, **123**, 2752; (5) 1923, **123**, 2767. Also *Trans. Faraday Soc.*, 1921, **17**, 525. (*Signed by*) W. C. M. Lewis, F. C. Guthrie, E. C. C. Baly, I. M. Heilbron.

HAILWOOD, ANTHONY JAMES, Hazel Bank, Hazel Road, Altrincham. British. Research Chemist in the British Dyestuffs Corporation, Ltd., Manchester. Formerly on the manufacturing staff of the same Corporation. B.Sc. with 1st Class Honours in Physics (Manchester University). *Signed by*) W. H. Perkin, G. R. Clemo, S. C. Bate.

HISCOCKS, EDWARD STANLEY, 5, Rosehill, Swansea. British. Research Student, Chemistry Dept., University College, Swansea. Part-time Lecturer in Chemistry to the Municipal Technical College, Swansea. Hons. Graduate (Wales) in Chemistry. Part-time Lecturer in Physical and Inorganic Chemistry to the Municipal Technical College, Swansea. (*Signed by*) J. E. Coates, Leonard E. Hinkel, Ernest E. Ayling.

HODGSON, HERBERT HENRY, M.A. (Cambridge), B.Sc. (London), Ph.D. (Heidelberg), F.I.C., 136, Paley Road, Bradford. British. Head of Colour Chemistry Dept., Technical College, Huddersfield, since Sept. 1918. Previous posts, 1908–1912, Lecturer and Research Chemist, Technical College, Bradford; 1912–1915, Head of Chemical Dept., Northern Polytechnic Institute, London, N.; 1915–1918, Chief Chemist to Messrs. Brotherton & Co. at Birmingham and Stourton (Leeds). *Papers:* (1) "Dissertation," Heidelberg, 1908; (2) "Some Reactions of Phenyl Iodide, Chloride, and Iodosobenzene Acetate," *Proc. Camb. Phil. Soc.*, 1908; (3) "Isomere organische Magnesiumverbindungen" (with J. Schmidlin), *Ber.*, **41**, 430–437; (4) "Triphenylessigsäure und Tritolylessigsäure" (with J. Schmidlin), *Ber.*, **41**, 438–447; (5) "The Iodination of Phenols, etc." (with W. M. Gardner), *J.C.S.*, 1909, **95**, 1819–1827; (6) "The Development of Sulphuric Acid from Sulphide Dyestuffs and from Free Sulphur" (with W. M. Gardner), *J. Soc. Chem. Ind.*, 1910; (7) "The Action of Sulphur on Amines. Part I. *o*-Toluidine," *J.C.S.*, 1912, **101**, 1693–1701; (8) "The Action of Sulphur on Amines. Part II. Aniline," *J.C.S.*, 1914, **105**, 952–956; (9) "Nitrosation of Phenols. Part I. 3-Chloro-4-nitrosophenol and its Conversion into Two Isomeric Chloroquinone Monoximes" (with F. H. Moore), *J.C.S.*, 1923, **123**, 2499–2507; (10) "The Preparation of 2- and 4-Nitro-1-naphthols" (with E. Kilner), *J.C.S.*, 1924, **125**, 808–811; (11) "Direct Sulphuration of Aniline," *J.C.S.*, 1924, **125**, 1855–1858; (12) "Mononitration of *p*-Chlorotoluene" (with P. Anderson), *J.C.S.*, Oct. Notes, 1924; 4 papers now before the Publication Committee. *Patents:* Some New Sulphur Compounds and Dyestuffs therefrom, 1912; Preparation of Meta Halogenated Phenols, Brit. Pat. 200714; Preparation of Dihalogenated Fluoranes, Brit. Pat. 205254; Preparation of Tautomers of Nitroso-*m*-halogenated Phenols, Brit. Pat. 206734; 2 now filing on *m*-Hydroxybenzaldehyde and Azo Dyestuffs from Alkyl Thiol Amines. (*Signed by*) James Bruce, L. Gordon Paul, R. W. Merriman.

HUGHES, DAVID, 18, Holmes Grove, Westbury on Trym, Bristol. British. Chemist. At present on the Staff of British Colloids, Ltd. Passed Qualifying Examination of the Pharmaceutical Society, 1894. Engaged for 10 years in Chemical and Clinical Laboratory Work on my own account in Bath and Clifton. Studied Bacteriology under Prof. Stanley Kent, Bristol University. Co-operated with Dr. A. L. Flemming, Bristol, in a monograph on the Spectroscopic Examination of Blood in Ethyl Chloride Anæsthesia. Desirous of keeping up to date in developments of Chemical Science and to be allowed the privilege of the Library. (*Signed by*) John Macvie Hill, Archibald Macpherson, John F. Ward, Geo. A. Turner.

HUGHES, KATHLEEN HARRIET, 8, Ormiston Drive, Knock, Belfast. British. Lecturer in Pure and Applied Chemistry, Municipal College of Technology, Belfast. Lecturer in Chemistry, M.C.T.B., 1920–1924. Temporary Assistant Chemist, Government Laboratory, Strand, 1917–1920. (*Signed by*) Henry Wren, Theophilus Harper, James W. Porter.

HUNT, ARTHUR FREDERICK, 6, Seabrooke Cottages, Front Lane, Cranham (nr. Upminster), Essex. Chemical Research Student. B.Sc. (Lond.), 1st Class Hons. Research Student at East London College under Dr. E. E. Turner. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

INGHAM, BERTRAM HOBART, Yew Bank, Langham Rd., Bowdon, Cheshire. British. Research Student. B.Sc. Hons., Victoria University, Manchester (*Signed by*) Arthur Lapworth, F. P. Burt, J. E. Myers, Henry Stephen, R. Robinson.

JOHNSON, JOHN DOBNEY, 6, Edward St., Loughborough, Leics. British. Research Student. B.Sc. Hons., London. Royal Scholar. Research Student. (*Signed by*) Jocelyn Thorpe, M. A. Whiteley, G. A. R. Kon, Arnold Stevenson.

JOHNSON, WILFORD JORDAYNE, "Devanha," South Rd., Brighton Beach, Victoria. Licensed Gold Assayer and Chemical Analyst. Associate, Australian Chemical Institute. 1913–1922 (except for War Service), Assistant to Mr. Henry W. Levy, Assayer and Metallurgical Chemist, Melbourne, Australia. September 1922 to date, in partnership with Mr. Henry W. Levy, in private practice as Assayers and Metallurgical Chemists. (*Signed by*) D. O. Shiels, Henry W. Levy, Robert Law.

JONES, CECIL BRELLISFORD OAKES, Old Sewage Works, Whitley, Coventry. British. Analytical Chemist to the Coventry City Council. Four years assistant to W. D. Scouller, Esq., M.Sc., A.I.C., F.C.S. Ten years chief assistant to John Haworth, Esq., F.I.C., F.C.S. Author of "Sewage Works Analyses" (*Surveyor*, April 25th, 1924). (*Signed by*) John Haworth, W. D. Scouller, James H. Kershaw.

JONES, WILLIAM WENALLT, 19, White Hart Lane, Wood Green, N. 22. British. Assist. Chemist, The British Drug Houses, Ltd., Graham St., City Road, N. 1. B.Sc. Wales, June 1922; 2nd Class Honours Chemistry. M.Sc. Wales, June 1924. One session's Research Experience at the University College of North Wales, Bangor. (*Signed by*) Francis H. Carr, Charles Alex. Hill, S. Sugden.

KENNEDY, ALAN RICHMOND, 88, Sellons Avenue, Harlesden, N.W. 10. British. Assistant Chemist (Thomas de la Rue & Co., 110, Bunhill Row, E.C.). Undergraduate (University of London) in Faculty of Science (graduation, 1925). Employed in commercial Laboratory (founded by Dr. Hugo Müller). Desirous of receiving Society's literature concerning particularly modern researches in Organic Chemistry. (*Signed by*) Hubert L. Lucking, P. C. L. Thorne, E. de Barry Barnett, Henry J. S. Sand.

KENYON, FRANK, Power Station, Creekmouth, Barking, Essex. British. Chemist to the New Electrical Station, Barking, County of London Electric Supply Co., Ltd. Associate of the Institute of Chemistry, Branch D. (*Signed by*) J. Kenyon, J. L. White, Harold Hunter.

KING, FREDERICK ERNEST, 101, Cavendish Road, Highams Park, Essex. British. Student (Research at East London College). (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones.

KNOTT, ERIC, 21, West Richmond St., Edinburgh. British. Lecturer in Chemistry and Physics at the Royal Dispensary and School of Pharmacy of Edinburgh. Student of the Royal Dispensary and School of Pharmacy of Edinburgh, 1919–21, from which place I obtained the Qualifying Certificate of the Pharmaceutical Society and also the Diploma of Pharmaceutical Chemist. For past three years engaged as Lecturer at above School in Chemistry and Physics. (*Signed by*) Russell G. Thin, A. Scott Dodd, William Duncan.

KRACOVSKI, JACOB, 11, Ernest St., London, E. 1. English. Research Student. B.Sc., 1st Class Hons. in Chemistry. At present engaged in research. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, M. A. Whiteley, E. H. Farmer.

LAMBOURNE, HERBERT, 44, Brighton Road, S. Croydon, Surrey. British. Head of the Chemistry Dept., Borough Polytechnic Institute, Borough Road, S.E. 1. Late Senior Lecturer in Organic Chemistry, University College, Nottingham. Research work on "Quinaldine and Derivatives," "Methyl-

stannonic Acid and Derivatives." M.A. (Cantab.), M.Sc. (Lond.), F.I.C. (*Signed by*) F. S. Kipping, J. B. Firth, E. B. R. Prideaux, F. C. Laxton.

LAWS, JOHN JOSEPH, 45, Fulham Rd., South Kensington. English. Chemist, Dentist, and Optician. Holding the Qualifying Certificate of the Pharmaceutical Society of G.B. (Lond.). Hon. Treasurer of the Chemists' Dental Society of Great Britain and Ireland (Reg. No. 15073). Hon. Gen. Secretary of the Institute of Chemists and Opticians. Examiner in Refraction to the Institute of Chemists and Opticians. Member of the Public Dental Services. At one time principal of the West End College of Chemistry and Pharmacy. Private tutor of Chemistry for many years. (*Signed by*) Percy Barrs, Robert W. Lindsey, James Harry Smith, Frank B. Arnold.

LE FEVRE, RAYMOND JAMES WOOD, 17, Broadway Avenue, St. Margarets, Twickenham, Mdx. British. University Undergraduate. Chemistry Student, East London College (2nd year of final). (*Signed by*) J. R. Partington, E. E. Turner, B. D. Shaw.

LEIPER, ALEXANDER JOHN SIMPSON, 74, Whitworth Road, South Norwood, London, S.E. 25. Scottish. Chemist. I wish to join the Chemical Society in order to keep in touch with up-to-date research and proceedings. I am an Associate of the Royal College of Science in Chemistry. (*Signed by*) M. A. Whiteley, Jocelyn Thorpe, James C. Philip.

LENNANE, ALFRED JAMES ANDREW, 22, Ryder St., St. James's, S.W. 1. British. Physician and Surgeon. Formerly Opium Analyst to the Indian Government. M.R.C.S., L.R.C.P. (*Signed by*) Frank Radcliffe, Thos. R. Owles, Samuel Gray Fenton.

LILEY, FREDERICK WILLIAM, 41, Beaconsfield Rd., West Croydon. British. Assistant, Croydon Borough Analyst. Student at King's College, London. 2 Years assistant to Croydon Borough Analyst. (*Signed by*) Lester Reed, Eric K. Rideal, Ed. Hinks.

LUNT, JAMES GILBERT, 17, York Avenue, Sefton Park, Liverpool. British. B.Sc. of Liverpool. Chemical Analysis, c/o Anglo-South American Meat Co., San Martin 235, Buenos Aires, Argentina. (*Signed by*) I. M. Heilbron, William Doran, Stanley J. C. Snedker.

MCVICKER, WILLIAM HAMILTON, 45, Wellington Park, Belfast. British. Chemical Research Student. B.Sc. (1st Class Honours), and M.Sc., Queen's University of Belfast. Musgrave Research Student, Queen's University of Belfast, 1923–25. Joint author of 7 papers as follows: *J.C.S.*, **123**, 642, 817, 820, 2147; **125**, 1743; *J. Amer. C. S.*, XLVI, 1351; *Phil. Mag.*, XLVIII, 628. (*Signed by*) A. Killen Macbeth, Ernest W. McClelland, A. W. Stewart, J. K. Marsh, H. Graham.

MANN, THOMAS, Alexander Terrace, Bransty, Whitehaven. British. Partner in firm of Hellon and Mann, Analytical and Consulting Chemists, Whitehaven. (*Signed by*) G. W. Martin, C. A. Mitchell, Bernard Dyer.

MASCARENHAS, VINCENT MARK, Bangalore. Indian Christian. Student, Indian Institute of Science, Bangalore. Bachelor of Arts of the University of Mysore with Chemistry as a main subject. Completed the work on the Chemistry of Indian Black Mustard Seed Oil, and that of Malabar Tallow (*Vateria Indica*) awaiting publication in the Journal of the Indian Institute of Science. (*Signed by*) J. J. Sudborough, M. O. Forster, Roland V. Norris.

MILES, FRANK DOUGLAS, Caldwell Road, West Kilbride, Ayrshire. English. Research Chemist. Asst. Lecturer in Inorganic Chemistry, Heriot-Watt College, Edinburgh, 1909–1915. Service in Dept. of Explosives Supply,

1915–1919. Senior Research Chemist, H.M. Factory, Gretna. Chief Research Chemist, Messrs. Burt, Boulton, and Haywood, 1919–1922. At present a member of the Research Section of Nobel Industries, Ltd. *Publications:* "Egyptian Blue," with H. P. Laurie and W. F. P. McLintock, *Proc. Roy. Soc.*, 1914. Also papers in *Proc. Roy. Soc. Edin.* (two, 1915), and in *Journ. Soc. Chem. Ind.*, 1920 and 1922. "A Volumetric Method for the Estimation of Lead," *J.C.S.*, 1915, **107**, 988; "The Solubility of Sulphur Dioxide in Sulphuric Acids" (with J. Fenton), *J.C.S.*, 1920, **117**, 59. Also author of forthcoming volume of Lunge's "Sulphuric Acid and Alkali" entitled, "Sulphuric Acid—Contact Process." (*Signed by*) John Weir, Norman Picton, W. Young.

NIGHTINGALE, EDWARD ARTHUR, 39, Pacific Rd., Fords Park Rd., Canning Town, E. 16. British. Commercial Analytical Chemist, Messrs. Burt, Boulton, and Heywood, Ltd., Coal Tar and Creosote Works, Silvertown, 1918–1920. Messrs. Pinchin, Johnson & Co., Paint and Varnish Manufacturers, Silvertown, 1920. Student at Borough Polytechnic for Paints, Oils, and Colours. Student at East Ham Technical College, Chemistry, 6 years' course. City and Guilds of London Institute, Coal Tar, 1st Class certificate. (*Signed by*) R. W. Griffiths, W. H. Barker, W. T. Clough.

OFFORD, FREDERICK WILLIAM, 66, Watford Road, Canning Town, London, E. 16. English. Analytical Chemist. National Certificate in Chemistry, "Higher" or "Advanced," 1923. Worked under J. Bendix, F.I.C., F.C.S. (1915–1920). (*Signed by*) E. W. Griffiths, E. G. Churchill, W. H. Barker.

OUTRIDGE, LIONEL EDWARD, "Fernhurst," The Avenue, Chingford, Essex. British. Research Student. B.Sc. (London), Honours Chemistry. Research student at East London College under Dr. D. C. Jones. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

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PARKER, WILLIAM BAYLEY, F.I.C., 3, Murray Road, Rugby, Warwickshire. Chief Chemist (Research and Works), The British Thomson-Houston Co., Ltd., Rugby. Chief Chemist to B.T.H. from April 1902, and Author of "Specifications for Foundry Pig Irons," Pt. I and II., Proceedings British Foundrymens' Association, 1912–13 and 1906; "Specifications for Alloys for High Speed Superheated Steam Turbine Blading," Jnl. Inst. of Metals, No. 2, 1915; "Purchasing Specifications for Resins and Shellac," Jnl. Oil and Colour Chemists' Association, Vol. V, 1922; "Variation of Refractive Index and Density of Benzene with Temperature," W. B. Parker and G. Thompson, *Trans. Chem. Soc.*, 1922, Vol. **121**. (*Signed by*) Percy F. Frankland, S. Judd Lewis, Gartha Thompson.

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PAYNE, WILLIAM SAMUEL, Moseley House, Rounds Green, Oldbury. English. Chemist. 5 years Laboratory Steward, Oldbury Secondary Schools. 3 years Laboratory Steward, Oldbury Technical Schools. 2 years Demonstrator and Assistant Chemistry Master, Oldbury Technical Schools. U.E.I. Certificate in Advanced Inorganic and Physical Chemistry, 1924. (*Signed by*) John G. Clarke, C. Mansfield Swain, E. Pritchett.

PEARSON, KENNETH JOHN, 105, Winterbourne Road, Thornton Heath.

British. Two years Assistant to the Croydon Borough Analyst. (*Signed by*) Lester Reed, Ed. Hinks, Henry P. Stevens.

PIKE, RICHARD EDWIN, 6, Haymarket, London, S.W. 1. British. Student. Pass B.Sc. (Lond.). Studying for Honours at Royal College of Science since October, 1923. (*Signed by*) H. B. Baker, H. F. Harwood, M. A. Whiteley, James C. Philip.

PLUMBRIDGE, DOUGLAS VICTOR, 21, Heathfield Rd., Wavertree, Liverpool. British. Research Chemist. Ph.D. (Munich). A.R.C.Sc. (London). A.I.C. On the staff of the Chemical Dept., Messrs. The Salt Union, Ltd., Western Point, Cheshire. (*Signed by*) A. Bramley, Norman M. Comber, James C. Philip.

PRESTON, JOHN MASSEY, The Dower House, Euxton, Chorley, Lancs. British. Private Research in Chemistry. B.Sc., 2nd Class Hons. Chem. (Liv.). A.I.C. (*Signed by*) E. C. C. Baly, H. Rogerson, F. C. Guthrie.

RAPER, RICHARD, 12, Mill Lane, Cambridge. British. Research Student. 1st Class Honours in Nat. Sci. Tripos, Parts I and II (Chemistry) of Cambridge University. Two years' research work under Dr. Mills, F.R.S., and two years' experience as Demonstrator in Cambridge University Chemical Laboratory. (*Signed by*) W. J. Pope, W. H. Mills, H. R. Stevens.

RULE, JOHN FREDERICK JAMES, 29, Alexandra Road, East Ham, E. 6. Research Student. Have passed the B.Sc. Hons. examination in Chemistry of London University, and I am undertaking Research Work under Professor Partington. (*Signed by*) J. R. Partington, W. H. Patterson, E. E. Turner.

SCORAH, LESLIE VIVIAN DONALD, 139, Dodworth Road, Barnsley (Yorks). British. Research Student. B.Sc. (Hons. Chem.) Sheffield. A.I.C. (*Signed by*) W. P. Wynne, G. M. Bennett, F. G. Tryhorn, Arthur W. Chapman.

SHEPPARD, GEORGE FREDERICK, 72, Mortlake Rd., Kew Gardens, Surrey. British. Chemist, Cl. II. Department of Government Chemist. Position as above. Student, Royal College of Science, London, 1900–2, passed examinations of the Associateship Course in Chemistry for Revenue Students. Past experience: Analytical work in above Department since November, 1902. (*Signed by*) Thos. J. Cheater, W. Williamson, Robert Robertson, Geo. Stubbs.

SHEVLIN, JOSEPH THOMAS, "Corwen," Frederick Road, Wylde Green, Birmingham. British. Patent Agent. Associate of the Chartered Institute of Patent Agents. Associate of the Institute of Physics. Associate of the Institution of Electrical Engineers. Fellow Physical Society of London. I am desirous of becoming a Fellow of the Society in order that I may be well versed in the more recent developments in Chemistry. (*Signed by*) G. G. Henderson, F. J. Wilson, E. W. Moss.

SMETHURST, ARTHUR FREDERICK, Nippon, Cedar Road, Sutton, Surrey. British. Undergraduate. Student in Chemistry at the Royal College of Science since October, 1922. (*Signed by*) H. B. Baker, H. F. Harwood, M. A. Whiteley, James C. Philip.

SMEWING, ETHEL MINNIE, 42, Park Avenue South, Crouch End, N. 8. British. Teacher. B.Sc. Hons. Chem. (Lond.). Teacher of Chemistry. (*Signed by*) J. F. Spencer, M. S. Crewdson, H. Crompton.

SMITH, ALTON EWART CLARENCE, Breydon, Oakmount Avenue, Southampton. British. Lecturer in Physical Chemistry, University College of Southampton. Lecturer as above since 1919. (*Signed by*) D. R. Boyd, C. K. Ingold, C. F. Cross.

SNELUS, SUZANNE MABEL LAVINIA, 67, Elgin Mansions, W. 9. British. Analytical and Consulting Chemist. Member of the Pharmaceutical Society

Associate of the Institute of Chemistry. Senior Analyst to Messrs. Parke Davis & Co. Chemist in Charge to Messrs. J. C. Arnfield & Sons. Assistant Research worker, Dr. F. W. Passmore. (*Signed by*) P. C. L. Thorne, E. de Barry Barnett, Henry J. S. Sand.

SPIERS, CLAUDE HYMAN, 34, Brondesbury Road, N.W.6. British. Research Chemist. M.A. (Cambridge). B.Sc. (London). Ph.D. (Cambridge). *T.*, 1924, **125**, 450. (*Signed by*) Jocelyn Thorpe, Arnold Stevenson, G. A. R. Kon, H. M. Spiers.

STERN, HAROLD JACOB, 17, Croxteth Grove, Sefton Park, Liverpool. British. Chemist to firm of paper stainers. Research on Photosynthesis, Liverpool University, 1921–22. Research in Organic Chemistry under Prof. W. H. Perkin, Oxford, 1922–24. B.Sc. (Hons. Chem.), Liv., 1921. Ph.D., Liv., 1923. B.Sc., Oxon., 1924. Baly, Heilbron, and Stern, 1923, **123**, 185. (*Signed by*) W. H. Perkin, Fredk. A. Mason, G. R. Clemo, S. G. P. Plant, E. Hope, F. Raymond Ing.

STILL, CHARLES JAMES, 50, Queen's Parade, Bangor, Co. Down. British. Lecturer in Bleaching and Dyeing, Municipal College of Technology, Belfast. B.Sc. (Lond.); M.Sc. and Ph.D. (Queen's Univ., Belfast). Joint author of several communications (in collaboration with Dr. Henry Wren) on Diphenylsuccinic Acids, published in *J. Chem. Soc.* (*Signed by*) Henry Wren, James W. Porter, Theophilus Harper.

SYED, MOHAMMAD HASSAN, Rupar (Amballa), India. Indian Muhammadan. Demonstrator, Maclagan Engineering College, Lahore, India. B.Sc. (Chemistry), Punjab University. Desirous of being in touch with the recent work in Chemistry. (*Signed by*) S. D. Muzaffar, S. J. Kohli, Edwin Theodore Dean.

THOMAS, MARY BEATRICE, Girton College, Cambridge. Lecturer in Chemistry and Director of Studies in Natural Sciences. Lecturer in Chemistry, Girton College, Cambridge. (*Signed by*) W. J. Pope, F. G. Hopkins, A. Hutchinson.

TIMMS, ERIC SPENCER, 96, Grange Park Rd., Thornton Heath. Research Student (Chemistry). B.Sc. (London), Honours Chemistry. Research Student at East London College under Dr. D. C. Jones. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

TITTERINGTON, ERIC, Abdine Palace, Cairo, Egypt. British. Private Chemist to H.M. the King of Egypt. Member of the Pharmaceutical Society of Great Britain. Engaged in the examination of food and all drugs used in the household of His Majesty. Attached to the Medical Staff of His Majesty for Physiological work. Appointed Examiner in Chemistry to the Cairo Medical School, 1924. (*Signed by*) Ayerst Henham Hooker, W. Morris Colles, C. S. Gibson.

TUDHOPE, THOMAS MARTIN AITKEN, 8, Anson Road, Tufnell Park, London, N. 7. British. Temporary Assistant Chemist in the Government Laboratory. B.Sc. (St. Andrews), with Special Distinction in Chemistry. Ph.D. (St. Andrews). Carnegie Research Scholar for two years (sessions 1921–1923). Engaged in Chemical Research at University College, Dundee, for three years. "Optically Active β-Phthalimino-β-phenylpropiophenones," McKenzie and Tudhope, *J.C.S.*, 1924, **125**, 923. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox.

VASS, CHARLES CYRIL NORREY, "Holmleigh," Harboro' Rd., Kingsthorpe, Northampton. British. Student. B.Sc. Ordinary (Leeds, 1924). (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman, H. M. Dawson, R. Whytlaw-Gray.

VILLAGE, JOHN HARRY, 61, Broxholme Lane, Doncaster. British. Chemist. B.Sc. Hons. (Lond.). For 5 years engaged as Assistant Chemist by the Koppers' Coke Oven Co. under G. E. Foxwell, M.Sc., A.Inst.P., F.C.S. Here I have assisted in numerous researches on coal and its by-products. Now in charge of Laboratory. (*Signed by*) G. E. Foxwell, P. G. Mander, G. D. Crosley.

VOGEL, ISRAEL, 16, Wellclose Square, London, E. 1. Research Student in Chemistry at the East London College. B.Sc., 1st Class Honours Chemistry. Neil Arnott Scholar and Bronze Medallist in Chemistry of the University of London. Author of "The Constitution of the Thionic Acids," *Chem. News*, **128**, 325–327, 342–345, 361 (1924). (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones.

WILSON, JOHN, 115, Canterbury Rd., North Harrow. British. Student engaged in Biochemical Research, Imperial College of Science and Technology, M.Sc. (Sheffield). (*Signed by*) S. B. Schryver, Harold Mastin, J. Knaggs.

WALKER, NELLIE, 15, Fintry Place, Broughty Ferry, Forfarshire. Lecturer in Chemistry, University College, Dundee (University of St. Andrews). M.A., B.Sc., Ph.D. (St. Andrews). Conjoint author of the following papers in the Journal of the Chemical Society: *J.C.S.*, 1914, **105**, 1131; *J.C.S.*, 1915, **107**, 1685; *J.C.S.*, 1922, **121**, 349; *J.C.S.*, 1923, **123**, 2875. (*Signed by*) Alex. McKenzie, J. C. Irvine, John S. W. Boyle.

WARD, WILLIAM JOSEPH VICTOR, 41, Marlowe Rd., Cambridge. English. Research Student. 1st Class Natural Sciences Tripos, Part II, Chemistry 1924, Cambridge. (*Signed by*) W. J. Pope, W. G. Palmer, W. H. Mills.

WHIPP, JAMES EWART, 15, St. John's St., Longsight, Manchester. Pharmacist. Student of the Institute of Chemistry. Fellow of the Biochemical Society. Fellow of the Royal Microscopical Society. Member of the Society of Chemical Industry. (*Signed by*) Henry Garnett, Harry Brindle, Chas. Turner.

WHITEHEAD, ALAN DOUGLAS, "Trevorian," 90, West Hill, Putney, S.W. 15. British. Chemist. Student in Dept. of Chemistry, University College, London, Sessions 1921–22, 1922–23, 1923–24. B.Sc. (Lond.), Honours in Chemistry. (*Signed by*) F. G. Donnan, A. Greeves, W. E. Garner.

WILLIAMS, LESLIE THOMAS DOUGLAS, 23, Queen's Gate Gardens, S.W. 7. British. Student. Associateship of the Royal College of Science. I am now performing research at the above college and am desirous of keeping abreast with modern progress in science. (*Signed by*) G. A. R. Kon, M. A. Whiteley, H. L. Riley.

WYLDE, JOHN HENRY, 203, Boleyn Rd., Forest Gate, E. 7. English. Asst. Chemist, Laboratory of the Gas Light and Coke Coy, Stratford Station. Student at the East Ham Tech. College. National Cert. in Chemistry, Part-time Course, Higher or Advanced (distinction Inorganic Chemistry). City and Guilds of London, Gas Engineering, Ordinary and Honours. (*Signed by*) E. W. Griffiths, W. H. Barker, W. T. Clough.

YARSLEY, VICTOR EMMANUEL, The View, Highfield, Chasetown, nr. Walsall. British. Salter Research Fellow, 1924. B.Sc., 1st Hons., School of Chemistry, B'ham. Associate of the Institute of Chemistry. (*Signed by*) G. T. Morgan, H. D. K. Drew, C. E. Wood.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

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ceutical and Chemical Laboratory. Ph.G. (Boston). Graduate of the Massachusetts College of Pharmacy, Boston, Mass. Member of the American Pharmaceutical Association. At present working on finding out the commercial utility of some of the indigenous plants. My aim in joining the Society is to come in contact with the members of the Society and enjoy the privileges given by the same. (*Signed by*) H. B. Tilden.

San, Moung Ba, B.A., 3, Stewart Road, Rangoon, Burma. Burmese. Assistant to the Chemical Examiner to the Government of Burma and Demonstrator in Physics and Chemistry at the Burma Government Medical School, Rangoon. Graduate of Calcutta University (1911–12). Winner of Chemistry Prize (term 1911–12) in the then Govt. College, Rangoon, now the Rangoon University College. No publications yet. 11 years' analytical experience in the Chemical Examiner's Laboratory, comprising examination of Mineral Oils, Drugs, Foodstuffs, Public Water supplies, and also Toxicological and Medico-legal analysis as well as Analysis of Ores, Minerals, and other commodities. (*Signed by*) Thein Kin, William Dallas.

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From the Publishers: Herren Urban & Schwarzenberg.

American Ceramic Society. Bibliography of magnesite refractories. Columbus 1924. pp. 8 + 41. (*Reference.*)

—— Bibliography of silica refractories. Columbus 1924. pp. 125. (*Reference.*) From the Society.

Annales de Chimie. Vols. II., LXIX., LXXXII., LXXXIII. Paris 1789, 1809, 1812. (*For circulation.*) [Incomplete.]

From Professor C. S. Gibson.

Birkbeck College. Centenary Lectures 1823—1923. London 1924. pp. xiv + 178. (*Recd.* 5/1/25.) From Dr. G. Senter.

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From the Publishers: Messrs. Edward Arnold & Co.

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Allgemeine Mineralogie. Berlin 1924. pp. xvi + 713. ill. *Gm.* 24. (*Recd.* 18/12/24.)

From the Publishers: Gebrüder Borntraeger.

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PHYSICS IN INDUSTRY. Lectures delivered before the Institute of Physics. Vol. II. By JOSEPH WILLIAM MELLOR, A. E. OXLEY, and CECIL HENRY DESCH. London 1924. pp. 48. ill. 3*s.* net. (*Recd.* 4/12/24.)

From the Publishers: The Oxford University Press.

REVUE GÉNÉRALE DES COLLOÏDES et de leurs applications industrielles. Year I, etc. Paris 1923 +. (*Reference.*)

From the Faraday Society.

SCHOTZ, SCHACHNA PEISACH. Synthetic organic compounds. London 1925. pp. 412. ill. 45*s.* net. (*Recd.* 19/12/24.)

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From the Publisher: M. Gaston Doin.

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ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Journal. Vol. VII., etc. Washington 1923 +. (*Reference.*)

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INTERNATIONAL RUBBER CONFERENCE. The Rubber Conference, Brussels, 1924: being the Official Report . . . together with the papers read and the discussions thereon. London 1924. pp. 218. ill. 5*s.* net. (*Recd.* 25/11/24.)

KENT-JONES, DOUGLAS WILLIAM. Modern cereal chemistry. Liverpool 1924. pp. x + 324. ill. 25*s.* net. (*Recd.* 24/11/24.)

KILLEFFER, D. H. Eminent American chemists: a collection of portraits of eminent Americans in the field of chemistry from the earliest days of the Republic to the present, together with short sketches of the work of each. New York [1924]. pp. v + 33 +33 portraits. (*Reference.*) 30*s.* net.

KISSLING, RICHARD. Chemische Technologie des Erdöls und der ihm nahestehenden Naturerzeugnisse: Erdgas, Erdwachs und Erdpech (Asphalt). 2nd edition. Braunschweig 1924. pp. xviii + 804. ill. *Gm.* 25. (*Recd.* 10/12/24.)

MARTIN, LOUIS CLAUDE. Optical measuring instruments: their construction, theory, and use. London 1924. pp. x + 270. ill. 17*s.* 6*d.* net. (*Recd.* 13/1/25.)

[MERCK, EMIL.] Merck's Reagenzien-Verzeichnis: enthaltend die gebräuchlichen Reagenzien und Reaktionen geordnet nach Autorennamen. 5th edition. [Darmstadt] 1924. pp. vi + 656. (*Reference.*) *Gm.* 18.

MOORE, RICHARD B. [and others]. Analytical methods for

certain metals including cerium, thorium, molybdenum, tungsten, radium, uranium, vanadium, titanium, and zirconium. (Bureau of Mines Bulletin, No. 212.) Washington 1923. pp. xviii + 326. ill. 3*s*. 6*d*. net. (*Recd*. 29/12/24.)

Otto, M. P. L'industrie des parfums d'après de la chimie moderne. Notations et formules. 2nd edition. Paris 1924. pp. xliv + 688. ill. 85 *fr*. (*Recd*. 5/12/24.)

Randell, Wilfrid L. Michael Faraday (1791—1867). London 1924. pp. 192. ill. 4*s*. 6*d*. net. (*Recd*. 24/11/24.)

Ruska, Julius. Arabische Alchemisten. II. Ğa'far alṢādiq, der sechste Imām. Mit einer Nachbildung der Handschrift Gotha A. 1292 (Haleb 338) in Manuldruck. Heidelberg 1924. pp. 128 + 62. *Gm*. 7.20. (*Recd*. 1/12/24.)

Sherman, Henry Clapp. Food products. 2nd edition. New York 1924. pp. xiv + 688. ill. 14*s*. net. (*Recd*. 25/11/24.)

Treadwell, W. D. Elektroanalytische Methoden. Berlin 1915. pp. x + 233. ill. (*Recd*. 24/11/24.)

United Kingdom. *Permanent Consultative Committee on Official Statistics*. Guide to current official statistics of the United Kingdom. Vol. II (1923): being a systematic survey of official statistics published mainly in 1923, together with an appendix relating to selected statistical publications issued prior to 1923. London 1924. pp. 306. (*Reference*.) 1*s*. net.

Weinland, Rudolf. Einführung in die Chemie der Komplex-Verbindungen (Wernersche Koordinationslehre) in elementarer Darstellung. 2nd edition. Stuttgart 1924. pp. xx + 538. ill. *Gm*. 24. (*Recd*. 24/11/24.)

Zipperer, Paul. Die Schokoladen-Fabrikation: eine Monographie der Kakaofrucht und ihrer Verwertung. 4th edition by Hermann Schaeffer and — Schröder. Berlin 1924. pp. viii + 338. ill. $5 net. (*Recd*. 13/12/24.)

III. *Pamphlets*.

Cohen, Barnett, Gibbs, H. D., and Clark, William Mansfield. Studies on oxidation-reduction. V. Electrode potentials of simple indophenols, each in equilibrium with its reduction product. (From the *U.S. Public Health Reports*, 1924, **39**.)

Evans, Edward Victor. Cantor Lectures on a study of the destructive distillation of coal. London 1924. pp. 49. ill.

Hunter, Harold. The chemical significance of optical dispersion. [London.] 1924. pp. 117. ill.

Robinovitch, Louise G., and Stiles, George W. A chemical basis for the treatment of tuberculosis: experiments on the action

of steapsin and insulin on tubercle bacilli. (From the *Amer. Rev. Tuberculosis*, 1924, **9**.)

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Food Investigation Board.* Special Report No. 20. The problems of apple transport overseas: a general survey and summary of the results obtained by a scientific expedition to Australia in 1923. By FRANKLIN KIDD and CYRIL WEST. London 1924. pp. vi + 16. ill.

—— *Fuel Research Board.* Technical Paper No. 10. Carbonisation of coal in continuous vertical retorts. A South Wales gas coal. (Mixture of Pentre and No. 3 Rhondda Seams from the Meiros Collieries, Llanharan.) London 1924. pp. iv + 26. ill.

SINNATT, FRANK STURDY, SIMPKIN, NEVILLE, and OWLES, ARCHIBALD BEWICK. The inorganic constituents of coal. Part IV. The melting point of coal ash. (*Lancs. & Cheshire Coal Research Assoc.* Bulletin No. 14.) London 1924. pp. 24. ill.

STERN, ARTHUR LANDAUER. Contributions to the chemistry of cellulose. I. Cellulose sulphuric acids. London 1894. pp. 28. (Two copies.)

TURNER, J. A. Mercurial poisoning: a report on poisoning from small quantities of mercurial vapor. (From the *U.S. Public Health Reports*, 1924, **39**.)

UNITED STATES. *Department of Agriculture.* Department Bulletin No. 1149. Absorption and retention of hydrocyanic acid by fumigated food products. By EDWARD L. GRIFFIN [and others.] Washington 1923. pp. 16. ill.

—— —— Department Bulletin No. 1152. Soy and related fermentations. By MARGARET B. CHURCH. Washington 1923. pp. 26. ill.

—— —— Department Bulletin No. 1166. Apple by-products as stock foods. By G. P. WALTON and GEORGE L. BIDWELL. Washington 1923. pp. 40. ill.

—— —— Department Bulletin No. 1250. Relation between the composition of California cantaloupes and their commercial maturity. By EDWARD MACKAY CHANCE, C. G. CHURCH, and F. E. DENNY. Washington 1924. pp. 26. ill.

VOEGTLIN, CARL, JOHNSON, JAMES MCINTOSH, and DYER, HELEN. Viscosity and toxicity of arsphenamine solutions. (From the *U.S. Public Health Reports*, 1924. **39**.)

WELCH, MARCUS BALDWIN. Notes on strength of timbers: with list of transverse tests on specimens in the Technological Museum. (*Sydney Technological Museum Bulletin*, No. 6.) Sydney 1923. pp. 12.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, February 5th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The following were formally admitted Fellows of the Chemical Society: E. Lakeman, W. Kilroy, D. McKie, R. F. Barnes, and S. Krishnamurti.

Certificates were read for the first time in favour of:

Niels Janniksen Bjerrum, Vendersgade 28, Copenhagen.
James Herbert Clegg, West Cliffe, Queens Park Road, Burnley.
Horace Cecil Cockroft, B.Sc., A.I.C., 6, Highfield Terrace, Halifax.
Francis Xavier Coyne, 160, Addison Street, Blackburn.
Robin George Westbury Farnell, A.R.C.S., A.I.C., Exeter College, Oxford.
Richard Randolph Garran, B.Sc., Orphir, St. George's Road, Toorak, Melbourne.
James Francis Halpin, F.I.C., 39, Benson Road, Forest Hill, S.E. 23.
John Stanley Heaton, Ph.D., B.Sc., 43, Birch Road, Crumpsall, Manchester.
John Cyril Hensman, M.A., A.I.C., Aldenham School, Elstree.
Horace William Hughes, B.Sc., 27, Ombersley Road, Balsall Heath, Birmingham.
David Bret Jehu, M.Sc., 34, High Street, Welshpool, Montgomeryshire.
Clifford Merton Jones, B.Sc., Buxton Crescent, Newton Hill, Wakefield.
David McDowall, 2, Kennishead Road, Thornliebank, Glasgow.
Richard Alan Morton, B.Sc., Ph.D., A.I.C., 2, Lumley Street, Garston, Liverpool.
Frederick Wilson Moulds, Hill Crest, Villa Road, Nottingham.
David Pomerantz, 15, Nottingham Place, Commercial Road, E. 1.
Robert Joseph Salmon, M.Sc., Holly Bank, Rowton, Chester.
Talrain Singh Prem Chandra Sharma, M.Sc., Engineering College Hostel, Hindu University, Benares, India.
John Robert Shepherd, M.Sc., A.I.C., Lady Hall Farm, Broughton-in Furness.
Leslie John Walker, 45, Devereux Road, Wandsworth Common, S.W. 18.
William Alexander Waters, B.A., 35, Shirley Road, Cardiff.
James Bernard Watson, 30, Mulgrave Road, West Hartlepool.

The following papers were read :

" The chemistry of petroleum. Part I. The occurrence of compounds of sulphur in the light distillate from the crude oil of Maidan-i-Naftun." By S. F. BIRCH and W. S. G. P. NORRIS.

" The chemistry of the three-carbon system. Part IV. A case of retarded mobility." By G. A. R. KON and R. P. LINSTEAD.

" Alternation in the molecular volumes of the normal monobasic fatty acids." By W. E. GARNER and E. A. RYDER.

Ordinary Scientific Meeting, Thursday, February 19th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society through the death of Dr. Horace T. Brown on February 6th, and announced that the Council had passed the following resolution :

" On behalf of the Chemical Society the Council desires to express its sense of the great loss the Society has sustained in the death of Dr. Horace T. Brown, who served on the Council as Vice-President, Ordinary Member of Council, Treasurer, and Foreign Secretary during a period of twenty years, and offers to his son and daughters deep sympathy in their bereavement."

Certificates were read for the first time in favour of :

Janardhana Ram Bhatt, B.A., Sre Sumangala College, Panadura, Ceylon.
Archibald Beresford Blunsden, The Bungalow, Westbury-on-Trym, Bristol.
Thomas Henry Bowles, Allandale, Meadowside Road, Cheam.
William Harrison Brindley, M.C., M.A., M.Sc.Tech., A.I.C., 11, Millmoor Terrace, Glossop.
Thomas James Elijah Gardner, 12, Bushwood Road, Kew.
Helen Simpson Gilchrist, 82, North Street, St. Andrews.
Frederick Denison Maurice Hocking, M.Sc., A.I.C., 18, Woodside Park Road, N. Finchley, N. 12.
Joseph Taylor Jackson, B.Sc., 192, Algernon Road, Lewisham, S.E. 13.
Ernest Edward Mabbott, B.Sc., 358, Fore Street, Edmonton, N. 9.
Edgar Kent Palmer, B.Sc.Tech., Rose Bank, Victoria Road, Hale, Cheshire.
John Brent Reed, B.Sc., A.I.C., 49, St. Mildred's Road, S.E. 12.
George James Robertson, M.A., B.Sc., Ph.D., The Manse, Stratkinness St. Andrews.
Leonard William Ernest Townsend, 35, Harewood Road, Collier's Wood, Merton, S.W. 19.
Edwin John Woodcock, Stonecot, Claremont Hill, Jersey.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

James Munsie Bell, Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.
John Cameron, Peking Union Medical College, Peking, Chihli, N. China.
Gordon McIntyre, B.Sc., Sarnia, Ontario, Canada.

Dr. B. Flürscheim and Dr. S. Sugden were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

Julius Nicholson Ashley, B.Sc., A.I.C.
George Alfred Bartram, B.Sc., A.I.C.
George Harry Beeby, B.Sc., A.I.C.
Arthur Henry Burdick Bishop.
Vincent Bloomer, B.Sc.
Claude McClellan Bottomley, B.Sc.
Frederick Stanley Brown, B.Sc., A.I.C.
Percy Chorley, M.Sc.
Herbert Isaac Coombs, B.A., B.Sc.
Alexander Steven Corbet, Ph.D., B.Sc., A.I.C.
William Haughton Crowe.
Alfred Davidson, B.Sc.
Ernest James Davis.
Walter Mark Duffin, B.Sc., A.R.C.S.
Arthur Hynard Durrant.
Frederick John Eaton, Ph.D., B.Sc., A.I.C.
George Alfred Edwards, B.A., B.Sc.
Harry Julius Emeléus, B.Sc., A.R.C.S.
Ralph Margrave Esdaile.
Edward Hugh St. Clair Flack, M.Sc.
Henry Bell Footner, B.Sc.
Desmond Geoghegan.
Clifton William Gibby, B.Sc., A.I.C.
Reginald Oswald Gibson, B.Sc., A.I.C.
Conrad Theodore Gimingham, F.I.C.
Jonathan Goodspeed.
Richard Greenhalgh, B.Sc.
Robert Owen Griffith, M.Sc., A.I.C.
Anthony James Hailwood, B.Sc.
Edward Stanley Hiscocks, B.Sc.
Herbert Henry Hodgson, M.A., Ph.D., B.Sc., F.I.C.
David Hughes.
Kathleen Harriet Hughes.
Arthur Frederick Hunt, B.Sc.
Bertram Hobart Ingham, B.Sc.
John Dobney Johnson, B.Sc.
Wilford Jordayne Johnson.
Cecil Brellisford Oakes Jones.
William Wenallt Jones, M.Sc.
Alan Richmond Kennedy.
Frank Kenyon, A.I.C.
Frederick Ernest King.
Eric Knott.
Jacob Kracovski, B.Sc.
Herbert Lambourne, M.A., M.Sc., F.I.C.
John Joseph Laws.
Raymond James Wood Le Fevre.
Alexander John Simpson Leiper, A.R.C.S.
Alfred James Andrew Lennane, M.R.C.S., L.R.C.P.
Frederick William Liley.
James Gilbert Lunt, B.Sc.
William Hamilton McVicker, M.Sc.
Thomas Mann.
Vincent Mark Mascarenhas, B.A.
Frank Douglas Miles.
Sadashiv Parashuram Nair, Ph.G.
Edward Arthur Nightingale.
Frederick William Offord.
Lionel Edward Outridge, B.Sc.
Thomas Webster Parker, A.R.C.S.
William Bayley Parker, F.I.C.
Stuart Russell Parsons, B.Sc., A.I.C.
William Samuel Payne.
Kenneth John Pierson.
Richard Edwin Pike, B.Sc.
Douglas Victor Plumbridge, Ph.D., A.R.C.S., A.I.C.
John Massey Preston, B.Sc., A.I.C.
Richard Raper, B.A.
John Frederick James Rule, B.Sc.
Moung Ba San, B.A.
Leslie Vivian Donald Scorah, B.Sc., A.I.C.
George Frederick Sheppard.
Joseph Thomas Shevlin.
Arthur Frederick Smethurst.
Ethel Minnie Snewing, B.Sc.
Alton Ewart Clarence Smith.
Susanne Mabel Lavinia Snelus, A.I.C.
Claude Hyman Spiers, M.A., Ph.D., B.Sc.
Harold Jacob Stern, Ph.D., B.Sc.
Charles James Still, Ph.D., M.Sc.
Mohammad Hassan Syed, B.Sc.
Mary Beatrice Thomas.
Eric Spencer Timms, B.Sc.
Eric Titterington.
Thomas Martin Aitken Tudhope, Ph.D., B.Sc.

Charles Cyril Norrey Vass, B.Sc.
John Harry Village, B.Sc.
Israel Vogel, B.Sc.
John Wilson, M.Sc.
Nellie Walker, M.A., Ph.D., B.Sc.
William Joseph Victor Ward, B.A.
James Ewart Whipp.
Alan Douglas Whitehead, B.Sc.
Leslie Thomas Douglas Williams, A.R.C.S.
John Henry Wylde.
Victor Emmanuel Yarsley, B.Sc., A.I.C.

The following paper was read :

"The nature of the alternating effect in carbon chains. Part II. The directing influence of the α-methoxyvinyl group in aromatic substitution." By C. K. INGOLD and E. H. INGOLD.

Dr. T. SLATER PRICE discussed "The action of light on the photographic plate."

ANNUAL GENERAL MEETING.

The Annual General Meeting will take place on Thursday, March 26th, 1925, at 4 p.m., when the PRESIDENT, Professor W. P. WYNNE, D.Sc., F.R.S., will deliver his Address.

ANNIVERSARY DINNER.

The Anniversary Dinner will be held in the Grand Hall of the Hotel Victoria, Northumberland Avenue, W.C. 2., on Thursday, March 26th, 1925 (the day of the Annual General Meeting), at 7 for 7.30 p.m. The presence of ladies will be welcomed.

Tickets, price 12*s.* 6*d.* each (including gratuities to waiters) can be obtained from the Assistant Secretary. It will facilitate arrangements if Fellows will apply for tickets at an early date, in any event before March 19th.

List of Papers, or Abstracts thereof, received between January 16th and February 19th, 1925. (This list does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"Colour and molecular geometry. Part III. A graphical presentation of the theory." By J. MOIR.

"Tesla-luminescence spectra. Part V. Some polynuclear hydrocarbons." By W. H. MCVICKER, J. K. MARSH, and A. W. STEWART.

"The surface tensions of aqueous solutions of various organic compounds." By P. R. EDWARDS.

"The cryoscopic method for adsorption." By H. L. RICHARDSON and P. W. ROBERTSON.

"Ring-chain tautomerism. Part XII. Derivatives of α-ethyl-ββ-dimethylglutaric acid." By G. A. R. KON, L. F. SMITH, and J. F. THORPE.

"A determination of the melting and transition points of potassium dichromate." By P. L. ROBINSON, G. E. STEPHENSON, and H. V. A. BRISCOE.

"Interaction of hydrogen and carbon dioxide on the surface of platinum." By C. R. PRITCHARD and C. N. HINSHELWOOD.

"The identity of uncineol with eudesmol." By A. R. PENFOLD.

"Further *X*-ray measurements on long-chain compounds (*n*-hydrocarbons)." By A. MÜLLER and W. B. SAVILLE.

"An *X*-ray investigation of the ketone series." By W. B. SAVILLE and G. SHEARER.

"The relationship of thyroxin to tryptophane." By C. S. HICKS.

"A new method of flame analysis." By O. C. DE C. ELLIS and H. ROBINSON.

"The movement of flame in closed vessels." By O. C. DE C. ELLIS and R. V. WHEELER.

"*cyclo*Telluropentanediones containing aliphatic and aromatic substituents." By G. T. MORGAN and C. J. A. TAYLOR.

"3-Chlorobenzopyrylium derivatives." By L. R. RIDGWAY and R. ROBINSON.

"A qualitative test for weak bases." By R. ROBINSON.

"The labile nature of the halogen atom in organic compounds. Part X. The action of hydrazine hydrate on the halogen derivatives of α-nitro-fatty acids." By A. K. MACBETH and D. TRAILL.

"The effect of colloids on the replacement of lead and copper from their salts by zinc." By L. T. M. GRAY.

"A new portable apparatus for the analysis of illuminating and other gases." By H. D. MURRAY.

"The action of halogen on phenylhydrazones. Part II. The action of chlorine." By J. E. HUMPHRIES, H. HUMBLE, and R. EVANS.

"Anomalous adsorption." By J. B. SPEAKMAN and A. E. BATTYE.

"The photo-decomposition of chlorine water and of aqueous hypochlorous acid solutions. Part I." By A. J. ALLMAND, P. W. CUNLIFFE, and R. E. W. MADDISON.

"Studies of dynamic isomerism. Part XVII. The mutarotation of aluminium benzoyl-camphor." By I. J. FAULKNER and T. M. LOWRY.

"Studies of dynamic isomerism. Part XVIII. The mechanism of mutarotation and of hydrolytic and prototropic change; with a criticism of Baker, Ingold, and Thorpe's doctrine of non-intervention." By T. M. LOWRY.

"Studies of dynamic isomerism. Part XIX. Experiments on the arrest of mutarotation in tetramethylglucose." By T. M. LOWRY and E. M. RICHARDS.

"The freezing points of hydrofluoric acid." By J. D. C. ANTHONY and L. J. HUDLESTON.

"The hydrolysis of iodine as measured by the iodine electrode." By H. D. MURRAY.

"Some aromatic chlorovinylarsines." By A. F. HUNT and E. E. TURNER.

"The mechanism of the reaction between arylhydrazine sulphonic acids and acetoacetic ester." By G. REEVES.

"The compounds formed by the action of bromine upon benzaldehyde-phenylhydrazone." By F. D. CHATTAWAY and A. J. WALKER.

"Periodic electrochemical phenomena." By E. S. HEDGES and J. E. MYERS.

"The nitration of meta-hydroxybenzaldehyde carbonate and ethyl carbonate." By F. A. MASON.

"A synthesis of 1 : 2-dihydroquinaldine." By F. A. MASON.

"The synthesis of 5 : 5'-dibromo-6 : 6'-dimethoxy thioindigo." By R. H. GRIFFITH and E. HOPE.

"The interaction of sodium chloride and alumina." By F. H. CLEWS.

"A resolution of benzoin." By F. J. WILSON and I. V. HOPPER.

"Semicarbazones of benzoin. Part I." By I. V. HOPPER.

"The 'activation' of graphite as a sorbent of oxygen." By D. H. BANGHAM and J. STAFFORD.

"The mechanism of the formation of malachite from basic cupric carbonate." By J. R. I. HEPBURN.

"A synthesis of oxyberberine. Part I." By W. H. PERKIN, J. N. RÂY, and R. ROBINSON.

"Variation of colour in the fluoresceine family." By J. MOIR.

"The equilibria underlying the soap boiling processes. Pure sodium palmitate." By J. W. MCBAIN and G. M. LANGDON.

"Some reactions of triethylphosphine." By J. N. COLLIE.

"Nitro- and amino-ethoxy-lutidine." By J. N. COLLIE and G. BISHOP.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ADAMKIEWICZ, ALBERT. Die Natur und der Nährwerth des Peptons: eine experimentelle Untersuchung zur Physiologie des Albumins. Berlin 1877. pp. viii + 128. From Dr. H. E. Cox.

ALLEN, ROBERT. Bismuth ores. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 62. ill. 3*s*. 6*d*. net. (*Recd*. 5/3/25.) From the Director.

ATACK, FREDERICK WILLIAM, assisted by LEONARD WHINYATES. The Chemists' Year Book 1924. American data in collaboration with FRANCIS M. TURNER, Jr. Manchester [1924]. pp. xii + 1164. ill. (*Reference*.) From Mr. L. Eynon.

BÖTTGER, WILHELM. Qualitative Analyse und ihre wissenschaftliche Begründung. 4th—7th edition. Leipzig 1925. pp. xvi + 644 + 34. *M*. 22. (*Recd*. 3/2/25.)
From the Publisher: Herr Wilhelm Engelmann.

CARPENTER, LEONARD. Mechanical mixing machinery. London 1925. pp. 138. ill. 6*s*. net. (*Recd*. 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

CONGRÈS INTERNATIONAL POUR LA RÉPRESSION DES FRAUDES. Compte rendu des travaux du deuxième Congrès, 1909. Paris 1910. pp. viii + 1496. From Dr. H. E. Cox.

DEADLY ADULTERATION and slow poisoning unmasked; or, disease and death in the pot and the bottle. By an enemy to fraud and villany. New edition. London [n. d.]. pp. viii + 190.
From Dr. H. E. Cox.

ELLIOTT, CYRIL. Distillation principles. London 1925. pp. 166. ill. 6*s*. net. (*Recd*. 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

GIBBS, WILLIAM E. The dust hazard in industry. London 1925. pp. 168. ill. 6*s*. net. (*Recd*. 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

GORE, GEORGE, SPARLING, MARCUS, and SCOFFERN, JOHN. Practical chemistry: including the theory and practice of electrodeposition; photographic art; the chemistry of food, with a chapter on its adulterations; and the chemistry of artificial illumination. London 1856. pp. xvi + 574. ill. From Dr. H. E. Cox.

GUYE, CHARLES EUGÈNE. Physico-chemical evolution. Translated by J. R. CLARKE. London 1925. pp. xii + 172. 6*s*. net. (*Recd*. 12/2/25.) From the Publishers: Messrs. Methuen & Co.

HALSE, EDWARD. Antimony ores. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 102. ill. 5*s*. net. (*Recd*. 5/3/25.) From the Director.

HENNINGER, ARTHUR [RODOLPHE MARIE]. De la nature et du role physiologique des peptones. Paris 1878. pp. 68.
From Dr. H. E. Cox.

HOFMANN, FRANZ. Die Bedeutung von Fleischnahrung und Fleischconserven mit Bezug auf Preisverhältnisse. Leipzig 1880. pp. iv + 120. From Dr. H. E. Cox.

JANKE, ALEXANDER. Allgemeine technische Mikrobiologie. I Teil: Die Mikroorganismen. Dresden 1924. pp. xii + 342. ill. *M.* 12. (*Recd.* 3/2/25.) From the Publisher: Herr Theodor Steinkopff.

LOWY, ALEXANDER, and HARROW, BENJAMIN. An introduction to organic chemistry. New York 1924. pp. x + 390. ill. 15*s.* net. (*Recd.* 12/2/25.)
From the London Publishers: Messrs. Chapman & Hall.

PATTERSON, AUSTIN M. A German-English dictionary for chemists. 5th printing, with addenda. New York 1924. pp. xvi + 344. (*Reference.*) 12*s.* 6*d.* net.
From the London Publishers: Messrs. Chapman & Hall.

REVUE GÉNÉRALE DES COLLOÏDES et de leurs applications industrielles. Year I, etc. Paris 1923 +. (*For circulation.*)
From the Biochemical Society.

SEYMOUR, HARTLAND. Agitating, stirring and kneading machinery. London 1925. pp. 140. ill. 6*s.* net. (*Recd.* 11/2/25.) From the Publishers: Messrs. Ernest Benn.

SPIELMANN, PERCY EDWIN. Bituminous substances: scientific progress of practical importance during the last fifteen years. London 1925. pp. xvi + 206. ill. 15*s.* net. (*Recd.* 21/1/25.)
From the Publishers: Messrs. Ernest Benn.

TUNGAY, SYDNEY J. Acid-resisting metals. London 1925. pp. 136. ill. 6*s.* net. (*Recd.* 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

URBAIN, GEORGES. Les notions fondamentales d'élément chimique et d'atome. Paris 1925. pp. iv + 172. 10 *fr.* (*Recd.* 10/2/24.) From the Publishers: MM. Gauthier-Villars et Cie.

WELLINGS, A. W. Chemical symbols, formulæ and calculations. London 1925. pp. viii + 96. 3*s.* net. (*Recd.* 16/1/25.)
From the Publishers: Messrs. Methuen & Co.

II. *By Purchase.*

ARENDT, RUDOLF. Technik der Experimentalchemie: Anleitung zur Ausführung chemischer Experimente. 5th edition. Edited by LUDWIG DOERMER and WALTER FRANCK. Leipzig 1925. pp. xxviii + 732. ill. *M.* 26.50. (*Recd.* 2/2/25.)

FREUNDLICH, HERBERT. The elements of colloidal chemistry. Translated by GEORGE BARGER. London 1925. pp. viii + 210. ill. 7*s.* 6*d.* net. (*Recd.* 19/1/25.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Lecture, held in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1, on Thursday, February 26th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

Sir WILLIAM HARDY, M.A., Sec.R.S., delivered his Lecture entitled: "Problems presented by Films on Solid Surfaces." A vote of thanks to the Lecturer, proposed by Professor H. E. Armstrong, F.R.S., seconded by Professor A. V. Hill, F.R.S., and supported by the Chairman, was carried with acclamation, and acknowledged by Sir William Hardy.

Ordinary Scientific Meeting, Thursday, March 5th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Sir Edward Thorpe	Feb. 16th, 1871.	Feb. 23rd.
Alexander Mitchell Williams	Dec. 7th, 1922.	Feb. 21st.

The PRESIDENT also announced that at a Special Meeting of the Council, held on February 26th, 1925, the following resolution was passed:

"On behalf of the Chemical Society, the Council desires to express its profound regret at the death of Sir Edward Thorpe, who for 54 years was a Fellow, and during 39 years served the Society as Member of Council, Vice-President, Treasurer and President, and while Treasurer initiated and supervised the production of the first three volumes of the Collective Indexes of the Society's Journal.

"The Council recognises that by Sir Edward Thorpe's death the

Society loses a wise counsellor and British Chemistry a distinguished investigator, and offers to Lady Thorpe its sincere sympathy in her bereavement."

The Fellows present expressed their concurrence in this resolution by rising from their places.

It was also announced that

(1) With a view to increasing the usefulness of the Library, the Council has made arrangements for the photographic copying by means of the Photostat, of material contained in the Library. Particulars as to cost, etc., can be obtained from the Librarian.

(2) The first lecture in connection with the Fison Memorial Fund, which was established to endow a Lectureship in memory of the late Dr. A. H. Fison, will be delivered by Professor J. J. Thomson, O.M., F.R.S., on Thursday, May 7th, 1925, at 5 p.m., the Right Hon. the Earl of Balfour presiding. The place of meeting will be announced later. Tickets of admission will be obtainable from Mr. S. E. Carr.

The following List of Nominations for vacant places on the Council was read from the Chair:

President: Arthur W. Crossley.

Vice-Presidents who have filled the office of President (3 vacancies): H. E. Armstrong, A. Scott, W. P. Wynne.

Vice-Presidents who have not filled the office of President (2 vacancies): J. B. Cohen, N. V. Sidgwick.

Secretary: T. Slater Price.

Foreign Secretary: F. G. Donnan.

Ordinary Members of Council:

(*a*) Town Members, *i.e.*, those resident within 50 miles of Charing Cross (5 vacancies): H. Bassett, F. W. Gamble, J. Kenyon, B. D. Porritt, G. Stubbs.

(*b*) Country Members, *i.e.*, those resident beyond 50 miles from Charing Cross (2 vacancies): F. A. Freeth, W. Rintoul, F. J. Wilson.

Dr. P. W. Austin and Dr. E. E. Turner were appointed Scrutators to assist in the counting of votes recorded in the election of the Country Members of Council.

The following were formally admitted Fellows of the Chemical Society: F. H. Banfield, F. Kenyon, A. H. Durrant, A. F. Smethurst, J. D. Johnson, R. E. Pike, C. H. Spiers, S. Dutt, J. Kracovski, H. J. Emeléus, I. Vogel, K. V. Thimann, S. S. G. Sircar, B. T. Narayanan.

The Treasurer drew attention to the fact that on Thursday, March 5th, 1885, exactly 40 years ago, a certificate of a candidate for election as a Fellow was read for the first time in favour of William Palmer Wynne. Commenting on the uniqueness of the occasion, the Treasurer expressed the hope that the President would long be spared to give the Society the benefit of his wise counsel. The meeting showed its hearty approval of the Treasurer's remarks, and the President expressed his sincere thanks for the kind reference.

Certificates were read for the first time in favour of:

Geoffrey Alger Blyde, East Cliffe, East Bank Road, Sheffield.
Frank Henry Charles Bull, B.Sc., A.I.C., 50, Cornwall Road, Bishopston, Bristol.
Harry Dean, 134, New Lane, Oswaldtwistle.
Irvine John Faulkner, Emmanuel College, Cambridge.
Thomas Flett, B.Sc., A.I.C., Anchor Cottage, Kirkwall, Orkney.
John Charles Giblin, B.Sc., A.I.C., 3, Kensington Terrace, Brecon.
Isabel Hodgson Hadfield, M.Sc., 65, Langham Road, Teddington.
Thomas Haworth, 8, Park Terrace, Fielding Lane, Oswaldtwistle.
William Jobson, 52, The Mall, Swindon.
Thomas William Jones, B.Sc., 36, St. Vincent Road, Westcliff-on-Sea.
John Keane, M.Sc., Ph.D., 6 Shamrock Villas, Drumcondra, Dublin.
Andrew Joseph Myles, 12, Gardner Road, Tue Brook, Liverpool.
Alfred William Nash, B.Sc., 18, Prospect Road, Moseley, Birmingham.
Henry Bowen Oakley, M.Sc., A.R.C.S., Wellcome Tropical Research Laboratories, Khartoum.
Harry Rawlings, B.Sc., 15, Station Road, Ramsey, Huntingdon.
Alan Lawrence Smith, M.Sc., 22, Dean Street, Blackpool.
George Thorn, B.Sc., Grove House, Beechen Grove, Watford.
Ernest Swann Watts, Eaglesfield, Limefield Road, Kersal, Manchester.
Archibald Steele Whamond, 22, Church Street, Alloa.
John Stanley Worthington, 27, Rowena Street, Great Lever, Bolton.

The following papers were read:

"Studies of dynamic isomerism. Part XVII. The mutarotation of aluminium benzoylcamphor." By I. J. FAULKNER and T. M. LOWRY.

"Studies of dynamic isomerism. Part XVIII. The mechanism of mutarotation, and of hydrolytic and prototropic change; with a criticism of Baker, Ingold, and Thorpe's doctrine of non-intervention." By T. M. LOWRY.

"Studies of dynamic isomerism. Part XIX. Experiments on the arrest of mutarotation in tetramethylglucose." By T. M. LOWRY and E. M. RICHARDS.

Ordinary Scientific Meeting, Thursday, March 19th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through the death of Joseph Arderne Ormerod, who was elected a Fellow on May 16th, 1872, and died on March 5th.

R. H. Purcell was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of :

James Lindsay Buchan, B.Sc., Hampden Club, N.W. 1.
John Alfred Valentine Butler, M.Sc., The Potteries, Winchcombe, Glos.
Annie Lavinia Byford, B.Sc., 73, Elderton Road, Westcliff-on-Sea.
James Craik, M.A., B.Sc., Ph.D., The University, St. Andrews.
Herbert Greetham Dane, M.Sc., The Diocesan Training College, Winchester.
Margaret Stedman Leonora Dixon, Homebush, Worcester Road, Sutton.
Donald Hanson, 7, Willow Bank, Halifax.
Joseph Hill, 58, Spring Street, Accrington.
Jim Hoyle, 11, Crow Lane, Ramsbottom.
Richard H. F. Manske, M.Sc., The University, Manchester.
Hugh Clonston Moir, B.Sc., A.I.C., 7, Craigielea Street, Dennistoun, Glasgow.
William George Rhodes, 318, Granville Road, Park, Sheffield.
Thomas Kennedy Walker, M.Sc., Ph.D., F.I.C., 4, Swythamley Road, Cheadle Heath, Stockport.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of :

Karl Thomas, M.D., The University, Leipzig.
Frederic N. Williams, P.O. Box 1117, Shreveport, La., U.S.A.

The following papers were read :

" The 'activation' of graphite as a sorbent of oxygen." By D. H. BANGHAM and J. STAFFORD.

" Ring-chain tautomerism. Part XIV. The structure of Balbiano's acid." By E. ROTHSTEIN, A. STEVENSON, and J. F. THORPE.

" The tendency towards intramolecular condensation in cyclic keto-esters. Part I. The formation and disruption of bicyclic dihydroresorcinols." By E. H. FARMER and J. ROSS.

" The structure of the enolic forms of β-ketoesters and β-diketones." By N. V. SIDGWICK.

PUBLICATIONS FUND.

In connection with the Appeal for the Publications Fund issued by the Treasurer, it has been decided that a list of donations and subscriptions received shall appear in the Proceedings for June. All donations and subscriptions received prior to the end of May will be included in the List.

LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

List of Papers, or abstracts thereof, received between February 19th and March 19th, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The isomerism of the oximes. Part XXI. Action of picryl chloride and of 2 : 4-dinitrochlorobenzene on aldoximes." By O. L. BRADY and L. KLEIN.

"Derivatives of semioxamazide. Part III." By F. J. WILSON and E. C. PICKERING.

"The stereochemistry of the hydronaphthalenes and related sesquiterpenes. Part I. Decahydro-β-naphthoic acid." By F. W. KAY and N. STUART.

"Irregularities in the condensation of certain nitriles with resorcinol." By E. CHAPMAN and H. STEPHEN.

"Studies in the benzothiazole series. Part III. The pseudobases of the *l*-substituted benzothiazole quaternary salts." By L. M. CLARK.

"Sulphur compounds removed from a Persian petroleum by means of sulphuric acid. Part I." By E. H. THIERRY.

"Ring-chain tautomerism. Part XIII. Three carbon ring-chain tautomerism in a bridged ring system." By J. W. BAKER.

"The measurement of the dielectric constants of liquids." By H. HARRIS.

"Note on the physiological action of certain benzothiazoles and mercaptan derivatives." By R. F. HUNTER.

"Note on the physiological action of certain arylamino-derivatives of monochloroacetic acid." By R. F. HUNTER.

"The hydrolytic properties of certain amino-acids." By L. P. BOSMAN.

"The reduction of anethole nitrosochloride." By J. B. SHOESMITH and R. H. SLATER.

"Investigations on the dependence of rotatory power on chemical constitution. Part XXV. Three optically active alcohols containing a phenyl group and some esters derived therefrom." By L. F. HEWITT and J. KENYON.

"The integral relations between the vibration frequencies of molecules." By E. C. C. BALY, R. A. MORTON, and E. ROGERS.

"The photochemical decomposition of nitrosyl chloride." By E. J. BOWEN and J. F. SHARP.

"Ray's supposed triethylene trisulphide." By G. M. BENNETT and W. A. BERRY.

"Hepta- and nono-dilactones." By G. M. BENNETT.

"A synthesis of pyrylium salts of anthocyanidin type. Part VI. Polyhydroxyflavylium salts related to chrysin, apigenin, lotoflavin, luteolin, galangin, fisetin, and morin." By D. D. PRATT and R. ROBINSON.

"Reactions depending upon the vapour at the interface of two immiscible liquids. Part II." By G. HARKER and R. K. NEWMAN.

"The hydrates of calcium carbonate." By J. HUME.

"The labile nature of the halogen atom in organic compounds. Part XI. The halogenation of acetylsuccinic ester." By A. K. MACBETH and D. TRAILL.

"A solid hydride of antimony." By E. J. WEEKS and J. G. F. DRUCE.

"A study of the effect of the concentration of aqueous sodium hydroxide solutions upon the rate of saponification of olive oil." By G. I. FINCH and A. KARIM.

"The formation of *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid from *d*-camphorquinone." By C. S. GIBSON and J. L. SIMONSEN.

"The reaction between aromatic aldehydes and phenanthraquinone in presence of ammonia." By A. C. SIRCAR and N. C. G. RAY.

"Studies in heterocyclic compounds. Part I." By A. C. SIRCAR and P. K. DE.

"The action of azides on toluquinone." By F. D. CHATTAWAY and G. D. PARKES.

"The partial pressures of water vapour and of sulphuric acid vapour over concentrated solutions of sulphuric acid at high temperatures." By J. S. THOMAS and W. F. BARKER.

"Investigations on the dependence of rotatory power on chemical constitution. Part XXVI. Four alcohols containing the vinyl group and some esters derived therefrom." By J. KENYON and D. R. SNELLGROVE.

"A synthesis of pyrylium salts of anthocyanidin type. Part VII. The preparation of the anthocyanidins with the aid of triacetylphloroglucinaldehyde." By D. D. PRATT and R. ROBINSON.

"A synthesis of pyrylium salts of anthocyanidin type. Part VIII. A new synthesis of pelargonidin chloride and of galanginidin chloride." By T. MALKIN and R. ROBINSON.

"The action of halogens upon *m*- and *p*-nitrobenzaldehyde phenylhydrazones." By F. D. CHATTAWAY and A. J. WALKER.

"Plant cuticles. Part I. Modern plant cuticles. Studies in the composition of coal." By V. H. LEGG and R. V. WHEELER.

"The explosion of ammonia with carbon monoxide and oxygen." By J. W. BEESON and J. R. PARTINGTON.

"3 : 3-Diethylpentane (tetraethylmethane)." By G. T. MORGAN, S. R. CARTER, and A. E. DUCK.

"Aromatic esters of acylecgonines." By W. H. GRAY.

"The additive formation of four-membered rings. Part VII. The synthesis and division of some dimethylene-1 : 3-oxaimines." By C. K. INGOLD.

"The decomposition of hydrogen peroxide by cobaltic hydroxide." By F. G. TRYHORN and G. JESSOP.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ACTUALITÉS DE CHIMIE CONTEMPORAINE. Publiées sous la direction de ALBIN HALLER. 3rd series. Paris 1925. pp. viii + 328. 12 *fr.* net. (*Recd.* 24/2/25.)

From the Publisher : M. Gaston Doin.

HANDBUCH DER SALVARSANTHERAPIE. Edited by W. KOLLE and K. ZIELER. Vol. II. Berlin 1925. pp. xiv + 878. ill. *M.* 34.40. (*Recd.* 16/3/25.) From the Publishers : Messrs. Urban & Schwarzenberg.

II. *By Purchase.*

GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE. 8th edition. By RICHARD JOSEF MEYER [and others]. Berlin 1924 +. (*Reference.*)

GNAMM, H. Die Gerbstoffe und Gerbmittel. (Chemie in Einzeldarstellungen, Vol. XII.) Stuttgart 1925. pp. xvi + 394. *M.* 24. (*Recd.* 14/3/25.)

HANSLIAN, RUDOLF, and BERGENDORFF, FR. Der chemische Krieg : Gasangriff, Gasabwehr und Raucherzeugung. Berlin 1925. pp. iv + 226. ill. *M.* 11. (*Recd.* 10/2/25.)

HOLDE, DAVID. Kohlenwasserstofföle und Fette sowie der ihnen chemisch und technisch nahestehenden Stoffe. 6th edition. Berlin 1924. pp. xxviii + 856. ill. *M.* 45. (*Recd.* 2/2/25.)

HOPPE-SEYLER, ERNST FELIX IMMANUEL. Handbuch der physiologisch- und pathologisch-chemischen Analyse. 9th edition. By HANS THIERFELDER. Berlin 1924. pp. xvi + 1004. ill. *M.* 69. (*Recd.* 2/2/25.)

KLÖCKER, ALB. Die Gärungsorganismen in der Theorie und Praxis der Alkoholgärungsgewerbe. 3rd edition. Berlin 1924. pp. xviii + 448. ill. *Rm.* 12. (*Recd.* 24/2/25.)

LEBERLE, HANS. Die Bierbrauerei. 2 vols. Stuttgart 1921–25. pp. xii + 307, xii + 589. ill. *M.* 31.80. (*Recd.* 9/3/25.)

LORD, NATHANIEL WRIGHT, and DEMOREST, DANA J. Metallurgical analysis. 5th edition. New York 1924. pp. xxii + 472. ill. 20*s.* net. (*Recd.* 19/1/25.)

MILLIKAN, ROBERT ANDREWS. The electron: its isolation and measurement and the determination of some of its properties. 2nd edition. Chicago 1924. pp. xiv + 293. ill. 8*s.* 9*d.* net. (*Recd.* 19/1/25.)

MÜLLER, ERICH. Elektrochemisches Praktikum. 4th edition. Dresden 1924. pp. xvi + 264. ill. *M.* 10. (*Recd.* 28/1/25.)

NERNST, WALTHER. Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes. 2nd edition. Halle (Saale) 1924. pp. viii + 232. ill. *M.* 12. (*Recd.* 10/2/25.)

RISTENPART, EUGEN. Chemische Technologie der organischen Farbstoffe. 2nd edition. Leipzig 1925. pp. xiv + 300 + 12 pattern plates. ill. *M.* 15. (*Recd.* 2/2/25.)

SOMMERFELD, ARNOLD. Atombau und Spektrallinien. 4th edition. Braunschweig 1924. pp. xii + 862. ill. *M.* 22. (*Recd.* 28/1/25.)

STRACHE, HUGO, and LANT, RICHARD. Kohlenchemie: Entstehung und chemisches Verhalten der Kohlen und ihrer Bestandteile, Untersuchungen der Kohlen. Leipzig 1924. pp. xvi + 600. ill. *M.* 24. (*Recd.* 2/2/25.)

SUTTON, FRANCIS. A systematic handbook of volumetric analysis. 11th edition. Revised throughout, with numerous additions, by WILLIAM LINCOLNE SUTTON and ALFRED EDWARD JOHNSON. London 1924. pp. x + 630. ill. 35*s.* net. (*Recd.* 19/1/25.)

TAYLOR, HUGH STOTT. [Editor.] A treatise on physical chemistry: a co-operative effort by a group of physical chemists. 2 vols. London 1924. pp. xii + 604 + 42, x + 701 to 1360 + 42. ill. 50*s.* net. (*Recd.* 21/1/25.)

III. *Pamphlets.*

COHEN, BARNETT, GIBBS, HARRY DRAKE, and CLARK, WILLIAM MANSFIELD. Studies on oxidation-reduction. VI. A preliminary study of indophenols: (*a*) dibromo substitution products of phenol indophenol; (*b*) substituted indophenols of the ortho type; (*c*) miscellaneous. (From the *U.S. Public Health Reports*, 1924, **39**.)

ELVOVE, ELIAS. A method for the estimation of total sulfur in neoarsphenamine and sulpharsphenamine. (From the *U.S. Public Health Reports*, 1924, **39**.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

ANNIVERSARY DINNER.

THE Anniversary Dinner of the Society was held in the Grand Hall, Hotel Victoria, on Thursday, March 26th, 1925, at 7 for 7.30 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair. The following is a list of those present:

Aeschlimann, J. A.
Anderson, Rt. Hon. Sir John, G.C.B., *Permanent Under-Secretary of State for Home Affairs.*
Anderson, Miss O. R.
Armstrong, H. E., F.R.S., *Past-President.*
Armstrong, Miss N.
Austin, P. C.
Austin, Mrs. P. C.
Backer, H. J.
Baker, H. B., C.B.E., F.R.S.
Baker, Mrs. H. B.
Baly, E. C. C., C.B.E.
Bassett, H.
Bennett, Miss D. M.
Bennett, J. C. S.
Bennett, G. M.
Bolton, E. R.
Bolton, Mrs. E. R.
Bolton, L. H.
Bolton, Mrs. L. H.
Boyd, D. R.
Brady, O. L.
Brewer, F. M.
Brown, R. B.
Brown, Mrs. R. B.
Burch, W. J. N.
Burgess, W. T.
Burton, H.
Carr, F. H., C.B.E.
Carr, Mrs. F. H.
Carr, Miss M.
Carr, S. E., *Assistant Secretary.*
Chapman, A. Chaston, F.R.S.
Chapman, Mrs. Chaston.
Chapman, A. W.
Chattaway, F. D., F.R.S.
Chemical Age.
Chemistry and Industry.
Clifford, E.
Clifford, F. W., *Librarian.*
Coates, J. E., O.B.E.
Cod, L. M.
Cohen, Ernst, *Nederlandsche Chemische Vereeniging.*
Cohen, Mrs. E.
Collins, S. W.
Cooper, A. J. Bullen.
Cooper, H. Creemer.
Corfield, C. E.
Corfield, Mrs. C. E.
Crossley, A. W., C.M.G., C.B.E., F.R.S., *President.*
Crossley, Mrs. A. W.
Crossley, K. H.
Daily Telegraph.
Dale, H. H., C.B.E., F.R.S.
Desch, C. H., F.R.S.
Dickes, Miss W. E.
Donald, M. B.
Donnan, F. G., C.B.E., F.R.S., *Foreign Secretary.*
Donnan, Miss.

Drew, R. B.
Druce, J. G. F.
Drummond, J. C.
Drummond, Mrs. M. H.
Dudley, H. W., O.B.E.
Dudley, Mrs.
Duncalfe, R.
Dunn, F. P.
Dyer, B.
Dyer, Mrs. B.
Eldridge, A. A.
Eldridge, Mrs. A. A.
Ellingham, H. J. T.
Fargher, R. G.
Fox, J. J., O.B.E.
Freeth, F. A., O.B.E.
Galletly, W. G.
Gardner, J. A.
Garner, W. E.
Gibbons, W. M., O.B.E., *Registrar, Sheffield University.*
Gibson, C. S., O.B.E., *Secretary.*
Gilling, C.
Gordon, J. G.
Gray, J. Hunter, K.C.
Gray, Mrs. J. Hunter.
Gray, W. H.
Greenaway, A. J.
Greeves, A.
Greeves, Mrs. A.
Gregory, Sir Richard.
Griffiths, O. S.
Haas, P.
Hamer, Miss F. M.
Hamer, J. C.
Hamer, Sir William.
Hamer, Lady.
Heath, Sir Frank, K.C.B., *Secretary, Department of Scientific and Industrial Research.*
Henderson, G. G., F.R.S., *President, The Institute of Chemistry.*
Henry, T. A.
Henry, Mrs. T. A.
Hewitt, J. T., F.R.S.
Heycock, C. T., F.R.S.
Hinkel, L. E.
Hinks, E., M.B.E.
Hinks, Mrs. E.
Hoffert, Miss D. A.
Holleman, A. F.
Holleman, Mrs. A. F.
Horton, E.
Hunter, H.
Hutchinson, H. B.
Jackson, Sir Herbert, K.B.E., F.R.S.
Jackson, Lady.
James, T. Campbell.
Jeans, J. H., *Sec. R.S.*
Johnston, T. B., *Dean, Guy's Hospital Medical School.*
Kenyon, J.
King, H.
King, Mrs. H.
Kingston, Miss H. L.
Lakeman, Miss E.
Laker, J.
Lambert, B.
Le Pla, Miss M., *Indexer.*
Lessing, Dr. R.
Lessing, Mrs. R.
Leuchars, W. W., *Prime Warden, The Dyers' Company.*
Levy, Miss E. R.
Lowndes, J.
Lowry, T. M., C.B.E., F.R.S.
McBain, J. W., F.R.S.
McCombie, H., D.S.O., M.C.
Maclean, Mrs. I. S.
Maclean, H.
Macnab, W., C.B.E.
Manning, A. B.
Masson, I., M.B.E.
Meulen, H. ter.
Meulen, Mrs. H. ter.
Miall, S.
Miall, Mrs. S.
Micklethwait, Miss F. M. G., M.B.E.
Mitchell, A. D.
Mitchell, Mrs. A. D.
Monier-Williams, G. W., O.B.E., M.C.
Moody, Mrs. G. T.
Moore, T. S.
Moore, Mrs. T. S.
Morgan, G. T., O.B.E., F.R.S.
Morning Post.
Morrell, G. F.
Morrell, Mrs. G. F.
Morris, H. J.
Mott, B., *President, The Institution of Civil Engineers.*
Newton, A. U.
Neilsen, H.
Neilsen, Mrs. H.
Nuthall, Tallant.
Ormandy, W. R.
Ormandy, Mrs. W. R.

Orton, K. J. P., F.R.S.
Paget, H.
Paget, Mrs. H.
Palmer, W. G.
Palmer, Mrs. W. G.
Pedersen, Kai.
Perkin, W. H., F.R.S., *Past-President.*
Philip, J. C., O.B.E., F.R.S.
Philip, Mrs. J. C.
Pickles, S. S.
Plimmer, R. H. A.
Pope, Sir William J., K.B.E., F.R.S., *Past-President.*
Porritt, B. D.
Pratt, W. R.
Pratt, Mrs. W. R.
Press Association.
Price, T. Slater, O.B.E., F.R.S., *Secretary.*
Price, Mrs. T. Slater.
Pringle, Sir John, C.B.
Pyman, F. L., F.R.S.
Pyman, Mrs. F. L.
Raven, Sir Vincent, K.B.E., *President, The Institution of Mechanical Engineers.*
Reid, R. B., *President, The Institute of Brewing.*
Roberts, E.
Robertson, Mrs. E. G.
Robertson, Sir Robert, K.B.E., F.R.S.
Robertson, Lady.
Rogers, H.
Rosedale, J. L.
Rowlands, M. J.
Russell, A. S.
Sargeant, F. Pilkington, *President, The Pharmaceutical Society.*
Scott, A., F.R.S., *Past-President.*
Scott, Mrs. A.
Sharp, T. M.
Sharp, Mrs. T. M.
Sidgwick, N. V., F.R.S.
Simonsen, J. L.
Simonsen, Mrs. J. L.
Simpson, G. C., C.B.E., F.R.S.
Simpson, Mrs. G. C.
Smith, C., *Editor.*
Smith, Miss M. L.
Smith, T. B.
Spielmann, P. E.
Stern, A. L.
Stern, Mrs. A. L.
Stubbs, G., C.B.E.
Stubbs, Mrs. G.
Sugden, S.
Taylor, Miss M.
Thomas, R. N. Garrod.
Thomson, J. Millar, F.R.S.
Thorpe, J. F., C.B.E., F.R.S., *Treasurer.*
Thorpe, Mrs. J. F.
Times.
Tinkler, C. K.
Tinkler, Mrs. C. K.
Tryhorn, F. G.
Tryhorn, Mrs. F. G.
Turner, E. E.
Turner, Miss E. G.
Turner, G. W.
Turner, T., *President, The Institute of Metals.*
Voelcker, E.
Voelcker, E. W.
Voelcker, J. A.
Whiteley, Miss M. A., O.B.E.
Widdows, Miss S. T.
Woolcock, W. J. U., C.B.E., *President, The Society of Chemical Industry.*
Wynne, Miss D. P.
Wynne, W. P., F.R.S., *Past-President.*

After the loyal toasts had been honoured the President announced that he had had a telegram from Professors Biilmann, Bjerrum, Bohr, Brönsted, and Sörensen sending their hearty greetings and congratulations to the Society. This was received with acclamation.

The following is a list of the Toasts proposed :—

1. " His Most Gracious Majesty The King."

2. " Their Majesties the Queen and Queen Alexandra, His Royal Highness the Prince of Wales, and the other members of the Royal Family."

By Sir H. Frank Heath, K.C.B., Secretary of the Department of Scientific and Industrial Research :—

3. "The Chemical Society," coupled with the name of the President.

By Professor Henry E. Armstrong, LL.D., F.R.S., Past-President :—

4. "The Retiring President, Professor W. P. Wynne, D.Sc., F.R.S."

By Professor Irvine Masson, M.B.E., D.Sc. :—

5. "The Federated Societies," coupled with the name of W. J. U. Woolcock, Esq., C.B.E., President of the Society of Chemical Industry.

By Professor F. G. Donnan, C.B.E., D.Sc., F.R.S., Foreign Secretary :—

6. "The Guests," coupled with the names of Professor Ernst Cohen, of Utrecht University (representing the Nederlandsche Chemische Vereeniging), and J. Hunter Gray, Esq., K.C., M.A.

Sir H. Frank Heath, K.C.B., in proposing the toast of "The Chemical Society," said :—

Mr. President, Ladies and Gentlemen, after I had accepted with some hesitation the invitation to address you this evening, and to propose this toast, I happened to be present at a public dinner where one of His Majesty's Judges said that after considerable experience of speeches of the kind he had come to the conclusion that most proposers of toasts began by explaining how unfitted they were for the task entrusted to them, and spent the rest of the time in proving it. Well, Ladies and Gentlemen, after that opinion from the Bench, there is nothing left for me but to throw myself on the mercy of the court.

I do, indeed, feel it to be a very great honour that a great scientific society like this should ask to have the principal toast of the evening proposed by a layman. You are not only a focus of research in pure science, you not only have a membership of 4,000 Fellows, but I see at these tables to-night inorganic and organic chemists, analytical and physical chemists, and not least of all, perhaps, biochemists. I won't suggest that the specialisation which is obviously taking place in your ranks has gone quite as far as the young American medical student of whom Dr. Howe told us in Philadelphia last autumn, who announced his intention of specialising in the ear, but had not made up his mind whether it was to be the right ear or the left. But specialisation there certainly is. Indeed, the foundation of the Society was an act of specialisation in 1841; when the Royal Society was first founded, I find from those

interesting records in *Nature* that the discussions ranged quite easily from naval architecture to the distillation of charcoal, from the anatomy of animal intestines to the discussion of a new digester for the brewing industry. Well, every one of those fields now has its own special society or societies. Specialisation must continue, I imagine, and increase, and yet to me as a layman I think there seems to be a movement in progress which must tend to counteract any disadvantages there might be from excessive specialisation; I mean the obvious tendency for different sciences to co-operate in the solution of the more difficult problems that are in front of you.

Professor Wynne, in his address this afternoon, referred to the Department with which I happen to be connected, and spoke of the share which chemists had undoubtedly had in the movement that led to the establishment of that Department. But I do not think that even you perhaps fully realise how close the link always has been, and I imagine always must be, between any organisation established to encourage scientific research and the chemists. Just look back. Professor Wynne's address was partly concerned in dealing with the review that Professor Meldola took before the war—I think in 1907—of the difficulties of the research worker in this country. Professor Meldola, a Past-President of this Society, was an original member of the Advisory Council of the Department of Scientific and Industrial Research and remained a member of that Council until his unfortunate death. Your new President, Dr. Crossley, is Director of Research to the largest Research Association for Industry that has come into existence since those difficult days of the war, the British Cotton Research Association, and that Association and Dr. Crossley are working in constant and continuous co-operation with the Department. Dr. Slater Price, another officer of this Society, is Director of the British Photographic Research Association; Sir Herbert Jackson, a former Vice-President, is Director of the Scientific Instrument Research Association; Dr. Pickard, a former member of your Council, is Director of the Leather Association; Dr. Scott, a Past-President, is a Director of the Laboratory established by the Department at the British Museum in order to study the best means of preserving antique objects of every kind; and finally there is your Treasurer, Professor Jocelyn Thorpe, who is to-day a member of the Chemistry Research Board of the Department and a member of many of its committees.

Now, my contact with all those distinguished men has made a double impression upon my mind. One is the adaptability of the chemist, and the other is his extraordinary power of penetration. Looking at the Research Association movement which I have

referred to already—incidentally there are twenty-four different industries which have organisations of this kind in this country, and the majority of the Directors of Research of those twenty-four Associations are chemists—I draw the conclusion that they must have great adaptability, because I happen to know that in many cases, and in some of the most outstanding cases, the chemists who have been called to those important posts knew nothing about the industry when they took up the appointment, and for that very reason have brought success. Professor Wynne told you this afternoon that those Associations have been useful because they have opened new posts to young men, and nothing could be more important than that. But I think he might possibly have added that these Associations have done more than that. I will tell you an experience of mine which explains. The other day I was in the largest textile mill in the world, and found that they have quite a large and busy research laboratory, and I was told that the reason that that laboratory had been established was because they had been so convinced of the value of research by the Association of which the firm was a member that they were determined to carry the matter further and have an organisation of their own within the works. That is going on all over the country; so that it is not merely if you look at it simply from the point of view of openings for young men—which after all is not the whole story—it is not merely that the Associations provide openings, but that in increasing measure the firms in the Associations as they come to realise the value of research will need the help of chemists and other men of science. And, sir, their power of permeation! Chemistry, it seems to me, has made its way already into almost every sphere of human life. You dictate to us, sir, what we are to eat, though I believe you are not entirely agreed as to the preservatives that should be used for our food; you give us new textiles to wear—or at least you give our wives new textiles to wear, and when we are ill you indicate to us, attracted as we are by the skilful advertisements of people who are out for that weakness of man that comes with illness, and you tell us where the medicines we are advised to take fail to come up to what they claim to be.

Now, sir, I could quite safely, with considerable safety, go on to tell you of the records of your great men who have been officers and Fellows of this Society. I could refer to the Central Library which you have established, which helps all the Societies connected with chemistry to have a nodal point from which they can gather their recorded information. I could speak of your research fund. I could tell you of the brave efforts you are making in spite of rising prices and a printers' strike to keep the publications going. But

if I did, I should only be telling you what you know far better than I do.

I am going to venture, sir, in view of the most excellent hospitality which you have offered me, and in view of the patience with which you, ladies and gentlemen, have listened to me up to the moment, I am going to venture to be bold, and to tell you how the present state of chemistry strikes a rank outsider.

I remember that when my brother-in-law, more than forty years ago, tried to teach me some chemistry, the molecule seemed to me a much more important thing than the atom. The atom, to my untutored mind, seemed a sort of axiom which you had to accept, but which compared with the interest of the molecule was a poor thing. Now I venture to think that possibly until comparatively recent times chemistry has concerned itself a good deal more with the molecule and its behaviour than with the atom. But is that condition going to last? The other night I heard a distinguished young biologist speaking of several sciences and claim as his belief that the central science of the future would be biology. He was prepared to take off his hat to physics and chemistry as important fundamentally, but the future lay with biology. One did not live in the cellars of a house, but in the upper storey. Well, as an outsider I am bound to say that I doubt that. To me, at any rate, and possibly to other people who are not chemists, chemistry seems to be taking increasingly a central position and bringing to its service the work, the tools, which other scientists on both sides of it are preparing. What has physics done recently from the point of view of chemistry? Has it not, by giving you the anatomy of the atom, and by revealing the structure of the space lattice, helped you to get a picture of three things—first, the mystery of chemical attraction, secondly, as Sir William Hardy, in his Bakerian lecture, pointed out, the phenomena presented by liquid and solid surfaces in close contact, and thirdly, the problem of catalysis. Those things are giving you, are they not, larger control over the speed and nature of reaction? But the engineer similarly is bringing in the tool of high pressure, and what will happen when the knowledge you already have, and these tools you already have, are brought to bear under the conditions of high pressure, it is very difficult to prophesy. And so you are forcing your way into the biological field. Another tool I fancy I see in your hands will be those mysterious accessory vitamins which link up your chemical work with those mysterious chemical reactions of the animal and vegetable organisms.

Well, sir, I have proved my incapacity for proposing this toast, and I will therefore ask you to drink to the health and future of the

Chemical Society, coupling with the toast the name of your President, Dr. Crossley.

Dr. ARTHUR W. CROSSLEY replied :—

I am sure the Society would wish me to thank you, Sir Frank Heath, very warmly for the way in which you have proposed this toast. My predecessor in this Chair has this afternoon answered, I think, fairly fully some of the remarks which you have made. He has expressed his appreciation of the efforts of the Department of Scientific and Industrial Research. Perhaps, as being somewhat intimately associated with that Department, I may be allowed to add one or two words. So far as my experience goes that Department is free from, shall we say, a Government monopoly—Red Tape, and is willing in every way possible to help anyone interested in the work it is doing. I have had some experience of the professional or professorial side of chemistry, and for the past five years I have had some experience of chemistry as applied to industry. I say, with full consideration of what I am saying, that in my opinion the Department has founded in the Industrial Research Associations a movement which is destined to play an all-important part in the future of this country. By no other means that I can conceive could science have been brought into those industries. I hope on some future occasion to speak somewhat more fully on this subject, and for the present, if you will not think it impertinent on my part, I should like to congratulate the Department on the big efforts which it has started and to say, "Don't be in the least discouraged by disparaging remarks that may be made about you."

I believe it is customary for the President on these occasions to make some reference to the affairs of the Society. This afternoon we had our Annual General Meeting, and by virtue of a decision arrived at, I find things weighing somewhat heavily on my shoulders. I refer to the decision which permits me to have the honour to occupy the position which I do at the present moment.

The election of one President, of necessity, means the retirement of someone who has occupied that post. It falls to more eloquent lips than mine to propose the toast of Professor Wynne this evening. I hope, however, that Professor Armstrong will forgive me if I say one or two words. When the time comes for Professor Wynne to apply for armorial bearings I would like to suggest that he take one single word for his motto, and that word is "Thorough." His sole aim has been efficiency, and in endeavouring to attain it he has not spared himself in the slightest degree. Few realise when he comes to a meeting and quietly says, "I think we should be well advised to do so and so," that this has possibly meant hours of thought, perhaps wrestling with the mystic language of charters and bye-

laws, perhaps the writing of numerous letters and documents. To do the right thing for the Society's welfare has been his sole object. I should like to speak on behalf of us all just one or two words to Professor Wynne. They are simple, but my long-standing friendship with him enables me to know, I think, that he will understand.

"Professor Wynne, we have learned to know something of the time, care and thought which you have expended on our behalf during the past two years. We appreciate; we are grateful."

The Chemical Society is rightly, in the opinion of its Fellows, a very exceptional and uncommon institution, indeed our forbears taught us to regard it as such. They did not found the Chemical Society of London, or England, or of Great Britain, they founded simply "the Chemical Society," and as such we are proud to regard it. We desire no addition: we ourselves are content to be chemists, without the added epithet of druggists which so many kind friends attempt to hurl at us. But I regret to say that when one consideration is taken into account we become quite unexceptional, quite common, and resemble most other societies, institutions, and individuals, inasmuch as we are finding it very difficult to make our income balance our expenditure. Up to the early days of 1914 we were quite a happy band, able to publish the original communications sent in by our Fellows, able to give our Fellows full value for their subscriptions and able to put by a small sum of money each year. In those days a page of the Journal cost 17*s.* 5*d.*; in 1921 the price had risen to £2 12*s.* 4*d.* It is true that at the present moment the price has fallen somewhat, but it is still well above twice the amount that it was in 1914. Moreover, the original communications are always on the increase, and we have now to make annual provision for the publication of 3,500 to 4,000 pages of Transactions alone. The situation is a very serious one from the point of view of the Society and it has given the Council furiously to think as to the possibilities of meeting it. The first step was to increase the subscription of our Fellows by 50 per cent. It is greatly to be regretted that it was found necessary to do so, for the majority of our Fellows are young men, and young chemists—in fact, I think I may say most chemists—are not over-burdened with this world's goods. The second step was to adopt the suggestion of the Treasurer to ask our Fellows to subscribe to a Publications Fund, the interest on which should be devoted to the upkeep of the Journal. We have raised in this way nearly two thousand pounds, but that is not enough, and we were faced this year with a possible adverse balance of some three thousand pounds. The Treasurer this afternoon told us we actually had a credit balance of some £210, but how has this been obtained? By ruthlessly cutting down the original communications

sent in for publication, to such an extent as to cause endless displeasure to authors and to leave it doubtful as to whether we are doing justice to their work; further, by asking Fellows to pay for the Annual Reports, which so far have always been distributed free, and by many other curtailments of our legitimate activities which, in my opinion, are greatly to the disadvantage of our Fellows and form a distinct danger to the prestige of British chemistry. Most societies, most institutions and most individuals themselves decide the pace at which they will live, and the pace is generally regulated by monetary possibilities. But the Chemical Society is again exceptional. The pace at which we are living has not been decided upon by ourselves, but has been decided upon by no less an authority than the nation.

I have stated that up to 1914 we were a happy band. In that year the nation spoke to us for the first time on record, I believe, but it spoke in no uncertain voice. It said, in the first place, "We are at war. We want certain drugs used for the alleviation of pain and suffering; we have so far obtained these supplies from abroad, and that source is now cut off. We are aware that these drugs have never previously been made in this country; we are aware that they require skilled labour for their production. Therefore we want you to prepare them for us." Well, those drugs were prepared by an organised effort on the part of the chemists of practically all the Universities and University Colleges in this country. Then came a second call. The nation said, "We want more explosives: T.N.T., picric acid, ammonium nitrate; we want acetone and dye-stuffs." Finally, there came a third call: "We want poison gas, poisonous and always more poisonous, and with each gas we want complete protection." I do not think it can be said that any of these calls were made in vain, or that the chemists of this country were found wanting in any way. So far as I know the chemists of this country, that is, the Chemical Society has never spoken back to the nation, but I suggest the time has come when this might be done, and in terms such as these:—

"In 1914 you asked us to do certain work for you, which we did to the best of our ability. We at once admit that some of our results were not forthcoming as speedily as we could have wished and in circumstances where speed was all important, due to the fact that the type of work which you asked us to do was new to us and we had perforce to gain experience. This experience has shown us clearly that in order to be prepared for any call which you may make upon us in the future, when delay may prove fatal, it is necessary that nothing should be left to chance, and it is therefore essential for us to carry out numberless researches so as to keep ourselves fully

informed of the possibilities of chemistry generally. Your requests of 1914 have greatly stimulated research activities in this country, and the publication of the increased number of papers has become a very serious matter to the Chemical Society, which can only meet the present situation by greatly curtailing its legitimate and rightful activities. In these special circumstances, will you not help us to carry on our legitimate work?"

I cannot think that such an appeal could possibly fall on deaf ears, for this very simple reason, that the Chemical Society through the efforts of its members has proved itself to be a national asset of the utmost magnitude and importance. Sir Frank Heath, once more I thank you for the way in which you have proposed the toast of the Chemical Society.

Professor Henry E. Armstrong (Past-President), in proposing "The Retiring President," Professor W. P. Wynne, said:—

Mr. President and Fellows of the Chemical Society, I ask you to lend me your ears and I hope I shall reach them. You have an unusual opportunity, an unusual spectacle, to offer to our guests to-night—that of a retiring President. The programme is wrongly printed. The "The" should be in Clarendon and "retiring" in italics. Presidents are not often retiring. Their business is to be unashamed and aggressive on behalf of the bodies they represent. A little more than two years ago I undertook two tasks: one, an easy one, was to convince the Society, the Council of your Society, that a particular person was *the* man for the office of President; the other, an almost impossible one, to cajole, to persuade, all but to force that particular person to recognise, as the walrus said, that his time was come to take on the many things pertaining to the President's office in our honourable body. It is little short of forty years ago, on March 27th, 1886, that he came to me as private assistant and had we been wise we should never have parted company. The years we worked together were the happiest and most fruitful of my life. We were not called upon to concentrate hydrogen ions; we never wasted time on noughts and crosses; no Lowry worried us with perpetual rechristenings of the already fully-named; we just quietly kept company with a hydrocarbon which was thoroughly well behaved and responsive. Our work was straightforward. There was no angle worship about it and we reported our results without fuss of any kind, in the briefest possible manner.

We put up ten signposts for the Di- and fourteen for the Trichloronaphthalenes and thereby demonstrated the truth of a doctrine fitly to be called, a *theory* of benzenoid structure, which I venture to say no *X*-ray analysis can upset. I think I may say

we were both proud of our exhibit at Wembley last year, when we thought of its implications. Our work pleased the Germans but it met with no recognition at home. It was unnoticed and that was a double compliment. It cost much toil during many years and a good deal of hard cash; neither of us made a halfpenny out of it.

I am told that Mr. Wells asks a couple of hundred pounds for a couple of thousand words. At all times, we could get what we wanted, what material we wanted, free of cost from Germany. We were never offered anything from our English works and our advice and assistance was never invited, although we worked in a technical college. Now, a great branch of the dye-stuff industry stands upon the foundation we built up. Yet neither before nor during the war, nor since, have we been asked to advise or assist in any way in the construction of the English edifice. Now, I modestly mention these points, in support of what the President said to-day as to the lack of co-operation between science and industry. When that address of his is printed, I trust that the measured terms in which he spoke on that subject will have their effect. I may say that the work was done in a sense *sub-rosa*, without official encouragement. I recollect on one occasion speaking to our hon. secretary, Sir John Watney, about research. His immediate reply was, "Your business is to teach boys, not to do research." That is the kind of encouragement we got in those days. This is the spirit that has been behind the comparative failure of our institutions to do original work, of which the President spoke to-day. It was not the primary fault of those who were working in the institutions.

I was glad to hear him speak out particularly on one subject—I think it was the keynote of his address—and say plainly that it is absurd for the Universities of this country all to attempt to do the same thing and on the same scale. Sir Frank Heath has told you of the tendency there is to specialise. A great lesson to be learnt by the Universities in this country is that they too must specialise. His University has no right to deal with anything but iron and steel and things of that kind. It will only be by specialising, that it will be possible for the several universities to effect the exchange of workers of which he spoke. Supposing we were to legislate to-morrow in the direction in which he spoke, all the research workers would drift to one or two places. That is a serious danger of any attempt of that kind.

Now to return to the man. My respect for his great ability as a worker, as a chemist and teacher and for the nobility of his character, has steadily increased with years. As a chemist, I

know of no better worker and teacher; as a man I have known no man so conscientious and self-sacrificing. I would recall to you the service he rendered as Editor in years gone by, of which our President gave so striking an illustration to-day. I wish the spirit he showed on that occasion could be manifest throughout the Society and I wish that Editors could be brought to take the same interest and at the same time show the same ability in their Editorial work that our late President displayed. You have heard how conscientious he has been. He has attended every possible meeting of the Society it has been possible for him to attend and he has done a great deal of outside work. Such a man deserves our thanks, not only for the work he has done, for the direct service he has rendered, more particularly must we thank him for the example he has set. Unsparing unselfishness is scarcely a present failing of the chemist, but the time is at hand when it must be your distinct characteristic.

Sir Frank Heath has rightly told you that after all it is not the atom but the molecule that is the real thing. The atom has no character until it joins up into the molecule. Speaking before the Institute of Chemistry recently, I said that chemists have reason to be proud of themselves on account of their achievements. At all events, the young women of the day are clad in cellulose and fine raiment mainly through your services. Even the Medical Research Council is faintly yearning for chemical aid. Sir Frank Heath spoke of Biology being the science of the future. Biology is nothing but chemistry when it comes to the real thing. Biology is making slow progress at the present time but most of the Bio-chemists, as I have said, are but bits of chemists. When they become chemists, there will be a real advance in vital chemistry and in medicine too. Still, with all this service to your score you have no recognised public standard and what is worse, no internal cohesion but lots of friction. You are not three hydrocarbons but more than thirty. Now is the time for you to show that you can come together, hold together, log roll together and organise together. There must be complete fusion of interests, I hold; an end must be put to the present chaos and inefficiency of publication. If necessary, to find funds, you must give up smoking. Your analyses will be more trustworthy if you do. There will be less tendency to believe in the transmutation of copper into lithium. No small temporary scheme will suffice. To be at all, you must be big.

Now, gentlemen, if you have any element of human feeling, you will sympathise with me in my determination to overcome to-night the modesty of your too-retiring President and join with

me in thanking him, with all possible warmth, for the distinguished way in which he has served the Society during the past two years and for the great example he has set by his unselfish devotion to the interests of our profession. I call upon you to join with me in drinking the future health and happiness of our late President, Professor Wynne.

Professor W. P. WYNNE, D.Sc., F.R.S., responding, said :—

I rise to thank you most heartily for the cordial way in which you have received the toast. I hope I may be allowed to regard it not as applying only to myself, but as including all those who have worked with me in the interests of the Society during the past two years. But for the loyal co-operation and cordial support of the officers, the Council and the office staff I could have done little or nothing, despite all the kind things Professor Armstrong has said in proposing the toast. He is my father in chemistry, and his eulogy is to be explained not by my merit but by the partiality often displayed by a parent.

As a father, Professor Armstrong is doubly fortunate, for, in addition to four distinguished sons who bear his name, he has a numerous chemical family of which I am proud to be the eldest. Two others of us, Sir William Pope and Professor Lowry, are also present this evening. As will have been gathered from what he said we may not be in complete agreement with our father's views on every subject—a not uncommon experience in families, chemical or otherwise—but that does not diminish in the slightest degree our affection for him or sincere appreciation of our fortunate upbringing.

Professor Armstrong referred to the date on which I became his private assistant. I had left South Kensington a few months earlier, and it was through Professor Japp's kind offices that this most happy chance came my way. If a reference may be permitted to the plea put forward this afternoon for the encouragement of migration, this crossing of Exhibition Road from the one College to the other did undoubtedly exercise a profound influence on my own career.

I had the good fortune to number among my teachers no fewer than seven Fellows of the Royal Society, five of them being Past-Presidents of this Society, and, on an occasion such as this, it is no less a pleasure than a duty gratefully to acknowledge my deep indebtedness to them. The first of these Fellows was Dr. George Gore, who, it may be remembered, published so long ago as 1865 an account of the modification in the properties of some seventy substances produced by complete desiccation, and thus was a pioneer in the field of research so closely associated with Professor

Brereton Baker's name. He was a self-made man. How he came to be chemistry master in King Edward's School, Birmingham, I do not know, but he had never been to a training college, and thus his originality had not been educated out of him. His method of judging the nature of our work was to suggest at the commencement of the class, that we should write a résumé of the previous lesson. This was assessed by the number of pages handed in at the end of a quarter of an hour, irrespective of the fact that some of them might contain six words and some of them sixty. That is the way in which I started to learn chemistry. Then, having left school, I went to evening classes after the day's work, and am a product of that system of "payment by results," under which science classes were farmed out to teachers, who were paid by fees based on successes achieved by their students in the examinations conducted by the Science and Art Department of those days. Despite the hard things which have been said about it, I do not think the system was wholly bad. At any rate it gave me my chance and to many others theirs. It provided, indeed, the only avenue to instruction in science subjects open to most students in the 'seventies of last century before University Colleges and Technical Schools came into existence. By its aid I went to South Kensington in 1881 and there had the great advantage of being a student under Sir Edward Frankland, Professor Percy Frankland and Professor Japp, who began my training in research. Thereafter followed the training as a teacher under Professor Armstrong, who taught me—nay, compelled me—to think; Sir Edward Thorpe, who brought me back to the old College, and Sir William Tilden, who last year, although in infirm health, did me the great honour of coming to the anniversary meeting and saying words which I shall never forget. I am to see him to-morrow, and I hope I may take to him from this gathering a message of affectionate regard and esteem. (Cheers.)

There is just one remark I should like further to make. Sir Frank Heath spoke in most appreciative terms of chemists and of their adaptability, for which we thank him. But it is only right to remember that the indebtedness to which he referred is not wholly on one side. I think the signal success which has attended the work of Sir William McCormick and Sir Frank Heath, neither of them men of science, in producing the result known as the Department of Scientific and Industrial Research, serves to show that success in such enterprises comes not only from a knowledge of men and affairs, but in no small measure from a sympathy with, followed by an understanding of, the type of problem to be solved.

As the thirty-ninth President, no longer retiring but retired, I salute my friend and colleague, the fortieth President, wishing him

as happy a time during his period of office as fell to my lot. Once again I thank you all most sincerely for the way in which the toast has been received. I do not deserve the praise; I have simply done my job.

The toast of "The Federated Societies" was given by Professor IRVINE MASSON, who said:—

There are, I suppose, few of us here who are so deeply learned in chemical politics as to be at once aware of what this term connotes; and I will therefore first adopt the old-fashioned plan of giving instruction by means of enumeration. The Chemical Society is affiliated with no fewer than seventeen others. Of the eighteen, four deal primarily with pure science—the Mineralogical, Faraday, Biochemical, and ourselves; twelve with the methods and the discoveries of pure science as applied to practical arts, namely the Society of Chemical Industry, Society of Public Analysts, Royal Agricultural Society, Institute of Brewing, Society of Dyers and Colourists, Society of Leather Trades' Chemists, Royal Photographic Society, Institute of Metals, Iron and Steel Institute, Ceramic Society, Society of Glass Technologists, Institution of Gas Engineers; and two are of a special character, namely, the Institute of Chemistry and the Association of British Chemical Manufacturers, which deal with chemists professionally and in their relation to the lay public.

What is especially made prominent by this list is, not so much the subdivision of pure chemistry, as the great number of ways in which the science as a whole has found a place in the business concerns of the nation. So evident is this, indeed, to chemists, that we have now and then to remind ourselves that if we have won the privilege of helping a little in the material welfare of our country, we cannot evade the responsibility which has thereby been entrusted to us. And, with this in view, the more we can do to foster intellectual sympathy between all kinds of chemists, the more will our science be able to serve the nation at large. And this is why there is a Federation of all these societies: it is a federation primarily *pro bono publico*, not merely *pro bono chemico*.

Let me indicate briefly two or three ways in which co-operation has usefully shown itself at present.

The Library of the Chemical Society has of late years been extended and is annually increased, with the set purpose of being useful not alone to its own Fellows but also to members of the other affiliated societies. Towards the heavy annual cost of this addition to its original function, many of these Societies have contributed; and now our Library, poorly housed though it is, is becoming a truly national asset. Last year, for instance, the

visits to consult our 30,000 volumes averaged about twenty-two per day; and of these, one-third of the consultations were made by members, not of the Chemical Society, but of other societies, while among the other two-thirds many were members of the Chemical Society and the others as well.

Another example is seen in the co-operation between the Chemical Society and the Society of Chemical Industry which has set going the Bureau of Chemical Abstracts. The Bureau has done a great deal of quiet work already, and it has before it the central problem of unifying the British publications which survey each month or fortnight the whole of the world's current literature of chemistry. Surely no obstacle short of insuperable bankruptcy should be allowed to stand in the way of an end so desirable.

A collective token of federation is, I take it, to be seen in that body of delegates, the Federal Council for Pure and Applied Chemistry. There is something in this Council which reminds one of the luminiferous ether. It was originally invented to offer a medium for the propagation of light and radiation of energy, and to overcome the difficulty of action at a distance. Yet, I have been told, experiments made with the object of detecting it in motion have failed; and some daring moderns have even questioned the necessity for believing in it, and have dubbed it a pure convention.

Now there is a name which I have to couple with this toast—that of Mr. Woolcock. Chemists, as such, are trained to deal with things which are in themselves non-human; yet, because these things, and we ourselves, must everywhere affect human affairs, we need human guidance. It is to wise and experienced men like Mr. Woolcock that we instinctively turn for such help; and not one of you does not know how well and generously Mr. Woolcock gives it—think of one example alone, chemistry at Wembley. Mr. Woolcock fulfils the function of an ideal catalyser; for he starts, facilitates, or hastens actions, without upsetting any equilibrium, and himself emerges apparently unchanged at the end.

I ask you to couple with the toast of the Federated Societies the name of Mr. Woolcock.

Mr. W. J. U. Woolcock in his reply stated :—

I feel my efforts to respond to this toast will be somewhat inadequate, the more so as on looking at the toast list and seeing the term, "The Federated Societies," I did not know what was meant by it. My chemical education is, as you know, very limited. Hitherto I have supposed that I knew just sufficient chemistry to understand what the real chemist was talking about when I had to take his advice. For once I have failed. Professor Masson, convincing as

he is on most subjects, lucid to a fault on his own particular subject, has left me absolutely in the dark as to what is meant by the "Federated Societies." I at first thought that possibly it was a misprint and that Sir William Pope was intended to reply on behalf of the Federal Council. The delightful language in which Professor Masson brushed on one side the Federal Council leaves me in no doubt that he is not referring to that body, but he gave us, in order that we might know exactly about what we are talking, a list of learned bodies which, in the hope or in the anticipation of the Chemical Society, will ultimately become federated. Let us hope that that will eventuate. In future when I have to think of a reason why I should be considered a chemist, I shall always think of what Sir Frank Heath said, and regard adaptability as a qualification in a claim for that distinguished name, because I think it is a qualification which those of us who lack some qualification in science may readily embrace and regard as practicable, and in that way seek admission to the inner circle, because it is very true that the chemist is an adaptable person, and those who have to have something to do with him need to be adaptable as well.

It has been my fortune during the past twelve months to study two chemists at very close range. In fact, if I had attempted to define the Federated Societies I should have thought of a rather shorter list, and thought of the Chemical Society, the Institute of Chemistry and the Society of Chemical Industry, because of the real federation which has existed between those three bodies for some little time, and perhaps never more closely than during the past twelve months. I have been able to study at short range the Presidents of the Chemical Society and the Institute of Chemistry. We have travelled together, and it is a common thing for Professor Henderson and myself to speak together in different towns. That kind of intimacy brings familiarity and a working together which can only be obtained in that way. I remember that some time ago we arrived in Birmingham together. We had been in Glasgow the night before and had as usual said the proper thing about each other. Professor Henderson, when we got to Birmingham, called my attention to a placard just outside the station, and, after a quick glance, said, "They know we are coming," but not taking it quite as quickly as Professor Henderson, I saw that he was mistaken and I studied it a little more closely. The two Macs advertised there were not ourselves.

During the past twelve months there has been hardly a local branch of the Society of Chemical Industry or of the Institute of Chemistry that has not had a joint dinner. This indicates a desire for co-operation among the rank and file of which those who are

temporarily the leaders of the chemical societies and associations in this country will have to take notice.

I do not myself believe it is possible for the Councils of the various Societies to lay down a definite scheme for federation and to attempt to impose that on the local branches of the various Societies, but I do think that at the present time there is a demand throughout the country that we shall do something to prevent this appalling overlapping and duplication in the production of chemical literature, and do something which will satisfy the man who likes to consider himself in the rank and file and who at the same time feels that there is a definite need for a closer union among the Societies and the Associations.

Well now, neither Professor Wynne nor Professor Henderson nor myself is capable of doing that sort of thing individually. Together, of course, we have found it very easy. If we were upon a job which required modesty of demeanour, Professor Palmer Wynne did it. If it required some of that native shrewdness and ruggedness of character, Professor Wynne and I pushed Professor Henderson into it. If, of course, it were a mere torrent of words that was required, you know what would happen. But unlike the Duke of Plaza Toro, we have no desire to lead our Societies from behind, and in our individual capacity—not in our representative capacity—we have prepared a scheme for a Chemistry House to which each of us felt entitled to put his name, not binding our respective Societies or Associations in any way. This is a scheme which we feel we can recommend to those of our friends who are prepared to listen to our recommendations. I feel that with you, Dr. Crossley, in the chair in succession to Professor Palmer Wynne—and if I may say so, I welcome you very heartily in the chair—the work will continue.

We of the " Federated Societies," yes, of the Federated in inverted commas Societies, thank you very much indeed for inviting us to-night, and thank Professor Masson for proposing the toast. We wish the Chemical Society every prosperity during the coming year, and hope that the traditions which have been built up during the past four or five years of close working and co-operation between the officers of the various Societies will be maintained. We trust that under your guidance those traditions will continue and we may be even more successful in the coming year than in the past.

Professor F. G. Donnan, C.B.E., D.Sc., F.R.S. (Foreign Secretary), proposed the toast of " The Guests," coupled with the names of Professor Ernst Cohen, of Utrecht University (representing the Nederlandsche Chemische Vereeniging), and Mr. J. Hunter Gray, K.C., M.A. He said :—

We have here to-night four distinguished representatives of

Holland, Professor H. J. Backer, Professor Ernst Cohen, Professor A. F. Holleman, and Professor H. ter Meulen. Three of them are accompanied by their wives. May I say that we wish these ladies also a very hearty welcome to London and to the Chemical Society dinner.

I believe it is true that although the population of Holland is relatively small, actually the largest number of Nobel prizes has been given to that nation, which is a wonderful tribute to the scientific output and ability of Holland. It is nothing new, for that country has always been perhaps the greatest centre of scientific culture in Europe. I have great pleasure in saying a few words about my friend Professor Cohen, of Utrecht, whose name I have the honour to couple with this toast. I think it is rather late in the evening to refer to the distinguished work of Professor Cohen, but he is the most eminent pupil of that great man, Professor J. H. van't Hoff, and is one of the greatest authorities on the effect of high pressure on chemical reactions, and many other things.

When I come to look at the list of other distinguished guests associated with this toast, I feel like a miserable sinner transported to Paradise and asked to propose the toast of all the holy Saints. The Rt. Hon. Sir John Anderson, G.C.B. (Permanent Under-Secretary of State for Home Affairs), is one of our guests, and may I assure him, speaking as one Secretary of State to another, that if in the conduct of the affairs of this great country he wishes for any advice, the President of the Chemical Society will be always willing to help.

I have also the pleasure of coupling with this toast another name, that of one of those modest men of law, Mr. J. Hunter Gray. I have had the honour to be associated with him in one or two cases. It is needless to speak about these great men, because we all spend our nights reading the *Evening Standard*, and our days reading *The Times*, and we have the greatest admiration for their work.

There is one thing I should like to say before I conclude, namely, in reference to a very important part of the toast, that of the ladies present to-night. We wish them all a very hearty welcome.

It is my great pleasure and honour now to give you the toast of "The Guests," coupled with the names of Professor Cohen and Mr. Hunter Gray.

Professor ERNST COHEN, who replied for the Dutch chemists present, said :—

During the toast of my friend Donnan I made some notes, but it seems to be impossible to make a response to all the remarks he made in the toast. I think it would take too much time. This afternoon I had a warning from the new President of your Society

that everyone must be brief. I think there is no nation more fond of conciseness in speech than the English. Take, for instance, your chemical abstracts. When an English chemist wants to describe the properties of any substance or fluid he says: B.P. 100, F.P. zero, D.C. 80, and for those who are not familiar with those telegraphic hieroglyphics I will add that B.P. means boiling point, F.P. freezing point, D.C. dielectric constant.

In English literature or poetry you find absolutely the same thing. I remember an English rhyme made up of initial letters which, for those who are not in a hurry, I will translate:

A fishy old fisher, called Fisher,
Fished fish on the edge of a fissure.
The fish with a grin
Pulled the fisherman in.
Now they're fishing for the Fisher within.

But the most striking conciseness is found in the language of English daily life. When I have to write a letter to the Foreign Secretary of the Chemical Society I write: F. G. Donnan, M.A., Ph.D., F.R.S., F.S.C.S., London, W.C.1, and so I could go on. If I were to follow these lines in responding, I would have to condense them into a few initials, which in plain English would mean, "I wish to the Council and the Fellows of the Chemical Society, good luck, welfare, prosperity and happiness."

Ladies and gentlemen, as I am a foreigner, you will allow me to express myself in a somewhat more elaborate way. In the first place, I have to thank the Council and the Fellows of the Chemical Society in the name of my Dutch colleagues who were so kindly invited to attend this dinner and the Annual Meeting this afternoon, and also to thank you in the name of the Dutch Chemical Society whose representatives are prevented from being here and celebrating with you the birthday of this Society with which so many illustrious names are linked.

There is a French saying which means, "Every meeting we finish by a dinner whenever we can, and it is by a dinner that we rule over man." But I make an alteration in the last line and say, "It is our dinners which delight ladies and men." The question arises as to the origin of the custom of finishing such a meeting with a dinner. We have had two dinners to-day; in the afternoon our President gave us mental food in his most interesting lecture, and now we have material food. Whence comes the custom of linking the two? It is your countryman, Joseph Priestley, to whom you are indebted for this most pleasant custom. Priestley has been pictured in a fascinating way in a caricature by one of your countrymen as sitting at a dinner, but at a dinner which he never attended.

Priestley was a very wise man. He also invented soda-water, a very good remedy for many persons who have attended a dinner. I have been so lucky as to find the caricature, and I have had it copied and will ask you all to accept a copy not only as a memento of this splendid invention by your countryman, but also as a memento of most pleasant hours spent in your company. I feel sure that my Dutch colleagues will feel with me that we have had a very interesting meeting and enjoyable dinner with you, and thank you all for the very kind way in which you have invited and entertained us.

Mr. J. HUNTER GRAY also replied, saying :—

Professor Donnan, and members of the Chemical Society, a few days ago I had the burden and privilege to make the last speech at another meeting and I had taken the greatest trouble to prepare an impromptu speech to deliver on that evening. It passed through my mind that I might palm it off once more, but I had no sooner come into this room than I found two members of this company—Sir Frank Heath and Professor Armstrong—who had heard my last impromptu effort. Therefore I am thankful I had made preparations for another impromptu speech.

This toast recalls to me a set of questions and answers which appeared recently in one of the newspapers. The publication of those questions and answers was for the purpose of demonstrating the super-excellence of a system of education in this country for which we paid so many millions of pounds annually. One question put was, What is a Guest? One bright youth answered, "A Guest is a joke." Well, I hope the guests are not worse than jokes to-night, because I would rather be a guest than a nuisance, especially as I am making the last speech on the toast list. The guest who talks too much is apt to become a nuisance, so I will be quite brief. Another answer was, "A Guest is a person usually of the male sex who eats and drinks as much as he can and pays nothing for it." I suspect that the young person who wrote that answer was a precocious member of the other sex. But we do, as guests, come within that definition.

We to-night are guests of a most eminent body of scientific men, and it is inevitable that our thoughts should be extraordinary when we hear about molecules and atoms and the somewhat dubious relationship between them, and we may play with unusual ideas. For example, usually when I look at the menu and note the various courses and I see there is one course entitled *Saumon d'Écosse* with some other French words, I should say that was good Scotch salmon. But no such thoughts came into my mind to-night. When I put my knife into that salmon, I wondered if I should find at least a dozen of those bodies Sir Frank Heath referred to, vitamins,

running about, and perhaps I might even find a few of those bodies known by some curious names, and see the poor little vitamin running away and calling in terror-stricken tones, " Yadil, Yadil."

But let me be serious. I am not one of those, although a mere lawyer, who think that the premier gifts of scientific genius have departed from this country. I believe that in the future, as in the past, our British men of science will remain in the van of scientific progress. The whole world has marvelled at the wonderful work done by them, and especially, may I say, by our chemists in the Great War, and believing, as I do, that any future warfare will depend more and more upon scientific progress, I have no fear, if only the public and the Governments of this country will give to science that encouragement which it demands and which it deserves.

I am proud to be associated with the great scientist Professor Cohen to-night in responding to the toast of the Guests. We, the Guests, thank you, our Host.

Ordinary Scientific Meeting, Thursday, April 2nd, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following:

Honorary Fellow.	Elected.	Died.
Guglielmo Körner	Jan. 20th, 1898.	March 28th.
Fellows.		
Charles Samuel Mummery	Dec. 5th, 1907.	March 27th.
Robert Atkinson Oddy	Feb. 21st, 1918.	March 12th.

The PRESIDENT announced:

1. That the Keith Gold Prize Medal of the Royal Society of Edinburgh awarded to the late Robert Traill Omond, LL.D., has been lent by Mr. Arnold Stevenson for exhibition in the Medal Case. It is hoped that other Fellows will add to the interest of the Society's Collection by loan or gift.

2. That the following Committees for 1925–1926 had been appointed by the Council:

Finance Committee: J. L. Baker, A. Chaston Chapman, F. P. Dunn, C. A. Hill, G. T. Moody, R. H. Pickard, and the Officers (Treasurer as Chairman).

House Committee: J. L. Baker, Sir Herbert Jackson, Alexander Scott, J. M. Thomson, Sir William Tilden, E. W. Voelcker, and the Officers.

Library Committee: P. P. Bedson, O. L. Brady, J. R. Partington (Chairman), Sir Thomas K. Rose, Alexander Scott, J. F.

Spencer, the Officers, and the Librarian, together with the following representatives of contributing Societies: J. L. Baker, R. B. Brown, J. C. Drummond, A. Harden, J. P. Longstaff, R. L. Mond, G. Senter.

Publication Committee: H. B. Baker, E. C. C. Baly, H. Bassett, O. L. Brady, H. W. Dudley, U. R. Evans, J. J. Fox, A. J. Greenaway, I. M. Heilbron, T. A. Henry, C. K. Ingold, H. McCombie, I. Masson, W. H. Mills, T. S. Moore, G. T. Morgan, J. R. Partington, J. C. Philip, R. H. Pickard, F. L. Pyman, N. V. Sidgwick (Chairman), W. P. Wynne, and the Officers.

Research Fund Committee: A. J. Allmand, H. B. Baker, E. C. C. Baly, J. B. Cohen, W. H. Mills, Sir Robert Robertson, R. Robinson, N. V. Sidgwick, Sir James Walker, W. P. Wynne, and the Officers.

The following were formally admitted Fellows of the Chemical Society: G. E. Gardam, G. E. Watts.

Certificates were read for the first time in favour of:

Neville Melton Bligh, A.R.C.S., A.I.C., 67, Castle Road, Bedford.
Hugh Alexander Millar Borland, M.Sc., A.R.C.S., 14, Cotham Road, Bristol.
Malcolm Sinclair Gaskill, 3, Buckingham Road, Hilton Park, Prestwich, Manchester.
Norman Hamer, Ash Mount, Holcombe, Manchester.
Ivor Gray Nixon, 75, The Vale, Golder's Green, N.W. 11.
Vincent Joseph Occleshaw, M.Sc., A.I.C., 22, Byrn Street, Ashton-in-Makerfield, Wigan.
Leon Rubenstein, B.Sc., 87, Eaton Grove, Swansea.
Alec Thomas Streather, B.Sc., A.I.C., 3, Wellington Road, Watford.
Violet Corona Gwynne Trew, 18, Adam Street, Portman Square, W. 1.

The following papers were read:

"The formation of *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid from *d*-camphorquinone." By C. S. Gibson and J. L. Simonsen.

"Aromatic esters of acylecgonines." By W. H. Gray.

"The decomposition of hydrogen peroxide by cobaltic hydroxide." By F. G. Tryhorn and G. Jessop.

RESEARCH FUND COMMITTEE.

A meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W. 1, must be received on or before Monday, June 1st, 1925.

All persons who received grants in June, 1924, or in June of

any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned by June 1st.

PUBLICATIONS FUND.

In connection with the Appeal for the Publications Fund issued by the Treasurer, it has been decided that a list of donations and subscriptions received shall appear in the Proceedings for June. All donations and subscriptions received prior to the end of May will be included in the List.

LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

BERICHTE, 1915 to 1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of Papers, or Abstracts thereof, received between March 20th and April 2nd, 1925. (This list does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The thermal decomposition of ammonia upon various surfaces." By C. N. Hinshelwood and R. E. Burk.

"Strychnine and brucine. Part III. The position of the methoxyl groups in brucine." By F. Lions, W. H. Perkin, and R. Robinson.

"Compounds of tervalent molybdenum. Part III. New oxalates." By W. Wardlaw and W. H. Parker.

"The composition of starch iodide." By H. D. Murray.

"Note on the atomic volume of manganese." By A. N. Campbell.

"Note on molybdenum semipentoxide." By W. Wardlaw and F. H. Nicholls.

"The action of hydrogen chloride on *cyclo*hexylideneazine and on *cyclo*pentylideneazine." By W. H. Perkin and S. G. P. Plant.

"The constitution of soap solutions in the presence of electrolytes: sodium laurate and potassium chloride." By W. C. QUICK.

"The tautomerism of dyads. Part III. The effect of the triple linking on the reactivity of neighbouring atoms." By E. H. INGOLD.

"The molecular condition of phenol in benzene solution." By J. C. PHILIP and C. H. D. CLARK.

"The solubility of sulphur dioxide in water and in aqueous solutions of potassium chloride and sodium sulphate." By J. C. HUDSON.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, MAY 7TH, 1925.

BJERRUM, NIELS JANNIKSEN, Copenhagen, Vendersgade 28. Danish. Professor in Chemistry at the Royal Veterinary and Agricultural College in Copenhagen. Researches on liquid potentials, on complex compounds, especially of chromium, on the ionisation of electrolytes, on the thermic dissociation of water and carbon dioxide, on the theory of titration, on the atomistic explication of ultra-red spectra, etc. (*Signed by*) F. G. Donnan, J. N. Collie, W. E. Garner.

BLUNSDEN, ARCHIBALD BERESFORD, "The Bungalow," Westbury-on-Trym, Bristol. English. Asst. Tech. and Analytical Chemist. Employed for over five years by The British Oil and Cake Mills, Ltd. (Bristol branch) in research, etc., in their laboratory and works. Evening study at the Merchant Venturers Tech. College, including lectures, advanced analysis, and research. City and Guilds of London Institute Final Certificate (Technological) in Oils, Fats, and Candle Manufacture. National Certificate in Chemistry. Desire to keep up-to-date with advance in the scientific world. (*Signed by*) Arthur Marsden, M. W. Jones, Chas. J. Waterfall, S. Siddons Wilson.

BLYDE, GEOFFREY ALGER, "East Cliffe," East Bank Road, Sheffield. British. Steel Maker at A. Blyde & Co., The Wallace Steel Works, Sheffield. Late Student of Metallurgy, Applied Science Department, The University of Sheffield. I am desirous of joining with a view to extending my knowledge of Chemistry and Metallurgy by the use of the Society's Library and Journals. (*Signed by*) John Evans, L. Archbutt, J. E. A. Blyde.

BOWLES, THOMAS HENRY, "Allandale," Meadowside Rd., Cheam, Surrey. British. Chemist, 1st Grade, Government Chemists' Department. 28 years Government Chemists' Department. (*Signed by*) R. Robertson, Geo. Stubbs, J. J. Fox.

BRINDLEY, WILLIAM HARRISON, 11, Millmoor Terrace, Glossop, Derbyshire. British. Demonstrator in Chemistry, Faculty of Technology, University of Manchester. M.C., M.A. (Cantab.), M.Sc.Tech. (Manc.), A.I.C. Demonstrator as above since 1921. Joint author of "An Attempt to Resolve Quaternary Phosphonium Compounds," and "Some Esters of Anisic Acid." (*Signed by*) Frank Lee Pyman, Fredk. M. Rowe, John K. Wood.

BUCHAN, JAMES LINDSAY, Hampden Club, London, N.W. 1. British.

Physico-chemical Research Student, University College, London. B.Sc. (Lond.), Hons. Chemistry. (*Signed by*) F. G. Donnan, W. E. Garner, D. McKie.

BULL, FRANK HENRY CHARLES, 50, Cornwall Road, Bishopston, Bristol. British. Works Chemist in the employ of Bristol Gas Company, Bristol. B.Sc. degree 1916 (Bristol University) (Subjects: Chemistry, Physics, Mathematics); Associate of the Institute of Chemistry, 1919; Full Technological Certificates in Gas Engineering and Gas Supply from City and Guilds of London Institute, 1923—4. (*Signed by*) F. Francis, J. W. McBain, M. E. Laing.

BUTLER, JOHN ALFRED VALENTINE, "The Potteries," Winchcombe, Glos. British. Assistant Lecturer in Chemistry, University College of Swansea. M.Sc. (Birmingham), 1922. Author of papers: *Trans. Faraday Soc.*, **19**, 659, 729, 734, 1924; *J. Phys. Chem.*, **28**, 438, 1924; *Phil. Mag.*, **48**, 746, 927; *Zeits. phys. Chem.*, **113**, 279, etc. *J.C.S.*, 1923, pp. 2370, 2380; 1924, pp. 963, 1101 (jointly with other authors). (*Signed by*) G. T. Morgan, S. R. Carter, J. E. Coates, L. E. Hinkel, E. E. Ayling.

BYFORD, ANNIE LAVINIA, 73, Elderton Rd., Westcliff-on-sea, Essex. British. Student of Chemistry. B.Sc. (Pass). Studying for B.Sc. Honours in Chemistry at Bedford College for Women. (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie, E. R. Levy.

CLEGG, JAMES HERBERT, "West Cliffe," Queens Park Rd., Burnley. British. Engineer and Manager, Burnley Corporation Gas Dept. Member of the Institution of Gas Engineers. My object in seeking membership of your Society is to extend my knowledge of and assist in the furtherance of Chemical Science. (*Signed by*) Raymond Ross, Ernest Hardiker, J. P. Leather.

COCKROFT, HORACE CECIL, 6, Highfield Terrace, Halifax. British. Schoolmaster. London, B.Sc., 2nd Class Hons. Chemistry, 1922; Associate of the Institute of Chemistry, Jan. 1923; Student at University College, Reading, 1919—1922. Research work on CuCN–KCN–H_2O system incorporated in paper, Bassett and Corbett, *J.C.S.*, Vol. **125**, 1924. (*Signed by*) Robt. D. Abell, H. Bassett, J. W. Dodgson.

COYNE, FRANCIS XAVIER, 160, Addison St., Blackburn, Lancs. English. Student at the Blackburn Technical College. Three years' work at a Manufacturing Chemist's as a chemist, in the laboratory. Proficiency in Chemistry, Physics, Mathematics, German, French, Latin, and Greek. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, Robert H. Pickard.

CRAIK, JAMES, The University, St. Andrews. British. Carnegie Research Fellow. M.A. 1920 (St. Andrews). B.Sc. 1921 (St. Andrews). Ph.D. 1924 (St. Andrews). Author of a paper entitled "The Mechanism of the Oxidation of Typical Carbohydrates with Hydrogen Peroxide and Hypochlorous Acid," *J. Soc. Chem. Ind.*, 1924, **43**, 171. At present engaged in Research Work in the Chemistry Department, University of St. Andrews. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

DANE, HERBERT GREETHAM, The Diocesan Training College, Winchester, Hants. British. Tutor and Lecturer (and Demonstrator) in Chemistry at the Winchester Training College. B.Sc. with First Class Honours in Chemistry, Sheffield, 1922. M.Sc. (Sheffield) 1923. Worked under Dr. J. Kenner 1921-22 on the Influence of Steric Factors on Intramolecular Condensation, see J. Kenner and E. Witham, *T.*, 1921, 1452. (*Signed by*) W. P. Wynne, F. G. Tryhorn, Arthur W. Chapman.

DEAN, HARRY, 134, New Lane, Oswaldtwistle, nr. Accrington. English.

Textile Chemist and Colorist. Assoc. Manchester Coll. of Technology (Bleaching, Dyeing, and Printing, including advanced Organic Chem. and Dyestuffs Intermediates). 3rd year College Certificate of Blackburn Tech. Coll. (Inorg. and Organic Chem. and allied subjects). (*Signed by*) Percy J. Rhodes, G. W. F. Holroyd, E. Knecht.

DIXON, MARGARET STEDMAN LEONORA, Homebush, Worcester Rd., Sutton, Surrey. British. Student. A student taking a B.Sc. Honours Degree in Chemistry at Bedford College for Women (University of London). (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie.

FARNELL, ROBIN GEORGE WESTBURY, Exeter College, Oxford. British. Chemist to the British Empire Sugar Research Association, 3, 5, 7, Old Queen St., S.W. 1. A.R.C.S. A.I.C. Research into the colloidal constituents of the juice of the sugar cane. (*Signed by*) James C. Philip, M. A. Whiteley, H. B. Baker.

FAULKNER, IRVINE JOHN, Emmanuel College, Cambridge. British. Research Student. (*Signed by*) T. M. Lowry, R. G. W. Norrish, L. P. McHatton.

FLETT, THOMAS, Anchor Cottage, Kirkwall, Orkney. British. Chemist. At present Works Chemist in a Factory. 4 Years' Course at Glasgow University, 1919—1923; Graduated B.Sc. (Applied Chem.) and was elected A.I.C., 1923; Works chemist at Thornley Binders, Ltd., since January 1924. (*Signed by*) G. G. Henderson, T. S. Patterson, R. Wright, S. Horwood Tucker.

GARDNER, THOMAS JAMES ELIJAH, 12, Bushwood Road, Kew, Surrey. English. Works Chemist (Consol Products, Ltd., Sunbury Common, Middlesex). 30 Years' experience in Manufacturing Chemistry, especially in the investigation and perfecting of Synthetical Essences and like products. I am anxious to keep in touch with the developments of modern Chemistry, particularly as applying to my own work. (*Signed by*) Francis W. Hodges, Frank A. Boys, Archibald Macpherson.

GARRAN, RICHARD RANDOLPH, Orphir, St. George's Rd., Toorak, Melbourne, Australia. Research student at the University of Melbourne. Bachelor of Science (Melbourne), 1st class Honours and Exhibition in Chemistry in first and second years, 2nd class in third year. Has since done a year's research (heterogeneous equilibrium) and is at present reading for Final Honour Examinations in Chemistry. (*Signed by*) A. C. D. Rivett, E. J. Hartung, W. Davies.

GIBLIN, JOHN CHARLES, 3, Kensington Terrace, Brecon, Wales. British. Science-master, Christ College, Brecon. Bachelor of Science (London, 1st Hons. Chem.). Associate of the Institute of Chemistry. (*Signed by*) W. J. Jones, Claude M. Thompson, E. P. Perman.

GILCHRIST, HELEN SIMPSON, 82, North St., St. Andrews. British. Research Chemist, Food Investigation Board, D.S.I.R. B.Sc. (St. Andrews), 1917. Ph.D. (St. Andrews), 1921. Author of a thesis on "The Preparation and Constitution of Synthetic Fats, containing a Carbohydrate Residue." Assistant in Chemistry, The University, St. Andrews, 1918—21. Joint author, with Principal Irvine, of (1) A Synthetic Fat, etc., *T.*, 1924, **125**, 1. (2) Condensation of Mannitol with Olive Oil, *ibid.*, 10. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

HADFIELD, ISABEL HODGSON, 65, Langham Rd., Teddington, Middlesex. English. Research Chemist. M.Sc., London University. Seven years' research work for the Aeronautics Advisory Committee. Member of the staff at National Physical Laboratory. (*Signed by*) Guy Barr, L. L. Bircumshaw, J. T. Hewitt.

HALPIN, JAMES FRANCIS, St. Chads, 39, Benson Road, Forest Hill, S.E. 23. British. Superintending Chemist, Government Chemist's Department. Superintending Chemist in the Government Laboratories. Fellow of the Institute of Chemistry. (*Signed by*) Robert Robertson, Geo. Stubbs, A. More, J. J. Fox.

HANSON, DONALD, 7, Willow Bank, Halifax. English. Works Chemist. Passed in Physics as subsidiary to taking Honours B.Sc. (External) of London University. Also 8 years' Laboratory and Technical Experience in Explosive Manufacture, Tar Distillation, Textile Chemistry, and Analytical Work. (*Signed by*) W. Sowden, G. C. Riley, W. J. Stansfield.

HAWORTH, THOMAS, 8, Park Terrace, Fielding Lane, Oswaldtwistle, Lancs. English. Assistant Gas Engineer and Manager, Oswaldtwistle Urban District Council. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

HEATON, JOHN STANLEY, 43, Birch Rd., Crumpsall, Manchester. British. Research Chemist. Student and research worker at Liverpool University for five years. B.Sc. (1st Hons.). Ph.D. Now engaged on research in textile industry. "The Investigation of Meso-thioanthracene Derivatives. Part I," Heilbron and Heaton, *J.C.S.*, 1923, **123**, 173. (*Signed by*) I. M. Heilbron, William Doran, F. C. Guthrie.

HENSMAN, JOHN CYRIL, M.A., A.I.C., Aldenham School, Elstree, Herts. British. Chemistry Master, Aldenham School. 1921, Cambridge Natural Sciences Tripos, Part I (Chem., Physics, Physiology); 1923, Cambridge Natural Sciences Tripos, Part II (Chemistry); 1923, elected to an Associateship of the Institute of Chemistry; 1923–4, Asst. Science Master, Rotherham Grammar School, Yorks.; 1924, Chemistry Master, Aldenham School. (*Signed by*) T. M. Lowry, W. H. Mills, Charles T. Heycock.

HILL, JOSEPH, 58, Spring St., Accrington, Lancs. English. Chemist (Works). Past Blackburn Tech. College, 4th year Day Course. Occupation: Chemist, East Lancashire Soap Works. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

HOCKING, FREDERICK DENISON MAURICE, 18, Woodside Park Road, N. Finchley, N. 12. British. Biochemist (and at present Final Year Medical Student, Univ. of London). M.Sc. (Lond.) with mark of distinction. A.I.C. (1920). A.C.G.F.C. and Streathfield Memorial Prize, 1919. (*Signed by*) A. Prideaux Dawson, Arthur J. Hale, H. M. Atkinson.

HOYLE, JIM, 11, Crow Lane, Ramsbottom. British. Finisher (Woollen). 2nd and 3rd Year Certificates Chemistry gained at Blackburn Technical College. 1st, 2nd, 3rd, and 4th Year Chemical Trades Course. U.L.C.I., with distinction in Magnetism and Electricity. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

HUGHES, HORACE WILLIAM, 27, Ombersley Rd., Balsall Heath, Birmingham. British. Schoolmaster. B.Sc. (Birmingham), Class 1 (1921). Principal Subjects: Metallurgy, Chemistry; Subsidiary: Strength of Materials. (*Signed by*) Harold Harris, Thomas Turner, Wm. Wardlaw.

JACKSON, JOSEPH TAYLOR, B.Sc. (Lond.), 192, Algernon Road, Lewisham, S.E. 13. British. Lecturer in Applied Chemistry at The Leathersellers' Company's Technical College, S.E. 1. Bachelor of Science, London University. Fellow Royal Microscopical Society, London. War service (France and Salonika), Sept. 1914–Jan. 1919. (*Signed by*) Arthur Harden, Charles Dorée, S. Judd Lewis.

JEHU, DAVID BRET, 34, High Street, Welshpool, Montgomeryshire. British (Welsh). Research Student. B.Sc., University of Wales, First Class Honours. M.Sc., University of Wales. Associate of the Institute of Chemistry. Paper

Jehu and Hudleston, *Trans.*, 1924, **125**, 1451. (*Signed by*) T. Campbell James, C. R. Bury, L. J. Hudleston, H. Medwyn Roberts.

JOBSON, WILLIAM, 52, The Mall, Swindon, Wilts. British. Analytical Chemist. Asst. Analyst in G. W. Rly. Chemical Laboratory, Swindon, for the last 25 years (less 4½ years' war service), appointed Chief Assistant, May 1922. Board of Education, S. and A. Dept., Inorganic Chemistry (Practical), Honours Part 1, 1903, Pass. (*Signed by*) W. R. Bird, T. C. Davison, T. Hartley.

JONES, CLIFFORD MERTON, Buxton Crescent, Newton Hill, Leeds Rd., Wakefield. British. University Student (post graduate). Science student at Queen Elizabeth's Grammar School, Wakefield (1914–1920). Laboratory assistant for two years (part time). Student in Science at University of Leeds, 1921 onwards. 2nd Class Honours B.Sc. in Chemistry, July 1924. (*Signed by*) J. B. Cohen, W. Lowson, W. A. Wightman.

JONES, THOMAS WILLIAM, 36, St. Vincent Road, Westcliff-on-Sea. English. Technical Chemist. B.Sc. (Hons. Chem.), London 1922. (*Signed by*) J. R. Partington, E. E. Turner, Stephen Miall, W. G. Shilling, F. A. Williams.

KEANE, JOHN, 6, Shamrock Villas, Drumcondra, Dublin. Irish. Assistant Lecturer in Chemistry, University College, Dublin. B.Sc. (First Hons.), 1917. M.Sc. 1918. Ph.D. 1922 (National University). (*Signed by*) A. G. G. Leonard, A. O'Farrelly, Sydney Young.

LUCY, ALFRED, 16, Chesney Street, Battersea, London, S.W. 11. British. Junior Assistant Chemist. Twelve years' Practical Chemical experience in Works and Research Laboratories (*i.e.*, The Gas Lighting Improvement Co., Ltd.), etc. Chemistry student, attended classes up to and including the B.Sc. Standard in Theoretical and Practical Inorganic and Organic Chemistry. Battersea Polytechnic certificates for Inorganic Chemistry and Oils, Fats, and Waxes. (*Signed by*) William A. Godby, J. L. White, John Wilson.

MABBOTT, ERNEST EDWARD, 358, Fore Street, Edmonton, N. 9. British. Student. B.Sc. Engaged upon Organic Research work at East London College. (*Signed by*) J. R. Partington, E. E. Turner, A. T. Healey.

McDOWALL, DAVID, 2, Kennishead Road, Thornliebank, Glasgow. British. Process Supervisor, Calico Printers, Ltd., 8 years, Manager, McDowall, Morrison & Co., Ltd., Chemical Manufacturers, and interested in research on behalf of Chemical Industry and in connection with Manufacturing Chemistry. (*Signed by*) Robert Craig McDowall, W. McHutchison, Andrew S. Matchett.

MANSKE, RICHARD H. F., The University, Manchester. British. Research Student in Chemistry, Victoria University, Manchester. B.Sc. 1923. M.Sc. 1924. Queen's University, Kingston, Canada. 1851 Exhibition Scholar, 1924—from Canada. (*Signed by*) Arthur Lapworth, R. Robinson, J. Kalff.

MOIR, HUGH CLOUSTON, 7, Craigielea St., Dennistoun, Glasgow. British. Chemist. Bachelor of Science (Applied Chemistry), Glasgow University. Associate of the Institute of Chemistry. Presently employed as Chemist by Wm. Beattie, Ltd., Dennistoun Bakery, 116, Paton St., Glasgow. (*Signed by*) G. G. Henderson, T. S. Patterson, S. Horwood Tucker.

MORTON, RICHARD ALAN, 2, Lumley Street, Garston, Liverpool. British. University Lecturer (Inorganic Chemistry). B.Sc., Ph.D. (Liv.), A.I.C. Several papers, *J.C.S.*, *Jour. Phys. Chem.* (*Signed by*) E. C. C. Baly, Harold Rogerson, I. M. Heilbron.

MOULDS, FREDERICK WILSON, Hill Crest, Villa Road, Nottingham. British. Chemist and Druggist. Member of the Pharmaceutical Society. Chemist

in charge of the Laboratories of Messrs. Newball & Mason, Ltd., Nottingham, and a director of the firm. Late student of the University College, Nottingham, where I studied Chemistry and Pharmacy, also Industrial Bacteriology. (*Signed by*) F. S. Kipping, J. B. Firth, F. C. Laxton, Wm. H. Sims.

MYLES, ANDREW JOSEPH, 12, Gardner Rd., Tue Brook, Liverpool. British. Works Manager and Chemist. 20 Years' experience in Tar Distillation and research work on Roads Compositions. Have written and read papers on treatment of and construction of modern road surfaces. Designed a viscometer for tar and bituminous compositions. (*Signed by*) George Tate, George S. Irvine, Thomas J. Roberts.

NASH, ALFRED WILLIAM, 18, Prospect Rd., Moseley, Birmingham. British. Professor of Oil Engineering and Refining. B.Sc. degree for original researches on the "Pyrogenesis of Hydrocarbons." "The Berginisation of Coal and Oil," author, *Journ. Inst. Pet. Technologists*, Vol. **10**, 43. "Fuel Oil Resources of the Future," joint author, *Journ. Inst. Pet. Tech.*, Vol. **10**, 47. "Somerset Oil-shales," joint author, *Journ. Inst. Pet. Tech.*, Vol. **10**, 47. 1907–22, engaged in Oil Refineries—eventually General Manager. 1922–present, Birmingham University, Senior Lecturer, afterwards Professor. (*Signed by*) G. T. Morgan, A. E. Dunstan, Harold Harris.

OAKLEY, HENRY BOWEN, Wellcome Tropical Research Laboratories, Khartoum, Sudan. British. Assistant Government Research Chemist. Diploma of Imperial College. M.Sc. London. A.R.C.S. London. In conjunction with Prof. J. C. Philip, *J.C.S.*, 1924, **123**, 1189. (*Signed by*) A. F. Joseph, James C. Philip, M. B. Donald.

PALMER, EDGAR KENT, Rose Bank, Victoria Rd., Hale, Altrincham. British. Post-graduate research. Oct. 1919–July 1923, Student at College of Technology, Manchester, in full-time degree course in the Chemical Technology of Textiles. July 1923, Grad. B.Sc.Tech. June 1924, Research under Prof. E. Knecht, Ph.D., and at present the same. (*Signed by*) Frank Lee Pyman, Edmund Knecht, John K. Wood.

POMERANTZ, DAVID, 15, Nottingham Place, Commercial Rd., E. 1. British. Student. Inter B.Sc. Two years at Royal College of Science for the 3 years necessary for the associateship (Chemistry). Am now doing the honours course at West Ham M. C. (*Signed by*) H. Bogdanor, George Dean, R. S. Glennie.

RAWLINGS, HARRY, 15, Station Road, Ramsey, Huntingdon. British. Science master (Chemistry). B.Sc. Lond., 2nd Hons. Chemistry, 1921. Assistant Analyst, Messrs. Boots Pure Drug Co., Ltd., 1915–17. Unpublished research on organic derivs. of tin, under Prof. Kipping at Univ. Coll., Nottingham, 1921 and early 1922. Chemistry student at Univ. Coll., Nottingham, 1917 and 1919–22. Am at present working for M.Sc. (Lond.) [May 1925], and desire access to the Library of the Society. (*Signed by*) F. S. Kipping, E. B. R. Prideaux, J. B. Firth.

REED, JOHN BRENT, 49, St. Mildred's Rd., London, S.E. 12. British. Assistant Research Chemist in the Research Laboratories of the South Metropolitan Gas Coy. Bachelor of Science, London. Associate of the Institute of Chemistry of Gt. Britain and Ireland. Student at Birkbeck College for the degree of Doctor of Philosophy. (*Signed by*) George Senter, S. Sugden, Walter T. J. Morgan, S. Medsforth.

RHODES, WILLIAM GEORGE, Park View, 318, Granville Rd. Park, Sheffield. English. Senior Science Master, Firth Park Secondary School, Sheffield. (*Signed by*) C. K. Ingold, John Evans, A. S. Russell.

ROBERTSON, GEORGE JAMES, M.A., B.Sc., Ph.D., The Manse, Strathkinness,

St. Andrews, Fife. British. Assistant in Chemistry and Carnegie Teaching Fellow in the University of St. Andrews. A thesis entitled "Investigations on Cellulose." Conjoint paper read by Principal Irvine before the American Chemical Society. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

SALMON, ROBERT JOSEPH, C.M.S. Medical Training College, Hangchow, Chekiang, China. British. Lecturer in Chemistry, Medical Training College, Hangchow. M.Sc. Manchester. (*Signed by*) Arthur Lapworth, Frederick Challenger, John F. Wilkinson, Harold Mastin, D. H. Bangham, Fred Fairbrother.

SHEPHERD, JOHN ROBERT, Lady Hall Farm, Broughton-in-Furness, Lancs. British. Chemist. M.Sc. (London) in Chemistry. A.I.C. (*Signed by*) Robert H. Pickard, J. Kenyon, J. L. White, A. Houssa, Harold Hunter.

SINGH, TERRAIN, alias PREM CHANDRA SHARMA, Engineering College Hostel, Benares Hindu University. Indian. M.Sc. Demonstrator in the Department of Industrial Chemistry of B.H.U. M.Sc. of the Benares Hindu University with a thesis on "The Effect of the Size of the Soil-particles and Electrolytes on the Equilibrium of Moisture between the Seed and the Soil." (*Signed by*) Phuldeo Sahay Varma, S. S. Bhatnagar, N. R. Dhar.

SMITH, ALAN LAWRENCE, Bank House, 22, Dean St., Blackpool. British. *Trans. Chem. Soc.*, 1923, **123**, 1046–1055, "The Interaction of Hydrogen Sulphide, Thiocyanogen and Thiocyanic Acid on Unsaturated Compounds." M.Sc., Victoria University. (*Signed by*) Henry Stephens, Frederick Challenger, F. P. Burt, D. H. Bangham, Fred Fairbrother, John F. Wilkinson.

THORN, GEORGE, Grove House, Beechen Grove, Watford. British. Science Master, Boys' County School, Harrow. B.Sc. (Bristol). (*Signed by*) F. Francis, J. W. McBain, F. W. Rixon.

TOWNSEND, LEONARD WILLIAM ERNEST, 35, Harewood Rd., Collier's Wood, Merton, S.W. 19. British. Assistant Chemist at the South Metropolitan Gas Co., 709, Old Kent Rd., S.E. Student, five years' laboratory training. (*Signed by*) S. Medsforth, E. de Barry Barnett, P. C. L. Thorne.

WALKER, LESLIE JOHN, 45, Devereux Road, Wandsworth Common, S.W. 18. British. Student at the School of Pharmacy of the Pharmaceutical Society of Gt. Britain, 17, Bloomsbury Sq., W.C. 1. Pharmacist, have passed Qualifying Exam. of Pharmaceutical Society of Gt. Britain. Chemistry is included in this Exam., and it is my intention to continue studies in same. At present studying for Major Exam. of Pharmaceutical Society. (*Signed by*) C. E. Corfield, F. Browne, F. H. Lowe.

WALKER, THOMAS KENNEDY, 4, Swythamley Road, Cheadle Heath, Stockport. British. Research Chemist to the Institute of Brewing, Research Scheme Committee. Degrees: M.Sc., Ph.D., Victoria University of Manchester. Fellow of the Institute of Chemistry. Two years' research for the Admiralty, and for two years as Assistant Chemist to Sir R. Robertson, F.R.S., in the Research Department, Royal Arsenal, Woolwich. Three years' research in Organic Chemistry with Professor A. Lapworth, F.R.S., at Manchester University. For the past three years I have been assisting Professor F. L. Pyman, F.R.S., in investigations on the preservative principles of hops under the Institute of Brewing Research Scheme. Publications: "Preparation of Sodium Ethoxide from Caustic Soda" (*Journ. Soc. Chem. Ind.*, 1921, **40**, 172T); "Condensation of Aryldiazonium Salts with Monoalkylated Malonic Acids" (*J.*, 1923, **123**, 2775); "Condensation of Aryldiazonium Salts and of Alkyl Nitrites with Cyanoacetic Acid Derivatives" (*J.*, 1924, **125**, 1622); five other papers dealing with the antiseptics of hops, of which one was published jointly with Professor Pyman and Harold Roger-

son, Esq. (*Journ. Inst. Brew.*, 1922, **19**, 929; 1923, **20**, 373; 1924, **21**, 570, 712). (*Signed by*) Frank Lee Pyman, Fredk. M. Rowe, Jas. Grant.

WATERS, WILLIAM ALEXANDER, 35, Shirley Road, Cardiff. British. Research Student in Chemistry (Resident B.A. of Gonville and Caius College, Cambridge). Cambridge Natural Sciences Tripos, Part I, Class I, Cambridge Natural Sciences Tripos, Part II (Chemistry), Class I. Shuttleworth Research Studentship in Chemistry at Caius College, Cambridge. (*Signed by*) Hamilton McCombie, Harold A. Scarborough, Eric K. Rideal.

WATSON, JAMES BERNARD, 30, Mulgrave Road, West Hartlepool. British. Metallurgical Chemist. Four years in the laboratory of the Technical College, West Hartlepool. Seven years as chemist in the Chemical and Metallurgical laboratory of the Central Marine Engine Works, West Hartlepool. (*Signed by*) J. W. Patterson, Gilbert Palmer, D. Arthur Ruell.

WATTS, ERNEST SWANN, "Eaglesfield," Limefield Road, Kersal, Manchester. British. Chief Chemist, E. Griffiths Hughes, Ltd., Manchester. Qualifying Examination of the Pharmaceutical Society of Great Britain. (*Signed by*) S. Ernest Melling, Harry Brindle, Chas. Turner.

WHAMOND, ARCHIBALD STEELE, 22, Church St., Alloa, Clackmannanshire. British. Analytical Chemist. Studied Chemistry at Heriot Watt College, Edinburgh, Day and Evening Classes, 1911–1914. March 1914–Nov. 1923, Assistant Chemist, Messrs. Wm. McEwan & Co., Ltd., Edinburgh (Army Service, Sept. 1914–Jan. 1919). Nov. 1923–present time, Chief Chemist, Messrs. Geo. Younger & Son, Ltd., Alloa. (*Signed by*) John M. Guthrie, A. Scott Dodd, John Doull.

WOODCOCK, EDWIN JOHN, "Stonecot," Claremont Hill, Jersey, C.I. British. Assistant Official Analyst. For the past 28 years Assistant to F. W. Toms, Esq., F.I.C., Official Analyst of Jersey, namely, the first five years as private assistant and since then as senior assistant analyst to the States of Jersey. (*Signed by*) F. W. Toms, Bernard Dyer, Alex. K. Miller, F. G. P. Remfry, G. Neville Huntly, R. Le Rossignol.

WORTHINGTON, JOHN STANLEY, 27, Rowena St., Great Lever, Bolton. British. Works Chemist. Experience in manufacture of Heavy Chemicals at Messrs. John Smith Junr. & Co., Ltd., Great Lever Chemical Works, Bolton, since 1908. Student in Advanced Chemical Tech. at Manchester College of Technology. At present have control of large Sulphuric Acid Plant. (*Signed by*) Arthur Worthington, Frank Lee Pyman, T. Trevor Potts.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

BELL, JAMES MUNSIE, Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, N.C., U.S.A. Canadian. Professor of Chemistry. Head of Chemical Department, University of N. Carolina. Formerly in Bureau of Mines, Washington, D.C., U.S.A. Numerous original publications, chiefly in the *Journal of the American Chemical Society*. (*Signed by*) James W. McBain.

CAMERON, JOHN, Peking Union Medical College, Peking, Chihli, North China. British (Scotch). Pharmacist to the above-named institution. Member of the Pharmaceutical Society of Great Britain. Publications as per attached list to date (17 articles). Instructor in Pharmacy in British Army in France, 1917–18. Lecturer in Pharmacy and Materia Medica in Peking Union Medical College, 1920–25. (*Signed by*) A. E. Newland.

MCINTYRE, GORDON, Sarnia, Ontario, Canada. Canadian. Chemist and Petroleum Technologist. Graduate McGill University, B.Sc., Ch.E. Chief

Chemist, Imperial Oil Refineries, Limited. (*Signed by*) Alfred Stansfield, Harold J. Roast.

THOMAS, Professor KARL, M.D., Leipzig, Liebig str. 16. German. Professor ordinar. für physiologische Chemie an der Universität, Leipzig, seit 1921. Mitarbeiter von Hoppe-Seylers Zeitschrift für physiologische Chemie (herausgegeben v. Kossel) und der Biochemischen Zeitschrift (herausgegeben von Neuberg). Schüler von W. Wislicenus, H. Thierfelder und Max Rubner, Mitglied der Biochemical Society. (*Signed by*) George Barger, Robert Robinson.

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FRANZEN, HANS. Margarine. (Chem. Tech. in Einzeldarstellungen.) Leipzig 1925. pp. viii + 100. ill. *Gm.* 10. (*Recd.* 31/3/25.) From the Publisher: Herr Otto Spamer.

INDUSTRIAL CHEMIST and chemical manufacturer: a journal devoted to the progress of applied chemistry and chemical engineering. Vol. I, etc. London 1925 +. (*Reference.*)
From the Publishers: The St. Margaret's Technical Press.

KÖNIGLICH PREUSSISCHEN AKADEMIE DER WISSENSCHAFTEN ZU BERLIN. Monatsberichte 1876 & 1881. Berlin 1877 & 1882. (*Reference.*) From the Royal Society.

LUNGE, GEORGE. The manufacture of acids and alkalis. Completely revised and rewritten under the editorship of ALEXANDER CHARLES CUMMING. Vol. IV. The manufacture of sulphuric acid (contact process). By FRANK DOUGLAS MILES. London 1925. pp. xvi + 428. ill. 36*s.* net. (*Reference.*)
From the Publishers: Messrs. Gurney & Jackson.

ROYAL TECHNICAL COLLEGE, [GLASGOW]. Journal: being a record of some of the research work carried out in the College by the staff and senior students. No. 1. Glasgow 1924. pp. 138. ill. (*Reference.*) From the Director.

THORPE, JOCELYN FIELD, and WHITELEY, MARTHA ANNIE. A student's manual of organic chemical analysis, qualitative and quantitative. London 1925. pp. x + 250. ill. 9*s.* net. (*Recd.* 19/3/25.) From the Authors.

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BACK, E., and LANDÉ, A. Zeemaneffekt und Multiplettstruktur der Spektrallinien. (Struktur der Materie in Einzeldarstellungen.) Berlin 1925. pp. xii + 214. ill. *M*. 14·40. (*Recd.* 8/4/25.)

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COHEN, JULIUS BEREND. Practical organic chemistry. 3rd edition. London 1924. pp. xvi + 520. ill. 6*s*. 6*d*. net. (*Recd.* 25/3/25.)

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FITGER, PETER. Racemisierungserscheinungen bei optisch-aktiven Sulfidsäuren. Lund 1924. pp. 134. *M*. 4. (*Recd.* 31/3/25.)

FOURNEAU, ERNEST. Organic medicaments and their preparation. Authorised translation by WILLIAM ARTHUR SILVESTER. London 1925. pp. x + 262. ill. 15*s*. net. (*Recd.* 17/3/25.)

GOOCH, FRANK AUSTIN, and BROWNING, PHILIP EMBURY. Outlines of qualitative chemical analysis. 5th edition. New York 1924. pp. viii + 184. ill. 7*s*. 6*d*. net. (*Recd.* 25/3/25.)

HODKIN, FREDERICK WILLIAM, and COUSEN, ARNOLD. A textbook of glass technology. London 1925. pp. xxiv + 552. ill. 42*s*. net. (*Recd.* 17/3/25.)

HOFMAN, HEINRICH OSCAR. Metallurgy of copper. 2nd edition. Revised by CARLE R. HAYWARD. New York 1924. pp. xiv + 420. ill. 25*s*. net. (*Recd.* 25/3/25.)

LAMBERT, THOMAS. Bone products and manures: a treatise on the manufacture of fat, glue, animal charcoal, size, gelatin, and manures. 3rd edition, revised and enlarged by HERBERT BIRTWHISTLE STOCKS. London, 1925. pp. viii + 284. ill. 10*s*. 6*d*. net. (*Recd.* 25/3/25.)

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NUGEY, A. L. Oil refinery specifications. Easton, Pa. 1924. pp. x + 210. ill. 25*s*. net. (*Recd.* 17/3/25.)

PARTINGTON, JAMES RIDDICK. A text-book of inorganic chemistry for university students. 2nd edition. London 1925. pp. xii + 1068. ill. 25*s*. net. (*Recd.* 25/3/25.)

PULSIFER, H. B. Structural metallography: an illustrated text with laboratory directions for students. Easton, Pa. 1924. pp. viii + 210. ill. 17*s*. 6*d*. net. (*Recd.* 17/3/25.)

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RINNE, FRIEDRICH. Crystals and the fine-structure of matter. Translated by WALTER S. STILES. London 1924. pp. x + 196. ill. 10*s*. 6*d*. net. (*Recd.* 17/3/25.)

STILLMAN, JOHN MAXSON. The story of early chemistry. New York 1924. pp. xiv + 566. 18*s*. net. (*Recd.* 25/3/25.)

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III. *Pamphlets.*

BOARD OF AGRICULTURE AND FISHERIES. Statutory rules and orders, 1908, No. 964. Adulterations. Fertilisers and feeding stuffs. The fertilisers and feeding stuffs (methods of analysis) regulations, 1908. London 1908. pp. 9.

GRÜN, RICHARD. Die Einwirkung des Sulfidgehaltes auf die Eigenschaften von Hochofenschlacken und Hüttenzementen. (From *Stahl und Eisen*, 1925, 45.)

HAROLD, CHARLES HENRY HASLER, and WARD, ARTHUR ROKEBY. Report on experimental work carried out at the Army School of Hygiene to demonstrate that chlorine gas in association with ammonia gas is a more efficient sterilizer of water than chlorine gas used alone or chloros or bleaching powder. (From the *J. Roy. Army Med. Corps*, 1924, 41.)

JOSEPH, ALFRED FRANCIS, MARTIN, FREDERICK JOHN, and HANCOCK, J. S. The electrical method for determining soil alkali. (From the *Cairo Sci. J.*, 1924, 12.)

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OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, May 7th, 1925, at 8 p.m., Professor J. C. PHILIP, O.B.E., D.Sc., F.R.S., Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Edward Wightman Bell	June 20th, 1889.	Jan. 29th.
Arthur Boake	Dec. 2nd, 1875.	April 12th.
William Dugdale Harland	Feb. 7th, 1878.	April 23rd.
Sir David L. Salomons	May 4th, 1876.	April 19th.
George Young	Dec. 4th, 1890.	April 3rd.

The CHAIRMAN announced:

1. That the following address of congratulation had been sealed and would be presented to the Royal University of Pavia on the occasion of the Centenary Celebrations of that University which were being held from May 20th to 22nd, 1925:

To the Rector, Senate, Professors, and Alumni of the Royal University of Pavia from The Chemical Society.

The Chemical Society sends cordial greetings and felicitations to the illustrious University of Pavia on the completion of no less than eleven centuries of high service to mankind.

As representatives of a Science rooted in antiquity, we gratefully acknowledge the debt we owe to the members of your University who throughout the ages preserved ancient learning and extended the boundaries of knowledge, giving to us our heritage. We do not forget that the celebrated Lanfranc, one of your earliest and greatest teachers, carried the torch of learning to our country as Archbishop of Canterbury. Since her foundation the University of Pavia has given to the world many men distinguished for learning

and science—Alexander Volta, who pointed out new paths which now we follow, Camillus Golgi, the great neurologist, and many others whose genius we gratefully acknowledge.

We join with those who will be hastening from all parts of the world to lay before you their tribute of praise, and we hope that in the future renewed prosperity will be added to your illustrious past.

Signed on behalf of the Chemical Society.

ARTHUR W. CROSSLEY, *President.*
JOCELYN THORPE, *Treasurer.*
(L.S.) T. SLATER PRICE, C. S. GIBSON, } *Secretaries.*
F. G. DONNAN, *Foreign Secretary.*

Sealed this Seventh day of May, One Thousand Nine Hundred and Twenty Five.

2. That a copy of the works of the late Walthère Spring had been presented to the Library by the Belgian Chemical Society, and that this volume can be purchased from Monsieur J. Wauters, Secrétaire, Société Chimique de Belgique, 83, Rue Souveraine, Brussels, price 40 francs, post free.

The following were formally admitted Fellows of the Chemical Society: Alan D. Whitehead, Stuart R. Parsons, Leslie S. Theobald, J. F. J. Rule, and A. H. B. Bishop.

Certificates were read for the first time in favour of:

Maung Hla Baw, R-1, 64th Street, Danneedaw, Rangoon.
Joseph John Blackie, c/o Messrs. Duncan, Flockhart & Co., 104, Holyrood Road, Edinburgh.
Samuel Cyril Blacktin, M.Sc., 173, Ecclesall Road South, Sheffield.
Nirmal Boran Brohmachary, B.Sc., Ghugudanga-Post, 24, Porganas, Calcutta.
Gertrude Margaret Bullick, B.Sc., 43, Belsize Park, Hampstead, N.W. 3.
Ralph Edgar Cable, Queen's Gardens, Hong Kong.
Leslie Marshall Clark, B.A., Ph.D., A.I.C., 38, Park Road, Hampton Wick.
Clive Kear Colwell, B.A., Ormesty, Great North Road, N. 2.
Jan Coops, 25, Sireelinckplein, The Hague, Holland.
William George Corderoy, B.Sc., 35, Century Road, Walthamstow, E. 17.
Oswald Pilkington Cronshaw, 141, Blackburn Road, Great Harwood, Blackburn.
John Alexander Currie, B.A., B.Sc., 44, Phillimore Gardens, W. 8.
Thomas Dillon, University College, Galway.
Octave Charles Marie Dony, 30, Rue Émile Banning, Brussels.
William Edward Gibbs, D.Sc., 4, Stanley Villas, Runcorn.
Ernest Hartshorne, B.Sc.Tech., 12, Muriel Street, Broughton.
Arthur Harvey, 12, Chaldon Road, Fulham, S.W. 6.
Charles Richard Hennings, Ph.D., 19, St. Dunstan's Hill, E.C. 3.
Noel Waterman Vere Jones, Eastnook, Pakefield, Lowestoft.
Frank William Linch, M.Sc., F.I.C., 89, Hazelbottom Road, Cheetham, Manchester.

Charles Lipshaw, 48, Lower Broughton Road, Salford.
James Arthur Prescott, The University, Adelaide.
Malik Karam Singh, B.Sc., Rawalpindi City, India.
Norman Heath Smith, B.Sc., Anglo-Persian Oil Co., Ltd., Abadan.
John Thurgood, B.Sc., Roseleigh, Elmwood Avenue, Harrow.
Shojiro Uchida, 12, Shinryudo-Machi, Azabu-Ku, Tokio.
John Henry Walker, A.I.C., Gourepore Works, Naihati, E.B.Ry., Bengal.

Messrs. H. Burton and J. N. Sugden were elected Scrutators, and a ballot for the election of Fellows was held, the following subsequently being declared elected as Fellows:

James Munsie Bell.
Niels Janniksen Bjerrum.
Archibald Beresford Blunsden.
Geoffrey Alger Blyde.
Thomas Henry Bowles.
William Harrison Brindley, M.C., M.A., M.Sc.Tech., A.I.C.
James Lindsay Buchan, B.Sc.
Frank Henry Charles Bull, B.Sc., A.I.C.
John Alfred Valentine Butler, M.Sc.
Annie Lavinia Byford, B.Sc.
John Cameron.
James Herbert Clegg.
Horace Cecil Cockroft, B.Sc., A.I.C.
Francis Xavier Coyne.
James Craik, M.A., B.Sc., Ph.D.
Herbert Greetham Dane, M.Sc.
Harry Dean.
Margaret Stedman Leonora Dixon.
Robin George Westbury Farnell, A.R.C.S., A.I.C.
Irvine John Faulkner.
Thomas Flett, B.Sc., A.I.C.
Thomas James Elijah Gardner.
Richard Randolph Garran, B.Sc.
John Charles Giblin, B.Sc., A.I.C.
Helen Simpson Gilchrist, B.Sc., Ph.D.
Isabel Hodgson Hadfield, M.Sc.
James Francis Halpin, F.I.C.
Donald Hanson.
Thomas Haworth.
John Stanley Heaton, B.Sc., Ph.D.
John Cyril Hensman, M.A., A.I.C.
Joseph Hill.
Frederick Denison Maurice Hocking, M.Sc., A.I.C.
Jim Hoyle.
Horace William Hughes, B.Sc.
Joseph Taylor Jackson, B.Sc.
David Bret Jehu, M.Sc., A.I.C.
William Jobson.
Clifford Merton Jones, B.Sc.
Thomas William Jones, B.Sc.
John Keane, M.Sc., Ph.D.
Alfred Lucy.
Ernest Edward Mabbott, B.Sc.
David McDowall.
Gordon McIntyre, B.Sc., Ch.E.
Richard H. F. Manske, M.Sc.
Hugh Clouston Moir, B.Sc., A.I.C.
Richard Alan Morton, B.Sc., Ph.D., A.I.C.
Frederick Wilson Moulds.
Andrew Joseph Myles.
Alfred William Nash, B.Sc.
Henry Bowen Oakley, M.Sc., A.R.C.S.
Edgar Kent Palmer, B.Sc.Tech.
David Pomerantz.
Harry Rawlings, B.Sc.
John Brent Reed, B.Sc., A.I.C.
William George Rhodes.
George James Robertson, M.A., B.Sc., Ph.D.
Robert Joseph Salmon, M.Sc.
Prem Chandra Sharma, M.Sc.
John Robert Shepherd, M.Sc., A.I.C.
Alan Lawrence Smith, M.Sc.
Karl Thomas, M.D.
George Thorn, B.Sc.
Leonard William Ernest Townsend.
Leslie John Walker.
Thomas Kennedy Walker, M.Sc., Ph.D., F.I.C.
William Alexander Waters, B.A.
James Bernard Watson.
Ernest Swann Watts.
Archibald Steele Whamond.
Edwin John Woodcock.
John Stanley Worthington.

The following papers were read:

"The tautomerism of dyads. Part III. The effect of the triple linking on the reactivity of neighbouring atoms." By Mrs. E. H. INGOLD.

"The rotatory dispersive power of organic compounds. Part XVI. Halogen-derivatives of camphor." By J. O. CUTTER, H. BURGESS, and T. M. LOWRY.

"The isomerism of the oximes. Part XXII. The configuration of the aldoximes." By O. L. BRADY and G. BISHOP.

"The parachor and chemical constitution. Part I. Polar and non-polar valencies in unsaturated compounds." By S. SUGDEN, J. B. READ, and H. WILKINS.

"The tautomerism of dyads. Part IV. New evidence of the tautomeric mobility of oximes." By J. P. GRIFFITHS and C. K. INGOLD.

Ordinary Scientific Meeting, Thursday, May 21st, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following:

	Elected.	Died.
Albin Haller (Honorary Fellow)	Feb. 6th, 1908.	May 1st.
Samuel Henry Davies	Feb. 15th, 1894.	May 9th.
John Mylne Mullaly	May 4th, 1922.	May 4th.

It was also announced that the Celebration of the Centenary of Faraday's discovery of benzene, which is being arranged by the Royal Institution in association with the Chemical Society, the Society of Chemical Industry, and the Association of British Chemical Manufacturers, will take place at the Royal Institution on Tuesday, June 16th, 1925. In the morning, at eleven o'clock, there will be a reception by the Duke of Northumberland of English and foreign delegates, and several short addresses will be delivered commemorative of Faraday's chemical work. In the evening, a banquet will be held in the Goldsmiths' Hall, the price of the tickets being £2 2*s*. each, including wine. Application for tickets for the reception and for the banquet, which are limited in number, should be made to the Secretary, The Royal Institution, Albemarle Street, W. 1.

Mr. H. G. Dane was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

Marion Alice Battie, B.Sc., A.I.C., The Orchard, Ivy Lane, Woking.
William Ambler Berry, B.Sc., 19, Blakeney Road, Sheffield.

Thomas Anthony Canning, Crindau Gas Works, Newport, Mon.
John Carroll Culbert, 172, North Road, Belfast.
Alexander John Dey, F.R.S.E., Rothiemay, Corstorphine, Edinburgh.
Stanley James Featherston, 33, Belmont Road, Beckenham.
James Hindle, 4, Plane Street, Blackburn.
Thomas Moore, B.Sc., 8, Cyprus Avenue, Belfast.
Alexander John Morrison, Testing Branch, Public Works Department, Sydney, N.S.W.
Frank Richard Morrison, Brae Street, Waverley, Sydney, N.S.W.
Ernest Charles Padgham, 30, Churchill Road, N.W. 2.
John Monteath Robertson, B.Sc., A.I.C., The Chemistry Department, The University, Glasgow.
Ernest Henry Warren, B.A., 1, Chamber's Lane, Willesden Green, N.W. 10.
James Watt, F.R.S.E., Craiglockhart House, Slateford, Edinburgh.
William John Willis, Hazel Mount, Carnforth.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

Howard Ecker, 1510, Dana Avenue, Cincinnati, Ohio, U.S.A.
William Beesley, Binnyston Gardens, Bangalore, India.
Alexander Smith, P.O. Box 103, Nairobi, Kenya Colony.

The following papers were read:

"The rotatory dispersion of derivatives of tartaric acid. Part II. Acetyl derivatives." By P. C. Austin and J. R. Park.

"The stability of additive compounds between esters and acids." By J. Kendall and J. E. Booge.

"Additive compounds in the ternary system, acid–ester–water." By J. Kendall and C. V. King.

"A spectroscopic study of the combustion of phosphorus trioxide and of phosphine." By H. J. Emeléus.

"The nature of the alternating effect in carbon chains. Part III. A comparative study of the directive efficiencies of oxygen and nitrogen atoms in aromatic substitution." By E. L. Holmes and C. K. Ingold.

LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

BERICHTE, 1915 to 1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of Papers, or Abstracts thereof, received between April 3rd and May 21st, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The ionisation of aromatic nitro-compounds in liquid ammonia." By M. J. FIELD, W. E. GARNER, and C. C. SMITH.

"α-Acenaphthoquinoline." By J. STEWART.

"Alcohols of the hydroaromatic and terpene series. Part IV. α- and β-Fenchyl alcohols and some esters derived therefrom." By J. KENYON and H. E. M. PRISTON.

"Perkin's reaction." By T. HOPKINS.

"Action of zinc alkyl halides on nitric esters." By T. HOPKINS.

"Polynuclear heterocyclic aromatic types. Part II. Some anhydronium bases." By J. W. ARMIT and R. ROBINSON.

"β-Piperonylpropionitrile and some derived substances." By W. BAKER and R. ROBINSON.

"The melting points of benzene derivatives." By T. BEACALL.

"Nitrosation of phenols. Part II. 3-Bromo-, 2-bromo-, 3-iodo-, and 2-iodo-phenols, with evidence favouring the nitroso form for 4-nitroso phenol." By H. H. HODGSON and F. H. MOORE.

"The Kekulé formula for benzene and the existence of isomeric ortho disubstitution products." By H. H. HODGSON and J. H. WILSON.

"A new method of diagnosing potential optical activity. Part I. The optical activity of chlorobromomethanesulphonic acid." By J. READ and A. M. MCMATH.

"The carboxy-phenyl camphoramic acids." By M. SINGH and R. SINGH.

"A simplified method of micro-combustion: the micro-Dennstedt method." By C. FUNK and S. KON.

"Interfacial tension." By J. R. POUND.

"Low temperature oxidation at charcoal surfaces. Part I. The behaviour of charcoal in the absence of promoters." By E. K. RIDEAL and W. M. WRIGHT.

"Osmotic pressure by the solubility method in concentrated solutions." By M. P. APPLEBEY and P. G. DAVIES.

"Synthetical experiments in the naphthyridine groups." By J. M. GULLAND and R. ROBINSON.

"Chlorobenzothiazole dibromide." By R. F. HUNTER.

"Note on the action of sodium of chlorobenzothiazole." By R. F. HUNTER.

"Investigations into the analytical chemistry of tantalum, niobium, and their mineral associates. Part III. A new method for

the separation of tantalum from niobium. Part IV. The detection and determination of tantalum in niobium compounds." By A. R. POWELL and W. R. SCHOELLER.

"The conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. Part VII. The influence of the phenyl group on the formation of the *cyclo*propene ring." By W. HAERDI and J. F. THORPE.

"Rapid determination of copper and iron in mixtures of their salts." By A. S. RUSSELL.

"The bromination of 4'-amino-1-phenyl-5-methyl benzothiazole and of 1 : 1-bisbenzothiazole." By R. F. HUNTER.

"Amino benzothiazoles. Part I. 1-Phenylamino benzothiazole and its homologues." By R. F. HUNTER.

"The directing influence of the methane sulphonyl group." By R. F. TWIST and S. SMILES.

"The dissociation constants of selenious acid." By J. S. WILLCOX and E. B. R. PRIDEAUX.

"The velocity of benzylation of certain amines. Part II." By D. H. PEACOCK.

"Measurements of energy absorption of certain photo-chemical reactions with iodine." By B. K. MUKERJI and N. DHAR.

"The action of hydrogen peroxide on limonene." By J. SWORD.

"Synthetical experiments in the *iso*quinoline group. Part I." By R. D. HAWORTH and W. H. PERKIN.

"Synthetical experiments in the *iso*quinoline group. Part II." By R. D. HAWORTH, W. H. PERKIN, and J. RANKIN.

"Synthetical experiments in the *iso*quinoline group. Part III." By R. D. HAWORTH and W. H. PERKIN.

"Synthetical experiments in the *iso*quinoline group. Part IV." By R. D. HAWORTH and W. H. PERKIN.

"Synthesis of ψ-protoberberine and ψ-protopapaverine." By J. S. BUCK, W. H. PERKIN, and T. S. STEVENS.

"Note on a laboratory method of preparing *p*-benzoquinone." By R. CRAVEN and W. A. T. DUNCAN.

"Hydroxybenzils." By J. T. MARSH and H. STEPHEN.

"Researches on sulphuryl chloride. Part III. Influence of catalysts on the chlorination of toluene." By O. SILBERRAD, C. A. SILBERRAD, and B. PARKE.

"The adsorption of water from the gas phase on plane surfaces of glass and platinum." By I. R. MCHAFFIE and S. LENHER.

"The action of phosphorus pentachloride on 2-*iso*nitroso-1-hydrindones." By R. D. HAWORTH and H. S. PINK.

"Oxidation products of oleic acid. Part I. Conversion of oleic acid into dihydroxystearic acid and the determination of the

higher saturated acids in mixed acids from natural sources." By A. LAPWORTH and E. N. MOTTRAM.

"The spatial structure of *cyclo*paraffins. Part I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene." By W. A. WIGHTMAN.

"The absorption spectra of the vapours of anthracene and anthraquinone, phenanthrene, and phenanthraquinone, and other quinones." By J. E. PURVIS.

"Investigations on the dependence of rotatory power on chemical constitution. Part XXVII. Some esters of *p*-toluene-sulphonic and -sulphinic acids." By H. PHILLIPS.

"Oxidations in turpentine and olive oil." By E. WALKER.

"Colour and molecular geometry. Part IV. Explanation of the colours of the cyanine dyes." By J. MOIR.

"The surface tensions of aqueous phenol solutions. Part II. Activity and surface tension." By A. K. GOARD and E. K. RIDEAL.

"Triad groups in complexes of octahedral symmetry." By J. D. M. Smith.

"*Iso*quinoline derivatives. Part IX. Preparation and reduction of *iso*quinoline and its derivatives." By R. FORSYTH, C. I. KELLY, and F. L. PYMAN.

"The nitration of *m*-meconine." By J. N. RÂY and R. ROBINSON.

"Chenopodium oil. Part II. The hydrocarbon fraction." By T. A. HENRY and H. PAGET.

"The amino-γ-pyridones." By W. H. CROWE.

"Studies of the glucosides. Part III. The synthesis of thioindican." By J. CRAIK and A. K. MACBETH.

"The reduction of the bromoanthraquinones." By E. DE B. BARNETT and J. W. COOK.

"The chlorination of acetanilide and the chloroamine-chloroanilide transformation." By F. G. SOPER.

"The thermal decomposition of ozone." By R. O. GRIFFITH and A. MCKEOWN.

"Studies of electrolytic polarisation. Part III. The diffusion layer." By S. GLASSTONE.

"Theories of polar and non-polar free affinities. A practical and theoretical reply to some recent criticisms and comparisons." By G. N. BURKHARDT and A. LAPWORTH.

"The reaction between sodium hypobromite and urea." By M. B. DONALD.

"Echitamine." By J. A. GOODSON and T. A. HENRY.

"The preparation of phthalamic acids and their conversion into anthrenilic acids." By E. CHAPMAN and H. STEPHEN.

"An *X*-ray examination of maleic and fumaric acid." By K. YARDLEY.

"The estimation of arsenic in organic compounds." By G. NEWBERY.

"The bromination of acyl derivatives of phenylhydrazine: the preparation of 2 : 4-dibromophenylhydrazine." By J. E. HUMPHRIES and R. EVANS.

"The system chromium trioxide–boric acid–water." By L. F. GILBERT.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, JUNE 18TH, 1925.

BATTIE, MARION ALICE, The Orchard, Ivy Lane, Woking, Surrey. British. Post-graduate student. B.Sc. Honours (Chemistry), Class II. Associate of the Institute of Chemistry. (*Signed by*) T. S. Moore, Mary Boyle, S. Smiles.

BAW, MAUNG HLA, R-1, 64th Street, Danneedaw, Rangoon. Burmese. Analytical Chemist, Messrs. E. M. D'Souza & Co., Rangoon, and Science Master, St. John's College, Rangoon. Passed the Intermediate Examination in Science of the Calcutta University in 1916, taking Chemistry, Physics, and Mathematics. Process Chemist (1916 to 1921) at the Seikkyi Refinery of Messrs. The Indo Burma Petroleum Co., Ltd.; and Process Chemist (1922) in the acid works of The Burma Chemical Industries, Ltd. Process Chemist (1923) with The Rangoon Pharmaceutical and Chemical Works, Rangoon. Since 1924 chemist in charge of the analytical laboratory of Messrs. E. M. D'Souza & Co., Rangoon, and Science Master, St. John's College, Rangoon. (*Signed by*) Maung Tun Tin, Maung Ba, Maung Ba San.

BERRY, WILLIAM AMBLER, 19, Blakeney Rd., Sheffield. British. Research Student at University of Sheffield. B.Sc., Hons. Chem., 1924. Joint author with Dr. G. M. Bennett of the Note, *J.C.S.*, 1925, **127**, 910. (*Signed by*) W. P. Wynne, T. M. Lowry, G. M. Bennett, F. G. Tryhorn.

BLACKIE, JOSEPH JOHN, c/o Duncan, Flockhart & Co., 104, Holyrood Road, Edinburgh. British. Pharmaceutical Chemist. Minor and Major Examination, Pharmaceutical Society of Great Britain. Laboratory Manager of Messrs. Duncan, Flockhart & Co., Manufacturing Chemists, Edinburgh. Examiner in Chemistry of the Pharmaceutical Society of Great Britain. (*Signed by*) George Barger, William Duncan, Eric Knott.

BLACKTIN, SAMUEL CYRIL, 173, Ecclesall Road South, Sheffield. British. Research Assistant. (Junior Assistant, Safety in Mines Research Laboratories, Badger Lane, Sheffield.) M.Sc. (Sheffield). (*Signed by*) W. P. Wynne, F. G. Tryhorn, J. Kenner.

BLIGH, NEVILLE MELTON, 67, Castle Road, Bedford. British. Science Master. A.R.C.S. (Chemistry), London, 1921. A.I.C., 1923. Formerly Senior Science Master, Wimborne Grammar School, Dorset. At present (Temporary) Senior Science Master, Stevenage Grammar School, Herts. (*Signed by*) H. B. Baker, James C. Philip, M. A. Whiteley.

BORLAND, HUGH ALEXANDER MILLAR, 14, Cotham Road, Bristol. British.

Teacher of Chemistry. A.R.C.S. (Lond.). M.Sc. (Bristol). Lecturer on Chemistry 1896 to present date (Secondary and Technical). Lecturer on Applied Chem., University of Bristol, 1910–19. (*Signed by*) Arthur Marsden, F. Francis, J. W. McBain, F. W. Rixon.

BROHMACHARY, NIRMAL BORAN, Ghugudanga-Post 24 Porganas, Calcutta, India. Hindu (Indian). Chemist to Messrs. B. K. Paul's Chemical and Pharmaceutical Works, Dum Dum, Calcutta. Passed the B.Sc. examination of the Calcutta University in 1920. Worked as an analytical and manufacturing chemist. Assistant of Messrs. Smith, Stanistreet & Co. for 2 years, and at present working as the Chemist for Messrs. B. K. Paul & Co. (for last three years). (*Signed by*) Dhirendra Nath Mukerji, Sudhindranarayan Ray, R. L. Jenks.

BULLICK, GERTRUDE MARGARET, 43, Belsize Park, Hampstead, N.W. 3. British. Hons. Student in Chemistry, Bedford College, Univ. of London. Graduate of Lond. Univ. B.Sc., June, 1924. (*Signed by*) Holland Crompton, J. F. Spencer, M. S. Crewdson, J. Stewart.

CABLE, RALPH EDGAR, Queen's Gardens, Hong Kong. English. Apothecary, Medical Department, Hong Kong. Lecturer (part time), University of Hong Kong, Med. Faculty, Practical Pharmacy. (*Signed by*) R. W. E. Stickings, A. J. Ewins, G. Newbery, P. Blenkinsop.

CANNING, THOMAS ANTHONY, Crindau Gas Works, Newport, Mon. English. Gas and Chemical Engineer, now General Assistant Technical Engineer to the Newport (Mon.) Gas Company. Certificates in Chemistry granted by Institution of Gas Engineers. Engaged 7 years in Gas Manufacture and allied work and the chemistry of same. I desire to become a Fellow of the Chemical Society in order to keep in touch with current chemical literature. (*Signed by*) Geo. R. Thompson, H. E. Cox, J. H. Canning.

CLARK, LESLIE MARSHALL, 38, Park Rd., Hampton Wick, Kingston-on-Thames. English. Chemist, National Physical Laboratory, Teddington. Late Scholar and Research Scholar, Sidney Sussex College, Cambridge. Late Assistant Demonstrator, Cambridge University Chemical Laboratory. B.A., Cantab. Ph.D., London. Associate of Institute of Chemistry. Joint author of papers in *J.C.S.*, 1923, **123**, 2353, and 2362. (*Signed by*) M. Johnson, Guy Barr, Percy G. Ward.

COLWELL, CLIVE KEAR, Ormesty, Great North Road, N. 2. English. Analytical and Consulting Chemist. B.A., Cantab. Paper in conjunction with A. J. Berry, M.A., in Chemical News. (*Signed by*) A. H. M. Muter, Cyril Dickinson, J. Kear Colwell.

COOPS, JAN, den Haag, 25 Sireelinckplein. Dutchman. Dr. ir. Delft. Assistant, Commercial University, Rotterdam. Author of some papers in *Rec. trav. chim.*, 1920, 1921, 1922, 1923, 1924, 1925, *Chem. Weekblad*, and *Kon. Akad. van Weten. Amsterdam*, etc. (*Signed by*) H. J. Backer, Ernest Cohen, A. Smits.

CORDEROY, WILLIAM GEORGE, 35, Century Rd., Walthamstow, E. 17. British. Student for Teaching Profession (entering profession next Sept.). 1st Honours (Chem.), B.Sc. (Lond.). [Studied at East London College, 1921–24.] (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones, Elwyn Roberts.

CRONSHAW, OSWALD PILKINGTON, 141, Blackburn Road, Great Harwood, near Blackburn. British. Chemist and Assistant Gas Engineer, Accrington District Gas and Water Board. For past 3 years Chief Chemist to the Accrington District Gas and Water Board, having full chemical control of all gas manufacturing operations, the manufacture of sulphate of ammonia,

etc. Hold 1st Class Certificates Gas Manufacture (City and Guilds). Distinction in Inorganic Chemistry (Lanc. and Cheshire Inst.). 1st Class Certificate Inorganic and Organic Chemistry at Blackburn College of Technology. Associate Member of Institution of Gas Engineers. (*Signed by*) James Booth, John S. Morrison, Robert C. McDowall.

CULBERT, JOHN CARROLL, 172, North Road, Belfast. British. Pharmacist. Pharmaceutical Chemist, Member of Pharm. Society of Ireland, ex-Member Council of Pharm. Society of Ireland. (*Signed by*) George Scott Robertson, W. H. Gibson, Henry Wren.

CURRIE, JOHN ALEXANDER, 44, Phillimore Gardens, London, W. 8. British. Student. Honours B.A., Chemistry, and B.Sc., Oxford. Now researching under Professor Donnan at University College, London. (*Signed by*) F. G. Donnan, W. E. Garner, C. W. Bonniksen.

DEY, ALEXANDER JOHN, Rothiemay, Corstorphine, Edinburgh. British. Manufacturing Chemist. Managing Director, T. and H. Smith, Ltd., Manufacturing Chemists. F.R.S.E. (*Signed by*) James Walker, Alex. C. Cumming, Alexander Lauder.

DILLON, THOMAS, University College, Galway. Irish. Professor of Chemistry, University College, Galway. Papers on Waxes, *Proc. R.D.S.*, 1909, vol. 12, No. 20; vol. 15, No. 10; *Proc. R.I.A.*, vol. 29, sec. B, No. 8. On separation of Isotopes of Lead, *Proc. R.D.S.*, 1922, vol. 17, p. 53. (*Signed by*) A. G. G. Leonard, Sydney Young, Emil A. Werner, A. O'Farrelly.

DONY, OCTAVE CHARLES MARIE, Bruxelles, 30 Rue Emile Banning. Belge. Professeur à l'Université de Bruxelles (Faculté de Science appliquées). Membre de l'Académie royale de Belgique. (*Signed by*) C. S. Gibson, Eric K. Rideal, T. M. Lowry, W. J. Pope, Henry E. Armstrong.

FEATHERSTON, STANLEY JAMES, 33, Belmont Rd., Beckenham, Kent. British. Analytical Chemist in Laboratory of Manufacturing Chemists, namely, Messrs. Hopkins & Williams, 16–17, Cross St., E.C. Honours Student in Chem. at Birkbeck Coll., University of London. 5 Years analytical work with manufacturing chemists. (*Signed by*) George Senter, F. Barrow, Samuel Sugden.

GASKILL, MALCOLM SINCLAIR, 3, Buckingham Rd., Hilton Park, Prestwich, Manchester. British. Chemical Engineer, West's Gas Improvement Co., Ltd., Manchester. Associate of the Manchester College of Technology. Chemist and Assistant Manager, Messrs. Hardman & Holden, Ltd., Chemical Manufacturers, Clayton. Present position, as above. Desirous of keeping in touch with modern developments of pure and applied chemistry. (*Signed by*) Harold G. Colman, William Buckley, Joseph Poulson.

GIBBS, WILLIAM EDWARD, 4, Stanley Villas, Runcorn. British. Chief Chemist to the Salt Union, Ltd. D.Sc. (Liverpool). Author of books: "Clouds and Smokes: The Properties of Disperse Systems in Gases," "The Dust Hazard in Industry." *Journ. Inst. Metals*, XV (1916), 1, pp. 41–191; *J.S.C.I.*, XLI, pp. 189–196; *Faraday Soc.*, XI, 1915, pp. 295–297, etc. (*Signed by*) W. C. McC. Lewis, I. M. Heilbron, E. C. C. Baly.

HAMER, NORMAN, "Ash Mount," Holcombe, nr. Manchester. British. Research and Analytical Chemist in Calico Printing, Dyeing, and Bleaching Works. As a student I have gained the Associateship of the Manchester College of Technology (Assoc. M.C.T.), whilst my duties as chemist cover a fairly wide field of analytical work, together with the investigation of the many and varied problems which are continually arising in the works. (*Signed by*) Arthur M. Morley, John K. Wood, Frank Lee Pyman.

HARTSHORNE, ERNEST, 12, Muriel St., Broughton, Manchester. British.

Chemist in the Laboratory of Dr. A. K. Miller, F.C.S. Degree of Bachelor of Technical Science in General Chemical Technology, Victoria University, Manchester. (*Signed by*) Alex. K. Miller, Frank Lee Pyman, John K. Wood.

HARVEY, ARTHUR, 12, Chaldon Road, Fulham, S.W. 6. British. Chemist. Formerly Agricultural Analyst, South Eastern Agricultural College (Univ. Lond.), Wye, Kent. Formerly lecturer on Applied Chemistry, Leathersellers College, London. Author of "Practical Leather Chemistry" and "Tanning Material," published by Crosby Lockwood & Son. Also several papers on leather chemistry in *J. Soc. L. Trades Chem.* Editor of Abstracts, *J. Soc. L. Trades Chem.* Member, British Association of Chemists, American Chemical Society, Society of Leather Trades Chemists. (*Signed by*) M. C. Lamb, A. B. Bradley, R. W. West.

HENNINGS, CHARLES RICHARD, 19, St. Dunstan's Hill, London, E.C. 3. German. Consulting Chemist. Qualified Pharmaceutical Chemist. Graduated in Chemistry. Ph.D., Freiburg. Papers as given before when first being admitted. (*Signed by*) Otto Oberländer, George P. Forrester, A. W. Edwards.

HINDLE, JAMES, 4, Plane St., Blackburn, Lancs. British. Student. Have been full-time day student in the Chemistry Dept. Municipal Technical College, Blackburn, for four years and am now preparing for Hons. Chemistry, B.Sc. (Lond.) there. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

JONES, NOEL WATERMAN VERE, Eastnook, Pakefield, Lowestoft. British. Student. Have been studying Chemistry for five years and wish to keep abreast of modern advances. (*Signed by*) E. de Barry Barnett, James W. Cook, Marcus A. Matthews.

LINCH, FRANK WILLIAM, 89, Hazelbottom Rd., Cheetham, Manchester. British. Research Chemist, British Dyestuffs Corporation. M.Sc., Lond. 1st Hons. Chemistry at B.Sc. F.I.C. Asst. Chief Chemist, H.M. Factory, Queensferry, 1915–1917. Chief Chemist, H.M. Factory, Avonmouth, 1917–1919. 1919 to date, Research Chemist, British Dyestuffs Corp., Blackley, Manchester. Action of sodium hypobromite on carbamide derivs. Part I. 3-Amino-coumarin. Both papers in Trans. 1912. (*Signed by*) G. R. Clemo, Colin H. Lumsden, Anthony J. Hailwood.

LIPSHAW, CHARLES, 48, Lr. Broughton Rd., Salford. British. Chemist to Messrs. Halliday & Co., Ltd., Bankfield Mills, Stockport. 4 years Laboratory Chemist, and Assistant Works Chemist, at Lowerhouse Printworks, Burnley. Student at the Royal Technical College, Salford. Diploma of the College, City and Guilds of London Institute, Final Certificates in Dyeing and Textile Printing. (*Signed by*) S. N. Brown, V. Edge, E. Clark, B. Prentice.

MOORE, THOMAS, 8, Cyprus Avenue, Belfast. British. Student. Graduate of London (with Honours) and of the Queen's University, Belfast. Fifth year research student in Photochemistry. (*Signed by*) Wm. H. McVicker, Joseph K. Marsh, A. W. Stewart, H. Graham.

NIXON, IVOR GRAY, 75, The Vale, Golder's Green, N.W. 11. English. Student. Have studied chemistry for over 6 years and desire to keep abreast of modern developments. (*Signed by*) E. de Barry Barnett, P. C. L. Thorne, James W. Cook.

OCCLESHAW, VINCENT JOSEPH, 22, Bryn Street, Ashton-in-Makerfield, nr. Wigan. British. Lecturer and Demonstrator in Inorganic Chemistry. M.Sc. (Liv.). A.I.C. (*Signed by*) E. C. C. Baly, J. T. Nance, A. O. Jones.

PADGHAM, ERNEST CHARLES, 30, Churchill Road, N.W. 2. British. Research Assistant at the British Museum Laboratory. Trained in Analytical

Chemistry under the late Dr. Ludwig Mond, F.R.S., and the late Dr. B. Mohr, 1891–1896. Assistant at the Davy Faraday Research Laboratory of the Royal Institution, 1896–1918. Research Assistant at The British Museum Laboratory since 1920. (*Signed by*) Alexander Scott, H. J. Plenderleith, John W. Heath.

PRESCOTT, JAMES ARTHUR, The University, Adelaide, South Australia. British (England). Professor of Agricultural Chemistry at the Waite Agricultural Research Institute of the University of Adelaide. Papers on Soil Chemistry in the "Journal of Agricultural Science," VI, 111; VIII, 65, 111, 136; IX, 216; X, 177; XIII, 333; also Bulletins of the Sultanic Agricultural Society, Egypt. Research Scholar, Rothamsted Experimental Station, 1912–1916. Chief Chemist, Sultanic Agric. Soc., Egypt, 1916–1924. Proceedings, vol. 30, No. 123, 1914. (*Signed by*) Edward H. Rennie, E. J. Russell, H. B. Dixon, Arthur Lapworth, Robert Robinson, H. J. Page.

ROBERTSON, JOHN MONTEATH, Nether Fordun, Auchterarder, Perthshire. Scottish. Research Assistant. B.Sc. (Hons. Chem.), Glasgow, 1923. A.I.C., 1924. Strang-Steel Research Scholar, 1923–24. Carnegie Research Scholar, 1924–25. (*Signed by*) S. Horwood Tucker, T. S. Patterson, G. G. Henderson, R. Wright, David T. Gibson.

RUBENSTEIN, LEON, Jesus College, Oxford (Rookwood, 87, Eaton Grove, Swansea). British. Research Student for Doctorate of Philosophy (Oxford University). First Class Honours, Degree of Bachelor of Science (Welsh Univ.). Bachelor of Science (Oxford Univ.). "Substitution in Vicinal Trisubstituted Benzene Derivatives" (November 1923). (*Signed by*) W. H. Perkin, S. G. P. Plant, J. F. S. Stone, R. H. Griffith, R. D. Haworth.

SINGH, MALIK KARAM, Rawalpindi City. Indian (British subject). Paper Expert. I am a B.Sc. (Physics and Chemistry). Was granted a "State Technical Scholarship" by the Govt. of India for the study of the Paper-making industry in Gt. Britain and other Western countries. Before going to England I worked for about twenty months in the Bengal Paper Mills, Raneegunj (near Calcutta), during 1918–20. Joined College of Technology, Manchester, in 1920. During 1920–21 I completed in one year, a two years' course in paper making, and in the final examination I got a 1st class both in the theoretical and practical parts of the subject. I also studied the following subjects: Organic Chemistry, Physical Chemistry, Chemistry of Dyeing, Chemistry of the Colouring Matters, Economics, Chemical Engineering, Heat Engines, and Construction of Works. In 1921–22 (about 15 months) I received practical training in the following three paper mills, in Aberdeen, Scotland, making different classes of paper: (1) The Donside Paper Mills; (2) The Alex Pirie Paper Mills at Stoneywood, and (3) The Mugiemoss Paper Mills at Bucksburn. During 1922–24 I conducted a special research on about a score of Indian raw materials, with a view to ascertain their suitability for making paper. I have paid short visits lasting from one to ten days to about a score of other paper mills and paper mill machinery manufacture workshops. I have seen almost all the paper mills in India. (*Signed by*) John K. Wood, Frank Lee Pyman, F. M. Rowe.

SMITH, NORMAN HEATH, Hillcroft, Spencer Avenue, Leek, Staffs. British. Process Chemist, at present with Messrs. Anglo-Persian Oil Co., Ltd., Abadan, Persia. B.Sc. (Tech.). Post grad. research on vegetable oils; 2½ years with Messrs. The British Aluminium Co., Ltd., as Asst. Chemist, and over 2 years with Messrs. Anglo-Persian Oil Co., Ltd. (*Signed by*) Colin E. Spearing, S. W. Hayter, H. Harper.

STREATHER, ALEC THOMAS, 3, Wellington Road, Watford. British. Works Chemist. B.Sc. (Honours Chemistry), Birmingham, 1922. Associate Institute of Chemistry. (*Signed by*) G. T. Morgan, S. R. Carter, C. E. Wood, F. W. Pinkard.

THURGOOD, JOHN, "Roseleigh," Elmwood Ave., Harrow, Middx. British. Analytical and Research Chemist. Engaged for 4 years in laboratory of Dunlop Rubber Co., Birmingham. Graduated B.Sc. at Birmingham University in 1922. At present engaged as Assistant Chemist to British Oxygen Co., Ltd., N. Wembley. (*Signed by*) G. T. Morgan, C. E. Wood, E. Holmes.

TREW, VIOLET CORONA GWYNNE, 18, Adam Street, Portman Square, W. 1. British. Student at Bedford College (London University). Reading for an Honours Degree in Chemistry. (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie.

UCHIDA, SHOJIRO, 12, Shinryudo-Machi, Azabu-Ku, Tokio, Japan. Japanese. Research Chemist of the Fuel Research Board of Japan. Undergraduate of Department of Chemistry, College of Technology, University of Tokio, Japan. (*Signed by*) W. A. Batley, V. H. Legg, M. J. Burgess, F. V. Tideswell.

WALKER, JOHN HENRY, A.R.T.C., A.I.C., Gourepore Works, Naihati, E.B. Ry., Bengal, India. Scotch. Chemist and Oil-mill Manager. Student Royal Technical College, Glasgow. Student with late Dr. J. Lewkowitsch. Sundry papers in *Analyst* and in *J.S.C.I.* Chemist and latterly mill-manager, Gourepore Co., Ltd., Linseed Oil. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson.

WARREN, ERNEST HENRY, 1, Chamber's Lane, Willesden Green, N.W. 10. English. Research Student. B.A., Cantab. (*Signed by*) Robert Robertson, Geo. Stubbs, P. J. Sageman.

WATT, JAMES, Craiglockhart House, Slateford, Edinburgh. British. Writer to the Signet. Chairman of Directors, T. and H. Smith, Ltd., Chemical Manufacturers. F.R.S.E. (*Signed by*) James Walker, Alex. C. Cumming, Alexander Lauder.

WILLIS, WILLIAM JOHN, Hazel Mount, Carnforth, Lancs. English. Chief Valuer to Michael Faraday and Partners, 77, Chancery Lane, W.C. 2. 3 years' Assistant Demonstrator, Inorganic Chemistry, Barrow Technical School. 3 years' Lecturer on Metallurgy and Iron Foundry Practice, Bradford Technical College. 1st Class Honours Inorganic Chemistry, Science and Art Department. 1st Class Honours and Bronze Medal, City and Guilds of London, Iron and Steel Manufacture. 1st Class and Silver Medal, City and Guilds of London, Salt Manufacture. 8 years Analytical Chemist, Barrow Hematite Steel Co., Ltd. 6 years Chief Chemist and Assistant Works Manager, Yorkshire Iron and Coal Co., Ltd. 5 years Chief Valuer to Michael Faraday and Partners, Surveyors and Valuers. (*Signed by*) T. A. Henry, A. E. Bond, Harry W. Dixon.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

BEESLEY, WILLIAM, Binnyston Gardens, Bangalore City, Mysore, India. British. Works' Chemist. Took course in Bleaching and Dyeing at the Manchester College of Technology. Technological Certificate and Silver Medallist in Dyeing, City and Guilds of London Institute. Six years Chemist Assistant with Messrs. Binny & Co., Ltd. Now Head Chemist, Bangalore Woollen Mills, India. (*Signed by*) E. Knecht.

ECKER, HOWARD, 1510 Dana Ave., Cincinnati, Ohio, U.S.A. American.

Research Director for The R. I. Johnston Paint Co., Cincinnati, Ohio. Graduate student from Ohio Mechanics Institute, Cin., Ohio. 1 year graduate work, Columbia College, N.Y. 6 years teaching at Ohio Mechanics Institute and for 3 years head of the department. Member of the American Chemical Society, Society of Chemical Industry, German Chemical Society. (*Signed by*) John H. Foulger.

SMITH, ALEXANDER, P.O. Box 103, Nairobi, Kenya Colony. Scot. Chemist and Managing Director, A. H. Wardle & Co., Ltd. Lecturer on chemistry for 2 years, School of Mines, South Africa. Pharmaceutical Society, minor certificate. Consulting Chemist to Kenya Marble Quarries. In charge Hygiene Laboratory (Dr. Kochs), Dar-es-Salaam, 12 months. (*Signed by*) G. T. R. Francis.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. British chemicals, their manufacturers and uses: being the official directory . . . containing a full list of members, with a classified list of British chemicals and a note of their industrial applications. London 1925. pp. 212. (*Reference.*) 10*s.* 6*d.* net.

From the Publishers: Messrs. Ernest Benn.

INDIAN CHEMICAL SOCIETY. Quarterly Journal. Vol. I, etc. Calcutta 1924 +. (Two copies.) From the Society.

INSTITUT INTERNATIONAL DE CHIMIE SOLVAY. Premier conseil de chimie, tenu à Bruxelles du 21 au 27 Avril 1922. Rapports et discussions . . . sur cinq questions d'actualité. Paris 1925. pp. xvi + 336. ill. (*Reference.*) 30 *fr.* net.

From the Publishers: MM. Gauthier-Villars & Cie.

NAMARI, ICHITARO. The electrolytic separation of magnesium from magnesia. Sakai 1924. pp. iv + 160. ill. (*Recd.* 15/4/25.)

From the Author.

PHILIP, JAMES CHARLES. Physical chemistry: its bearing on biology and medicine. 3rd edition. London 1925. pp. viii + 368. ill. 8*s.* 6*d.* net. (*Recd.* 7/5/25.) From the Author.

RUMBOLD, W. G. Bauxite and aluminium. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 110. ill. 6*s.* net. (*Recd.* 17/4/25.) From the Director.

SCIENTIFIC WORKER, The, and the B.A.C. Bulletin. Official organ of the National Union of Scientific Workers and the British Association of Chemists. New series. Vol. I, etc. London 1924 +. (*Reference.*)

From the Publishers: The National Union of Scientific Workers.

SPRING, WALTHÈRE. Œuvres complètes, publiées par la Société Chimique de Belgique. 2 vols. Bruxelles 1914–1923. pp. iv + 900, iv, 901 to 1860. ill. 40 *fr.* (*Recd.* 9/4/25.)

From the Société Chimique de Belgique.

STAUDINGER, HERMANN. Introduction to qualitative organic analysis. Authorised translation by WALTER THEODORE KARL BRAUNHOLTZ. London 1925. pp. xvi + 112. 6*s*. 6*d*. net. (*Recd.* 8/4/25.) From the Publishers: Messrs. Gurney & Jackson.

TABLES ANNUELLES DE CONSTANTES et données numériques de chimie, de physique et de technologie. Vol. V. 1917–1922. Part i. Paris 1925. pp. xlii + 804. (*Reference.*)
From the Comité International.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. III, Part ii. Vol. IV, Part i. Berlin 1925. pp. 289 to 544, 272. ill. *M*. 20. (*Recd.* 15/4/25.)
From the Publishers: Herren Urban & Schwarzenberg.

II. *By Purchase.*

ANDERSON, ROBERT J. The metallurgy of aluminium and aluminium alloys. New York 1925. pp. xxxii + 914. ill. 42*s*. net. (*Recd.* 27/4/25.)

BABBITT, HAROLD E. Sewerage and sewage treatment. 2nd edition. New York 1925. pp. xvi + 516. ill. 25*s*. net. (*Recd.* 13/5/25.)

BRAGG, SIR WILLIAM HENRY, and BRAGG, WILLIAM LAWRENCE. *X*-rays and crystal structure. 5th edition. London 1925. pp. xii + 324. ill. 21*s*. net. (*Recd.* 13/5/25.)

BURRELL, GEORGE A. The recovery of gasoline from natural gas, with a discussion of motor fuels. New York 1925. pp. 600. ill. 35*s*. net. (*Recd.* 13/5/25.)

BURTON, ELI FRANKLIN. The physical properties of colloidal solutions. 2nd edition. London 1921. pp. viii + 222. ill. 12*s*. 6*d*. net. (*Recd.* 21/4/25.)

COFFIGNIER, CHARLES. Colours and varnishes. Translated from the French by A. HARVEY. London 1925. pp. viii + 258. ill. 12*s*. 6*d*. net. (*Recd.* 13/5/25.)

COLLOID SYMPOSIUM MONOGRAPH. Papers presented at the second National Symposium on Colloid Chemistry, June 1924. Edited by HARRY N. HOLMES. New York 1925. pp. viii + 368. ill. 25*s*. net. (*Recd.* 21/4/25.)

GOUGH, HERBERT JOHN. The fatigue of metals. London 1924. pp. xx + 304. ill. 25*s*. net. (*Recd.* 13/5/25.)

HATSCHEK, EMIL. [Editor.] The foundations of colloid chemistry; a selection of early papers bearing on the subject. Edited on behalf of the Colloids Committee of the British Association. London 1925. pp. 174. 18*s*. net. (*Recd.* 13/5/25.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 4th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of Mr. Charles E. Soane, who was elected a Fellow on February 3rd, 1887, and who died on May 17th.

The PRESIDENT announced that the following address of congratulation had been sealed and will be presented on June 16th, 1925, to the Royal Institution on the occasion of the celebration of the Centenary of the discovery of benzene by Michael Faraday:

To the President, Officers and Members of the Royal Institution of Great Britain.

The Chemical Society welcomes the opportunity of associating itself with the Royal Institution in celebrating the centenary of the Discovery of Benzene by Michael Faraday, a discovery which was destined to have such far-reaching effects on the foundation and development of structural organic chemistry and to lead to the establishment of many new and important industries. We remember with pride that in 1868 the Chemical Society instituted a Triennial Lecture to commemorate the work of Faraday, for we recognise in him the pioneer of many of the principles underlying the chemical science of to-day.

We desire to join with the other Learned Societies and Academies of the world in offering our homage to the memory of this great and distinguished man.

Signed on behalf of the Chemical Society,

ARTHUR W. CROSSLEY, *President.*
JOCELYN THORPE, *Treasurer.*
T. SLATER PRICE, } *Secretaries.*
C. S. GIBSON, }
F. G. DONNAN, *Foreign Secretary.*

Sealed in Council this Fourth Day of June, One Thousand Nine Hundred and Twenty Five.

Mr. W. A. Wightman was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

William Bouch O'Brien Goudielock, 28, Fairfield Lane, Barrow-in-Furness.
Jnanendra Nath Ray, M.Sc., The University, Manchester.
Phyllis Mary Sanderson, 7, Cresswell Place, S.W. 10.
Eric Alfred Speight, B.Sc., A.R.C.S., 61, Arthur Road, Wimbledon Park, S.W. 19.
Gordon Mitchell Wright, M.A., B.Sc., University Chemical Laboratory, Cambridge.

The following papers were read:

"The spatial structure of *cyclo*paraffins. Part I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene." By W. A. WIGHTMAN.

"Chenopodium oil. Part II. The hydrocarbon fraction." By T. A. HENRY and H. PAGET.

"Echitamine." By J. A. GOODSON and T. A. HENRY.

Ordinary Scientific Meeting, Thursday, June 18th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT announced:

1. That, as Fellows would know, the Council has had before it for some time past the possibility of unifying chemical abstracts in pure and applied chemistry in the English language, and as stated in the Report of Council for 1923—1924, the Bureau of Chemical Abstracts was created to effect such unification. The Council, at its meeting that afternoon, had under consideration the following proposals of the Bureau, that

(1) The format adopted for the unified publications should be double column quarto.

(2) The type should be that now employed in the "A" Abstracts.

(3) The existing overlap, estimated to be at least 10%, should be eliminated,

as well as the further suggestion that, in the event of these proposals being adopted, one annual index covering both sections of the Abstracts should be supplied to all members of the two Societies concerned.

The Council has adopted the following resolution:

"That the Council concurs in the Bureau's proposals for the unification of the Abstracts in Pure and Applied Chemistry, and urges the Fellows, in the interests of co-operation and of

the consolidation of British Chemical Abstracts, to accept loyally such changes of format and arrangement as these proposals may involve."

It was further intimated that the proposals of the Bureau have also been accepted by the Council of the Society of Chemical Industry.

The President expressed the hope that Fellows would loyally support the efforts being made in the direction of unifying British chemical abstracts.

2. That the Faraday Society will hold a General Discussion on "Photochemical Reactions in Liquids and Gases" at Oxford on October 1st and 2nd next. The subject will be discussed under two main heads: (1) Einstein's Law of Photochemical Equivalence, (2) The Mechanism of Photochemical Reactions. Part I will be opened by Professor A. J. Allmand (King's College) and Part II by Professor M. Bodenstein (Berlin).

Fellows of the Chemical Society will be welcomed at this meeting, and it is hoped to accommodate all who attend the meeting at Exeter College and Lincoln College. Those desirous of attending are asked to communicate at once with the Secretary of the Faraday Society, 90, Great Russell Street, London, W.C. 1, from whom full particulars may be obtained.

3. That a communication has been received from the Committee of the van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1926 is about 1400 Dutch florins.

A Committee, consisting of Professor A. F. Holleman (President), Professor F. M. Jaeger, Professor A. Smits, and Mr. J. P. Wibaut (Secretary), has been appointed to award Grants. Applications should be sent before November 1st, 1925, by registered post to: "Het Bestuur der Koninklyke Akademie van Wetenschappen, bestemd voor de Commissie van het 'van't Hofffonds,' Trippenhuis, Kloveniersburgwal, Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

4. That Volume V of the Annual Tables of Constants and Numerical Data is now ready, and is obtainable from Monsieur Charles Marie (9, Rue de Bagneux, Paris VI) who will be glad to send particulars on application.

Messrs. J. B. Reed and P. W. B. Harrison were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of :

Joseph Raymond Dolphin, B.Sc., Chemical Department, The University, Birmingham.
Henry Wilfrid Keenan, 80, Upper Richmond Road, East Sheen, S.W. 14.
Bertram Grey Leatherbarrow, Hill Crest, Station Road, Brimington, Chesterfield.
Henry Nicholson, M.Sc., Aberlady, Osborne Road, Stockton-on-Tees.
Robert Saxon, B.Sc., Westfield Terrace, Baildon, Yorks.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

Bertram Cuthbert, c/o The British Australian Cotton Association, Ltd. Oil Mills, Brisbane.
Albert Louis Auguste Sigot, Institut de Chimie, 2, Rue Goethe, Strasbourg.

Mr. H. C. Sayer and Dr. H. Burgess were elected Scrutators, and a ballot for the election of Fellows was held, the following subsequently being declared elected as Fellows :

Marion Alice Battie, B.Sc., A.I.C.
Maung Hla Baw.
William Beesley.
William Ambler Berry, B.Sc.
Joseph John Blackie.
Samuel Cyril Blacktin, M.Sc.
Neville Melton Bligh, A.R.C.S., A.I.C.
Hugh Alexander Millar Borland, M.Sc., A.R.C.S.
Nirmal Boran Brohmachary, B.Sc.
Gertrude Margaret Bullick, B.Sc.
Ralph Edgar Cable.
Thomas Anthony Canning.
Leslie Marshall Clark, B.A., Ph.D., A.I.C.
Clive Kear Colwell, B.A.
Jan Coops.
William George Corderoy, B.Sc.
Oswald Pilkington Cronshaw.
John Carroll Culbert.
John Alexander Currie, B.A., B.Sc.
Alexander John Dey.
Thomas Dillon, M.A., D.Sc.
Octave Charles Marie Dony.
Howard Ecker.
Stanley James Featherston.
Malcolm Sinclair Gaskill.
William Edward Gibbs, D.Sc.
Norman Hamer, Assoc.M.C.T.
Ernest Hartshorne, B.Sc.Tech.
Arthur Harvey.
Charles Richard Hennings, Ph.D.
James Hindle.
Noel Waterman Vere Jones.
Frank William Linch, M.Sc., F.I.C.
Charles Lipshaw.
Thomas Moore, B.Sc.
Ivor Gray Nixon.
Vincent Joseph Occleshaw, M.Sc., A.I.C.
Ernest Charles Padgham.
James Arthur Prescott, M.Sc., A.I.C.
John Monteath Robertson, B.Sc., A.I.C.
Leon Rubenstein, B.Sc.
Malik Karam Singh, B.Sc.
Alexander Smith.
Norman Heath Smith, B.Sc.Tech.
Alec Thomas Streather, B.Sc., A.I.C.
John Thurgood, B.Sc.
Violet Corona Gwynne Trew.
Shojiro Uchida.
John Henry Walker, A.R.T.C., A.I.C.
Ernest Henry Warren, B.A.
James Watt.
William John Willis.

The following papers were read :

" Investigations on the dependence of rotatory power on chemical constitution. Part XXVII. Some esters of *p*-toluene-sulphonic and sulphinic acids." By H. PHILLIPS.

" The enhanced reactivity of newly formed molecules. Part I. The conversion of cyclols into ketones." By F. R. Goss and C. K. INGOLD.

" Constituents of *Myoporum lætum*, Forst (' The Ngaio '). Part I." By F. H. McDOWALL.

" A synthesis of datiscetin." By J. KALFF and R. ROBINSON.

" The relative directive powers of groups of the forms RO– and RR'N– in aromatic substitutions. Part IV. A discussion of the observations recorded in Parts I, II, and III." By J. ALLAN, A. E. OXFORD, R. ROBINSON, and J. C. SMITH.

" A new aspect of the photochemical union of hydrogen and chlorine, and a quantitative study of the induction period." By R. G. W. NORRISH.

The Council has made the following Grants from the Research Fund :

	£	*s.*	*d.*
Bromination products of caronic acid. R. G. Atkinson. ...	12	0	0
Mechanism of tautomeric change. J. W. Baker	15	0	0
Photographic investigation of explosion waves. C. Campbell ...	5	0	0
Chemistry of the aminotriazole derivatives (*contd.*). P. K. Dutt.	5	0	0
Chemistry of the acridine molecule (*contd.*). P. K. Dutt ...	5	0	0
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Acid chlorides of the type chlorothiol benzoyl chloride and their products. E. W. McClelland	5	0	0
Influence of various substituents on the reactivity of organic compounds. I. Cyanohydrin formation. R. H. F. Manske...	10	0	0
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Three-carbon tautomerism (*contd.*). E. A. Speight	15	0	0
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Influence of water vapour on reactions of the type: Solid $\rightleftharpoons$ solid + gas. B. Topley	5	0	0
Physical properties of straight-chain alkyl benzenes and their derivatives (*contd.*). E. E. Turner	5	0	0
Investigation of sulphur trioxide (*contd.*). I. Vogel	5	0	0
Synthetical experiments in the *iso*quinoline series. R. Campbell	10	0	0
Separation of platinum from iridium and rhodium with special reference to complex nitrites. D. F. Withers	10	0	0
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LIST OF FELLOWS, 1925.

The List of Fellows for 1925 is now in active preparation and will be supplied to those Fellows who make application to the Assistant Secretary by the 31st July, 1925. In order that the new List may be as complete as possible, Fellows are invited to notify any change of address, or other alteration, before that date.

BERICHTE, 1915–1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of papers, or Abstracts thereof, received between May 22nd and June 18th, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting or which have appeared in the Journal.)

"A low voltage standard cell." By H. MASTIN.

"Hydrogen and oxygen electrode titrations of some dibasic acids and of dextrose." By H. T. S. BRITTON.

"Sulphur sesquioxide." By I. VOGEL and J. R. PARTINGTON.

"The relation of homogeneous to catalysed reactions. The catalytic decomposition of hydrogen iodide on the surface of gold." By C. N. HINSHELWOOD and C. R. PRICHARD.

"The decomposition of carbon monoxide in the corona due to alternating electric fields. Part I." By M. CRESPI and R. W. LUNT.

"The formation and stability of spiro-compounds. Part XII. Further evidence for the multiplanar configuration of the *cyclo*heptane ring." By J. W. BAKER.

"The condensed ternary system phenol–water–salicylic acid." By C. R. BAILEY.

"The hydration of strong electrolytes and some properties of salt solutions." By J. N. SUGDEN.

"The action of sulphur on amines. Part III. *o*-, *m*-, and *p*-Chloroanilines." By H. H. HODGSON and J. H. WILSON.

"The system sodium sulphite–sodium hydroxide–water." By D. L. HAMMICK and J. A. CURRIE.

"Synthetical experiments in the *iso*quinoline group. Part V. Synthesis of substances allied to oxyberberine." By R. D. HAWORTH, W. H. PERKIN, and H. S. PINK.

"Amino benzothiazoles. Part II. The naphthylamino naphthiazoles and their bromo derivatives." By R. F. HUNTER.

"Negative adsorption: the surface tensions and activities of some aqueous salt solutions." By A. K. GOARD.

"The structure of α-campholytic acid. A correction." By J. P. C. CHANDRASENA, C. K. INGOLD, and J. F. THORPE.

"The interaction of carbon dioxide and hydrogen on the surface of tungsten." By C. N. HINSHELWOOD and C. R. PRICHARD.

"Note on potassium antimonoxalate." By L. H. A. HOLMES and E. E. TURNER.

"Studies on the Walden inversion. Part IX. The influence of the solvent on the sign of the product in the conversion of β-bromo-β-phenylpropionic acids to β-hydroxy-β-phenylpropionamides." By G. SENTER and A. M. WARD.

"'Co-ordination' and the periodic table." By I. AUCKEN.

"Anode phenomena in the electrolysis of potassium ethyl malonate." By J. B. ROBERTSON.

"The isomerism of the styryl alkyl ketones. Part II. The isomerism of the homologues of 2-hydroxystyryl, and of 3-methoxy-, and 4-hydroxy-styryl methyl ketones." By A. MCGOOKIN and D. J. SINCLAIR.

"Hydrogen electrode studies of the precipitation of hydroxides. Part I. Magnesium, manganous, ferrous, cobalt, nickel, and thorium." By H. T. S. BRITTON.

"Stereoisomeric azo-dyes." By G. T. MORGAN and D. G. SKINNER.

"4- and 4'-Methoxybenzoylbenzoin." By H. GREENE.

"The relative rates of conversion of phenoxyphenyldichloroarsine and its chloro-derivatives into chlorophenoxarsines." By E. ROBERTS and E. E. TURNER.

"Chemistry of petroleum. Part II. The action of sodium hypochlorite on types of sulphur compounds found in petroleum distillates." By S. F. BIRCH and W. S. G. P. NORRIS.

"Derivatives of δ-*o*-aminobenzoylvaleric acid." By M. J. PATERSON and S. G. P. PLANT.

"The action of formic acid on certain sesquiterpenes." By J. M. ROBERTSON, C. A. KERR, and G. G. HENDERSON.

"Syntheses of disulphoxides." By D. T. GIBSON, C. J. MILLER, and S. SMILES.

"The effect of gum arabic and other emulsifiers on the acid hydrolysis of esters in heterogeneous systems." By R. C. SMITH.

"Lithium arc spectrum for polarimetric use." By P. C. AUSTIN.

"Bismuth dihydride." By E. J. WEEKS and J. G. F. DRUCE.

"Reduction product of the hydroxyanthraquinones. Part VI." By A. G. PERKIN and G. YODA.

"A wandering of the acetyl group during methylation." By O. KUBOTA and A. G. PERKIN.

"The supposed formation of 1 : 2 : 4-oxadi-imine rings from nitroso-compounds and methylenearylamines." By G. N. BURKHARDT, A. LAPWORTH, and E. B. ROBINSON.

"The reaction of bromine with aliphatic acids. Catalytic effect of acyl halides." By H. B. WATSON.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

CLARKE, FRANK WIGGLESWORTH. The data of geochemistry. 5th edition. Washington 1924. pp. 842. (*Recd.* 26/5/25.)
From the Author.

DANIELS, GEORGE WILLIAM. Refrigeration in the chemical industry. London 1925. pp. x + 141. ill. (*Recd.* 29/5/25.)
From the Publisher: Mr. A. J. Rayment.

EASTMAN KODAK COMPANY. Abridged scientific publications from the Research Laboratories. Vol. VIII, 1924. Rochester, N.Y. 1925. pp. 156 + vi. ill. (*Reference.*)
From the Eastman Kodak Company.

IMPERIAL COLLEGE CHEMICAL SOCIETY. Journal. Vol. IV, containing the papers read during the session 1924—1925. London 1925. pp. 54. ill. (*Reference.*) From the Society.

KLAR, M. The technology of wood distillation with special reference to the methods of obtaining the intermediate and finished products from the primary distillate. Translated [from the 2nd German edition] by ALEXANDER RULE. With an additional chapter by the translator. London 1925. pp. xvi + 496. ill. 25*s.* net. (*Recd.* 8/6/25.)
From the Publishers: Messrs. Chapman & Hall.

MORRICE, ALEXANDER. A treatise on brewing: wherein is exhibited the whole process of the art and mystery of brewing the various sorts of malt liquor; with practical examples upon each species. Together with the manner of using the thermometer and saccharometer; elucidated by examples, and rendered easy to any capacity, in brewing London porter [etc.]. London 1802. pp. [xii] + v to 180 + [xii]. ill. (*Reference.*)
From Dr. Alexander Scott.

NATIONAL BENZOLE ASSOCIATION and UNIVERSITY OF LEEDS. *Joint Benzole Research Committee.* Second report. London 1925. pp. 246. ill. (*Recd.* 18/5/25.)

From the National Benzole Association.

ORGANIC SYNTHESES: an annual publication of satisfactory methods for the preparation of organic chemicals. Vol. IV. Edited by OLIVER KAMM [and others]. New York 1925. pp. viii + 90. 7*s.* 6*d.* net. (*Recd.* 22/5/25.)

From the London Publishers: Messrs. Chapman & Hall.

TIBA. Revue Générale de Teinture Impression Blanchiment Apprêt et de Chimie Textile et Tinctoriale et Revue de la Soie Artificielle. Year II, etc. Paris 1924 +. (*Reference.*)

From the Publishers.

II. *By Purchase.*

BIRTWHISTLE, GEORGE. The principles of thermodynamics. Cambridge 1925. pp. x + 164. ill. 7*s.* 6*d.* net. (*Recd.* 10/6/25.)

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE 1925: a catalogue of heavy and fine chemicals, raw material, machinery, plant and equipment applicable to production industries. Compiled with the co-operation of leading British manufacturers by LEONARD HILL. Edited by DUDLEY MAURICE NEWITT. London 1925. pp. 260. ill. (*Reference.*) 21*s.* net.

DUKES, CUTHBERT. The bacteriology of food. London 1925. pp. xii + 180. ill. 7*s.* 6*d.* net. (*Recd.* 10/6/25.)

FRIEND, JOHN NEWTON. [Editor.] A text-book of inorganic chemistry. Vol. III. Part i. The alkaline earth metals. By MAY SYBIL BURR (née LESLIE). London 1925. pp. xxvi + 346. (*Reference.*) 20*s.* net.

HOWE, H. E. [Editor.] Chemistry in industry: a coöperative work intended to give examples of the contributions made to industry by chemistry. New York 1924. pp. xiv + 372. ill. 6*s.* net. (*Recd.* 16/4/25.)

JÖRGENSEN, ALFRED. Micro-organisms and fermentation. 5th edition. Revised by the Author with the assistance of S. H. DAVIES. London 1925. pp. xiv + 468. ill. 30*s.* net. (*Recd.* 10/6/25.)

JOHNSON, J. B. Materials of construction. Rewritten by M. O. WITHEY and JAMES ASTON. Edited by F. E. TURNEAURE. 6th edition. New York 1925. pp. xx + 866. ill. 30*s.* net. (*Recd.* 13/5/25.)

KLOOSTER, HENRY S. VAN. Lecture and laboratory experiments in physical chemistry. 2nd edition. Easton, Pa. 1925. pp. x + 274. ill. 12*s.* net. (*Recd.* 15/5/25.)

LADOO, RAYMOND B. Non-metallic minerals: occurrence—preparation—utilization. New York 1925. pp. viii + 686. ill. 30*s*. net. (*Recd.* 10/6/25.)

LORD, LEONARD J. Practical butter and cheese making. London 1925. pp. 200. ill. 10*s*. 6*d*. net. (*Recd.* 13/5/25.)

MELLOR, JOSEPH WILLIAM. Modern inorganic chemistry. New edition. London 1925. pp. xx + 1104. ill. 12*s*. 6*d*. net. (*Recd.* 15/5/25.)

NEWMAN, FRANK HERBERT. The production and measurement of low pressures. London 1925. pp. 192. ill. 16*s*. net. (*Recd.* 10/6/25.)

NORTH, SYDNEY H., and GARBE, J. B. Low temperature distillation, home oil supply and the utilization of "waste" coal. London 1925. pp. vi + 216. ill. 15*s*. net. (*Recd.* 13/5/25.)

O'BRIEN, W. B. Factory practice in manufacture of azo dyes. Easton, Pa. 1924. pp. viii + 176. ill. 22*s*. 6*d*. net. (*Recd.* 16/4/25.)

PARRY, ERNEST JOHN. Parry's cyclopædia of perfumery. 2 vols. London 1925. pp. vi + 840. (*Reference.*) 36*s*. net.

RICHMOND, HENRY DROOP. The laboratory book of dairy analysis. 3rd edition. London 1925. pp. viii + 118. ill. 5*s*. net. (*Recd.* 15/5/25.)

SIM, JAMES. Steam condensing plant in theory and practice. London 1925. pp. xiv + 272. ill. 18*s*. 6*d*. net. (*Recd.* 10/6/25.)

THOMPSON, MAURICE DE KAY. Theoretical and applied electrochemistry. Revised edition. New York 1925. pp. xx + 552. ill. 20*s*. net. (*Recd.* 13/5/25.)

THOMSON, SIR JOSEPH JOHN. The electron in chemistry: being five lectures delivered at the Franklin Institute, Philadelphia. [Philadelphia] 1923. pp. vi + 144. ill. 10*s*. 6*d*. net. (*Recd.* 15/5/25.)

VEDDER, EDWARD B. The medical aspects of chemical warfare. With a chapter on the naval medical aspects of chemical warfare by DUNCAN C. WALTON. Baltimore 1925. pp. xvi + 328. ill. 32*s*. 6*d*. net. (*Recd.* 26/5/25.)

WELLS, HARRY GIDEON. The chemical aspects of immunity. New York 1925. pp. 254. 20*s*. net. (*Recd.* 18/5/25.)

WILLIAMS, GEORGE BRANSBY. Sewage disposal in India and the East. Calcutta 1924. pp. x + 230. ill. 17*s*. 6*d*. net. (*Recd.* 13/5/25.)

WOOD, THOMAS BARLOW. Animal nutrition. London 1924. pp. viii + 226. 4*s*. 6*d*. net. (*Recd.* 15/5/25.)

WORLD POWER CONFERENCE, First. London 1924. Transactions. 5 vols. London [1925]. pp. xxiv + 1506, xviii + 1600, xvi + 1502, xx + 1816. (*Reference.*)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, October 15th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	*Died.*
Richard Burtles	May 3rd, 1923.	July 3rd.
Charles Frederick Chandler	Feb. 1st, 1872.	Aug. 25th.
William Henry Deering	April 1st, 1869.	Sept. 5th.
William Joseph Dibdin	April 15th, 1880.	June 8th.
Samuel Jackson	Dec. 15th, 1892.	July 27th.
Francis Robert Japp	Feb. 6th, 1879.	Aug. 1st.
Reginald A. Joyner	Dec. 6th, 1917.	Oct. 8th.
Daniel Rankin Steuart	Dec. 15th, 1881.	Aug. 1st.
Leonard E. Vlies	Feb. 21st, 1918.	July 26th.

The PRESIDENT announced that :

1. The first of the two Informal Lectures to be held this Session will be delivered in the Rooms of the Society on Thursday, November 26th, 1925, by Professor R. Robinson, D.Sc., F.R.S., who has chosen as his subject :

> "Recent Researches on the Structural Relationships of Some Plant Products."

Special attention is drawn to the fact that the lecture will be delivered at 6 *o'clock* instead of at 8 *o'clock* as stated on the meeting card.

2. Following the innovation made in October, 1923, it has been decided to hold next month a united dinner for British Chemists. The dinner, to be called "British Chemistry Dinner" is under the auspices of the Chemical Society, the Institute of Chemistry, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Institution of Petroleum Technologists, the Society of Public Analysts, the Bio-Chemical Society, the Oil and Colour Chemists' Association, and the Chemical Industry Club,

and will be held at the Connaught Rooms, Great Queen Street, W.C. 2, on Friday, November 13th, 1925, at 6.30 for 7 p.m. Dr. W. R. Ormandy, Chairman of the Chemical Industry Club, will preside.

The price of the tickets is 15*s*. each (not including wine) for lady or gentleman, and as the accommodation is limited to about 400, early application is advisable.

Besides the Loyal Toasts, there will be only two other Toasts, namely, "The Profession and Industry of Chemistry" and "The Guests." After dinner, there will be dancing and musical items.

Application for tickets (15*s*. each), with remittance, should be sent to the Secretary of the Chemical Industry Club, 2, Whitehall Court, S.W. 1.

3. The Selection Committee of the Harrison Memorial Prize will meet shortly to consider the award of the Harrison Prize.

The Prize, of the value of about £150, is to be awarded to the chemist of either sex being a natural born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, during the previous five years has conducted the most meritorious and promising original investigations in any branch of pure or applied chemistry and published the results of those investigations in a scientific periodical or periodicals.

Provided that in the opinion of the Selection Committee there is a candidate of sufficient distinction to warrant an award of the Prize, the award is to be made in December, 1925.

The Selection Committee is prepared to receive applications, nominations or information as to candidates eligible for the Prize. Any such information must be received by The President, The Chemical Society, Burlington House, Piccadilly, W. 1, not later than Tuesday, December 1st, 1925.

4. As Fellows are already aware, the Council has approved the proposals of the Bureau of Chemical Abstracts (see Procs. for June, 1925), aiming at the unification of abstracts of chemical papers in this Country. As a consequence of the arrangements made, "British Chemical Abstracts" will appear as from January, 1926, in two sections, namely, A (Pure Chemistry) and B (Applied Chemistry), and will be in the same format and type, without overlap, and with one common index at the end of the year. The format adopted is that at present employed for the "B" Abstracts; beginning, therefore, with January, 1926, Fellows will receive the Abstracts in Pure Chemistry in quarto double-column size. This clearly means a break with the past, so far as the Chemical Society is concerned, but the Council trusts that in the interests of co-operation the Fellows will accept these changes with loyalty.

5. The price of the Annual Reports for 1925, Vol. XXII, will be the same as for Vol. XXI, namely 5*s*. 6*d*. post free to those Fellows who apply by Christmas Day, 1925. Application should be made to the Assistant Secretary, and must be accompanied by a remittance for 5*s*. 6*d*.

6. Volume I of the Memorial Lectures has been reproduced by a photographic process, and is now on sale at the Publishers, Messrs. Gurney & Jackson, 33, Paternoster Row, E.C. 4, price to Fellows 9*s*. post free.

7. Sets of the Berichte from 1915–1924 (10 years) can be obtained on application to the Assistant Secretary at the reduced price of £22, plus carriage.

8. In continuance of the arrangement made with the American Chemical Society, the *Journal of the American Chemical Society*, *Industrial and Engineering Chemistry*, and *Chemical Abstracts*, can be obtained by Fellows at the following reduced rates:

Price for any one journal $7.25, post free,
Price for any three journals $17.50, post free,

while *Chemical Reviews* is offered to Fellows at $4.50, post free. Applications should be made as soon as possible to Dr. Charles L. Parsons, Secretary, American Chemical Society, 1709, G. Street N.W., Washington, D.C., U.S.A.

The *Journal of Physical Chemistry* is obtainable by Fellows at $8.00 post free, published at $10.00. Application should be made to the *Journal of Physical Chemistry*, Ithaca, N.Y., U.S.A.

9. A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms obtainable from the Assistant Secretary, must be received on or before Tuesday, December 1st, 1925. Applications from Fellows will receive prior consideration.

All persons who received Grants in December, 1924, or in December of any previous year, whose accounts have not been closed by the Council, are reminded that Reports must be returned by December 1st.

The following were formally admitted Fellows of the Chemical Society: G. M. Bullick, C. G. Trew, I. C. P. Smith, W. G. Corderoy, E. H. Warren, I. A. Smith, C. F. Flint, R. R. Garran, N. M. Bligh, and E. C. Padgham.

Certificates were read for the first time in favour of:

Robert Leslie Andrew, Dominion Laboratory, Wellington, New Zealand.
Louis Baissac, Curepipe Road, Mauritius.
William Francis Barker, Ph.D., Rhodes University College, Grahamstown, S. Africa.
Ralph Basden, The Technical College, Newcastle, N.S.W.

Frank Bell, 11, Edwy Parade, Gloucester.
Arthur Neville Copnall Bennett, B.Sc., 27, Dale Road, Luton.
John Cecil Bird, B.Sc., A.I.C., 72, Dyne Road, Kilburn, N.W. 6.
Lionel Christopher William Birkett, B.Sc., Moor House, North Road, Spennymoor.
James Boyd, F.I.C., P.O. Box 1162, Johannesburg.
Frank Symonds Bradhurst, c/o Messrs. Holbrooks, Ltd., Danks Street, Waterloo, Sydney.
John Hildred George Carlile, B.Sc., A.R.C.S., 29, Orlando Road, Clapham, S.W. 4.
Leslie James Chalk, B.Sc., 14, Shrubbery Road, Southall.
Rama Charan, B.Sc., B.Sc.Tech., 12, Bank Road, Allahabad.
Edward Mortimer Crowther, D.Sc., F.I.C., Rothamsted Experimental Station, Harpenden, Herts.
Frank Edwin Dickinson, Research Establishment, Sutton Oak, St. Helens.
William Donovan, M.Sc., Dominion Laboratory, Wellington, New Zealand.
John Stanley Dunn, M.A., Ph.D., A.I.C., 39, Victoria Park, Cambridge.
Edwin Francis Edwards, c/o Messrs. Holbrooks, Ltd., Waterloo, Sydney.
John Moelwyn Edwards, 92, Jamaica Road, Rotherhithe, S.E. 16.
James Walter Shanks Gemmell, B.Sc., Helen's Villa, Fleming Place, St. Andrews.
Francis Reginald Glover, 98/100, St. Peters Street, Nottingham.
Felix John Theodore Grigg, M.Sc., A.I.C., Government Buildings, Christchurch, New Zealand.
John Hall, M.Sc., A.I.C., 202, Burton Road, Derby.
Herbert Sim Hirst, B.Sc., Trinity College, Cambridge.
Toru Iwadare, c/o Banyu Pharmaceutical Co., Ltd., 174, Shimomeguro, Tokyo, Japan.
David Christopher Mendis Jayewardene, Fern Bank, Moratuwa, Ceylon.
Charles Benjamin Johnson, 134, Preston New Road, Blackburn.
Walter Idris Jones, Ph.D., B.Sc., 7, Manor Street, Cambridge.
Charles King, 141, Bath Street, Glasgow.
Frederick Karl Victor Koch, B.Sc., A.R.C.S., 9, Crossfield Road, Hampstead, N.W. 3.
Charles Dudley Langford, B.Sc., A.R.C.S., 43, Ashbourne Avenue, Temple Fortune, N.W. 11.
Henry Guinness de Laszlo, B.A., Ph.D., 3, Fitzjohn's Avenue, Hampstead, N.W. 3.
Sam Lenher, B.A., 15, Gordon Street, W.C. 1.
William Macartney, c/o Messrs. Grattan & Co., Ltd., Belfast.
William Francis Martin, F.I.C., 27, Shandon Crescent, Edinburgh.
Arthur Moore, Highfield, Oakworth, Keighley.
John Blackburn Murgatroyd, 90, St. George's Square, S.W. 1.
Chitsukhlal Hiralal Nanavati, 80, Esplanade Road, Fort, Bombay.
Anna Maria O'Mara, 83, Elsham Road, Holland Park, W. 14.
Norman Frederick Parker, B.A., A.I.C., 45, Sellons Avenue, Harlesden, N.W. 10.
Marjorie Ellen Pring, B.Sc., 66, St. Augustine's Avenue, S. Croydon.
Herbert Charles Roberts, 15, Estcourt Terrace, Headingley, Leeds.
George Baty Scott, 37, Woodbridge Road, Knowle, Bristol.
Rupert Boswood Scammell, B.Sc., c/o Messrs. F. H. Faulding & Co., Ltd., Castlereagh Street, Redfern, Sydney.
Tpo Shin, Agricultural Farm, Mandalay.

Dalip Singh, Ph.D., near Tehsil P.O., Lahore.
William Veale Thorpe, B.A., 270, Balham High Road, S.W. 12.
William Milburn Towler, B.Sc., 28, Denton Avenue, Roundhay, Leeds.
David Traill, B.Sc., 58, Chalmers Street, Dunfermline.
Donald Morrison Turner, 40–42, Lexington Street, W. 1.
Geoffrey Turner, B.Sc., 85, Winchester Avenue, Leicester.
Frederick Henry Webb, St. Malo, Jameson Road, Harpenden, Herts.
Hugh Amphlett Williams, 249, Kennington Road, S.E. 11.
Robert Harding Williams, 131, Anlaby Road, Hull.
John James Benjamin Wolfe, 24, Greyhound Road, Hammersmith, W. 6.
John Frederick Zimmermann, 17, Stile Hall Gardens, Chiswick, W. 4.

The following papers were read:

"The effect of ultra-violet light on dried hydrogen and oxygen." By H. B. BAKER and M. CARLTON.

"A new per-oxide of barium." By M. CARLTON.

"The production of oxide-films on copper at ordinary temperatures." By U. R. EVANS.

"The structural isomerism of the oximes. Part III. The benzilmonoximes." By A. H. ATACK and F. W. ATACK.

List of papers, or abstracts thereof, received between June 18th and October 15th, 1925. (This list does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"The action of sulphuretted hydrogen on a neutral solution of potassium permanganate." By H. B. DUNNICLIFF and S. DAYAL.

"Note on the preparation of thiocarbanilide." By S. J. C. SNEDKER.

"Studies with the microbalance. Part II. The photochemical decomposition of silver chloride." By E. J. HARTUNG.

"Preparation, hydrolysis and reduction of the isomeric fluorobenzyl bromides." By J. B. SHOESMITH and R. H. SLATER.

"The action of silica on electrolytes. Part II." By A. F. JOSEPH and H. B. OAKLEY.

"The formation and growth of silver nuclei in the decomposition of silver oxalate." By J. Y. MACDONALD and C. N. HINSHELWOOD.

"Researches in the menthone series. Part I." By J. READ and A. M. R. COOK.

"Studies in adsorption by the application of optical methods. Fixation by dispersoids of methylene-blue within the disperse phase." By A. FODOR and R. RIWLIN.

"The physical chemistry of the metal–ammonium complexes. Part I. The blue of the copper–ammonium complexes." By S. S. BHATNAGAR, M. PRASAD and D. NATH.

"The correlation of absorption spectra with ionisation in violuric acid." By R. A. MORTON and A. H. TIPPING.

"Absorption spectra and lactam-lactim tautomerism." By R. A. MORTON and E. ROGERS.

"The heat of combustion of salicylic acid." By E. BERNER.

"An electrometric and phase rule study of some basic salts of copper." By H. T. S. Britton.

"The distribution of pyridine between water and benzene." By R. M. Woodman and A. S. Corbet.

"The velocity of decomposition of oxalic acid in solution." By D. L. Watson.

"The absorption of gases in colloidal solutions." By A. Gatterer.

"A circulation apparatus for gases." By N. G. Chatterji and G. I. Finch.

"2 : 4-Dinitrophenylhydrazine as a reagent for aldehydes and ketones." By O. L. Brady and G. V. Elsmie.

"The methylation of the oximes of benzil." By O. L. Brady and H. M. Perry.

"The alkaline oxidation of some carbohydrates by means of dyestuffs, considered quantitatively." By E. Knecht and E. Hibbert.

"Unstable states of solutions of sodium behenate." By M. E. Laing and collaborators.

"Note on the preparation of *p*-nitrophenylhydrazine." By H. H. Hodgson and H. G. Beard.

"The preparation of 2-nitro-1-halogen naphthalenes and of β-nitronaphthalene." By H. H. Hodgson and E. Kilner.

"The swelling and dispersion of some colloidal substances in ether–alcohol mixtures." By E. W. J. Mardles.

"The relationship of salts in dilute aqueous solution as determined by their influence on the critical solution temperature of the system phenol–water." By J. H. Carrington, L. R. Hickson, and W. H. Patterson.

"The colorimetric dissociation constants of dinitrocatechol and dinitroresorcinol." By F. C. Laxton, E. B. R. Prideaux, and W. H. Radford.

"The cyanine dyes. Part IX. The mechanism of the condensations of quinaldine alkiodides in presence of bases." By W. H. Mills and R. Raper.

"Dibenzylquinaldine." By W. H. Mills and A. T. Akers.

"The action of nitrous acid upon amides and other 'amino' compounds." By R. H. A. Plimmer.

"Olefinic terpene ketones from the volatile oil of flowering *Tagetes glandulifera*. Part I." By T. G. H. Jones and F. B. Smith.

"On the interaction between copper and sulphuric acid." By C. W. Rogers.

"Trypanocidal action and chemical constitution. Part II. Arylamides of 4-aminophenyl-arsinic acid." By H. King and W. O. Murch.

"The butyl esters of the simpler amino-acids. Part I." By W. T. J. Morgan.

"The influence of salts in ethyl alcohol solution on the mutual miscibility temperature of the system ethyl alcohol–paraffin." By E. J. Howard and W. H. Patterson.

"Condensations of the sodium derivatives of trimethylene glycol and glycerol." By A. Fairbourne and G. E. Foster.

"An investigation of the effect of differential aëration on corrosion by means of electrode potential measurements." By A. L. McAulay and F. P. Bowden.

"The recognition of allotropy in metals." By D. Stockdale.

"Solubility influences. Part I. The effect of some salts, sugars, and temperature on the solubility of ethyl acetate in water." By S. Glasstone and A. Pound.

"Experiments on the synthesis of apofenchocamphoric acid. Preparation of αα-dimethyl-β'-carboxyadipic acid." By K. C. Roberts.

"Electrometric study of the reactions between alkalis and silver nitrate solutions." By H. T. S. Britton.

"Electrometric separation of the iodide, bromide and chloride of silver." By H. T. S. Britton.

"Reduction products of the hydroxyanthraquinones. Part VII." By W. B. Miller and A. G. Perkin.

"Chloro-derivatives of *m*-hydroxybenzaldehyde." By H. H. Hodgson and H. G. Beard.

"The nitration of *m*-bromophenol." By H. H. Hodgson and F. H. Moore.

"The reduction of arsenic compounds by sodium hyposulphite. The production of subsulphides of arsenic." By W. Farmer and J. B. Firth.

"The electrical conductivities of hydrochloric acid and potassium chloride in water and acetone–water mixtures." By T. K. Brownson and F. M. Cray.

"Metallocyclic compounds. Part I. Compounds of tellurium." By H. D. K. Drew.

"The action of hydrogen fluoride on compounds of selenium and tellurium. Part I. Selenium dioxide." By E. B. R. Prideaux and J. O'N. Millott.

"The resolution of an asymmetric arsenic compound into its optically active forms." By W. H. Mills and R. Raper.

"The electrical conductivity of phosphorus pentachloride." By G. W. F. Holroyd, H. Chadwick, and J. Mitchell.

"Hydrogen electrode studies of the precipitation of basic chromates, borates and carbonates." By H. T. S. Britton.

"The relation between chemical constitution and pungency in acid amides." By E. C. S. Jones and F. L. Pyman.

"The rate of reaction of bromine with aqueous formic acid." By D. L. Hammick, W. K. Hutchison and F. R. Snell.

"The quaternary salts of benzoxazoles." By L. M. Clark.

"$\gamma\gamma'$-Dichloropropyl sulphide." By G. M. Bennett and A. L. Hock.

"Synthesis in the thianthren series. Part II." By M. Sen and J. N. Rây.

"Some lactonic esters derived from phenacyl bromide by condensation with ethyl sodiomalonate and analogous substances." By R. M. Rây and J. N. Rây.

"The velocity of decomposition of heterocyclic diazonium salts. Part I. Diazonium salts of the pyrazole and pyrazolone series." By J. Reilly and D. Madden.

"Orientating effects in the diphenyl series." By H. G. Dennett and E. E. Turner.

"The relative directive influence of polar and steric effects on ring closure." By R. W. J. Smith and E. E. Turner.

"The configuration of the ammonium ion." By W. H. Mills and E. H. Warren.

"Symmetrical substitution derivatives of trimethylene bromide and pentamethylene bromide." By W. H. Mills and L. Bains.

"Further studies on a new chlorinating agent preparation of polychloro-derivatives of toluene." By O. Silberrad.

"The equilibrium in the systems aluminium sulphate–copper sulphate–water and aluminium sulphate–ferrous sulphate–water at 25°." By V. J. Occleshaw.

"Reactions of the meso-hydroxyanthrones." By M. A. Matthews.

"The influence of different nuclei on the absorption spectra of substances." By J. E. PURVIS.

"The occurrence of sylvestrene." By B. S. RAO and J. L. SIMONSEN.

"The partial formaldehyde vapour pressures of aqueous solutions of formaldehyde. Part II." By W. LEDBURY and E. W. BLAIR.

"Trypanocidal action and chemical constitution. Part III. Arsinic acids containing the glyoxaline nucleus." By I. E. BALABAN and H. KING.

"The preparation of tertiary arsines by the Friedel-Crafts reaction." By A. F. HUNT and E. E. TURNER.

"Equilibrium in the system : $CH_3COOCH_3+H_2O \rightleftharpoons CH_3OH+CH_3COOH$." By G. J. BURROWS.

"The parachor and chemical constitution. Part III. Orientation isomerism in aromatic compounds." By S. SUGDEN and H. WILKINS.

"The aluminioxalates of some optically active bases." By T. B. CHILD, E. ROBERTS, and E. E. TURNER.

"On the equilibrium between methylformate, methanol and hydrogen, and some related equilibria." By J. A. CHRISTIANSEN.

"Hydrogen electrode studies of the reactions between solutions of salts of weak metallic bases and the acetate, oxalate and tartrate of sodium, with a note on the effect of dextrose on zirconium chloride solution." By H. T. S. BRITTON.

"The conversion of *r*-phenyl-α-naphthyl-glycollic acid into ketones." By A. MCKENZIE and H. J. TATTERSALL.

"Studies of equilibrium in systems of the type $Al_2(SO_4)_3$–$M''SO_4$–H_2O. Part II. Aluminium sulphate–nickel sulphate–water at 30°." By R. M. CAVEN and T. C. MITCHELL.

"The system silver sulphate–aluminium sulphate–water at 30°." By R. M. CAVEN and T. C. MITCHELL.

"Change of crystal habit of some salts when crystallised from silicic acid gel." By H. A. FELLS and J. B. FIRTH.

"The ionic activity product of water in glycerol–water mixtures." By J. COLVIN.

"2-*m*-Xylidino-5-ethoxy-4 : 5-dihydrothiazole." By V. K. NIMKAR and F. L. PYMAN.

"The change in the absorption spectra of aromatic nitro-compounds in liquid ammonia with time." By W. E. GARNER and H. F. GILLBE.

"Nitrosyl sulphuric acid. Part I." By G. A. ELLIOTT, L. L. KLEIST, and H. W. WEBB.

"The action of acetylenetetrabromide on organic bases." By J. D. FULTON.

"Production of *cyclo*telluripentanedionedichlorides." By G. T. MORGAN (with F. J. CORBY, O. C. ELVINS, E. JONES, R. E. KELLETT, and C. J. A. TAYLOR).

"Interactions of tellurium tetrachloride and monoketones." By G. T. MORGAN and O. C. ELVINS.

"A note on the sulphonation of 4-chloro-phenol." By J. M. GAUNTLETT and S. SMILES.

"Some analogues of adrenalone. Part I." By F. MATTHEWS.

"The relationship between the optical rotatory powers and the relative configurations of optically active compounds. Part II. The relative configurations of the optically active mandelic acids and β-phenyl-lactic acids." By G. W. CLOUGH.

"Synthesis of 2 : 3 : 5-trimethyl glucose." By J. C. IRVINE and J. W. H. OLDHAM.

"The oxidation of certain sesquiterpenes with chromyl chloride and chromic acid." By D. T. GIBSON, J. M. ROBERTSON, and J. SWORD.
"Tesla-luminescence spectra. Part VI. Some amino-derivatives." By W. H. MCVICKER, J. K. MARSH, and A. W. STEWART.
"Glyceryl glucoside." By H. S. GILCHRIST and C. B. PURVES.
"A comparison of methods of measuring the polarity of surfaces." By N. K. ADAM, R. S. MORRELL, and R. G. W. NORRISH.
"cyclo*Hexane*spirocyclo*hexane*." By W. S. G. P. NORRIS.
"The effect of heat on chloral hydrate." By J. D. MOUNFIELD and J. K. WOOD.
"The solubilities of sodium, potassium and calcium ferrocyanides. Part I." By M. P. APPLEBEY and M. FARROW.
"Isomeric change of aromatic compounds. Part I. The conversion of diacylanilides into acylaminoketones." By A. W. CHAPMAN.
"Nitrosyl sulphuric acid." By F. J. WILSON and H. W. WEBB.
"The constitution of the metallic ozonides." By E. C. C. BALY and R. W. RIDING.
"The influence of substituents on the stability of Schiff's bases. Part I. Hydrolysis of nitro- and methoxy-benzylidene anilines." By E. M. LANGMAN, W. HEALEY, and P. K. DUTT.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ABDERHALDEN, EMIL. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I, Chemische Methoden, Teil 6, Heft. iii, Abt. III, Physikalisch-chemische Methoden, Teil A, Heft v. Berlin 1925. pp. [268] + xxiv, [136]. ill. *M.* 12.30, *M.* 5.70. (*Recd.* 12/9/25.) From the Publishers: Herren Urban & Schwarzenberg.

AUSTRALIAN JOURNAL OF EXPERIMENTAL BIOLOGY AND MEDICAL SCIENCE. Vol. I, etc. Adelaide 1924 +. (*Reference.*)
From the Publishers.

BERRY, ARTHUR JOHN. Volumetric analysis: with a chapter on simple gravimetric determinations. 3rd edition. Cambridge 1925. pp. viii + 152. ill. 9*s.* net. (*Recd.* 9/10/25.)
From the Syndics of the Cambridge University Press.

BRUN, P. L'industrie des cyanures. Paris 1925. pp. 470. ill. 20 *fr.* net. (*Recd.* 22/9/25.)
From the Publisher: M. Gaston Doin.

BUNBURY, HUGH MILLS, and DAVIDSON, ALFRED. The industrial applications of coal tar products. London 1925. pp. xii + 284. 42*s.* net. (*Recd.* 7/9/25.)
From the Publishers: Messrs. Ernest Benn.

COHEN, JULIUS BEREND, and RUSTON, ARTHUR G. Smoke: a study of town air. [2nd] edition. London 1925. pp. xii + 108. ill. 8*s.* 6*d.* net. (*Recd.* 14/10/25.)
From the Publishers: Messrs. Edward Arnold & Co.

EASTMAN KODAK COMPANY. Aerial haze and its effect on photography from the air. Rochester, N.Y. 1923. pp. 84. ill. (*Recd.* 16/6/25.) From the Eastman Kodak Company.

GARDNER, WILLIAM. Companion to the first edition of Chemical synonyms and trade names. London 1925. pp. vi + 56. (*Reference.*) 7*s.* 6*d.* net.

From the Publishers: Messrs. Crosby Lockwood & Son.

HAUSBRAND, EUGEN. Principles and practice of industrial distillation. Translated from the 4th German edition by EDWARD HOWARD TRIPP. London 1925. pp. xx + 300. ill. 21*s.* net. (*Recd.* 12/9/25.) From the Publishers: Messrs. Chapman & Hall.

HOLMYARD, ERIC JOHN. Chemistry to the time of Dalton. London 1925. pp. 128. ill. 2*s.* 6*d.* net. (*Recd.* 16/10/25.)

From the Author.

INSTITUTE OF PHYSICAL AND CHEMICAL RESEARCH. Scientific papers. Vol. I, etc. Tokyo 1924 +. (*Reference.*)

From the Institute.

INSTITUTION OF CHEMICAL ENGINEERS. Transactions. Vol. 2, 1924. London [1925]. pp. 110. ill. (*Reference.*)

From the Institution.

JACOBSON, CARL ALFRED. A pronouncing chemical formula speller and contest guide. Baltimore 1925. pp. xviii + 280. (*Reference.*) 20*s.* net.

From the English Agents: Messrs. Baillière, Tindall & Cox.

LEATHES, JOHN BERESFORD, and RAPER, HENRY STANLEY. The fats. 2nd edition. London 1925. pp. viii + 242. 12*s.* 6*d.* net. (*Recd.* 15/10/25.)

From the Publishers: Messrs. Longmans, Green & Co.

LEPESCHKIN, W. Lehrbuch der Pflanzenphysiologie auf physikalisch-chemischer Grundlage. Berlin 1925. pp. vi + 298. ill. *Gm.* 15. (*Recd.* 7/9/25.)

From the Publisher: Herr Julius Springer.

MARTINDALE, WILLIAM HARRISON, and WESTCOTT, WILLIAM WYNN. The extra pharmacopœia. 18th edition. Vol. II. London 1925. pp. xlii + 728. (*Reference.*) 20*s.* net.

From the Publishers: Messrs. H. K. Lewis & Co.

MATAGRIN, A. L'industrie des produits chimiques et ses travailleurs. Paris 1925. pp. xviii + 486. ill. 12 *fr.* net. (*Recd.* 7/9/25.) From the Publisher: M. Gaston Doin.

MEDICAL RESEARCH COUNCIL. Special Report Series, No. 71. The aetiology and pathology of rickets from an experimental point of view. By V. KORENCHEVSKY. London 1922. pp. 172 + 18 plates. 4*s.* net.

—— Special Report Series, No. 77. Studies of rickets in Vienna

1919–22. (Report to the Accessory Food Factors Committee appointed jointly by the Medical Research Council and the Lister Institute.) London 1923. pp. 230 + 13 plates. 7*s*. 6*d*. net.

MEDICAL RESEARCH COUNCIL. Special Report Series, No. 91. An investigation of the Salmonella group, with special reference to food poisoning. By WILLIAM GEORGE SAVAGE and P. BRUCE WHITE. London 1925. pp. 160. 3*s*. 6*d*. net.

—— Special Report Series, No. 92. Food poisoning: a study of 100 recent outbreaks. By WILLIAM GEORGE SAVAGE and P. BRUCE WHITE. London 1925. pp. 112. 2*s*. 6*d*. net.

—— Special Report Series, No. 93. Experimental rickets: the effect of cereals and their interaction with other factors of diet and environment in producing rickets. By EDWARD MELLANBY. London 1925. pp. 66 + 40 plates. 3*s*. 6*d*. net.

From Professor J. C. Drummond.

MEIJER, WILLEM. Pyrazolonen. Groningen 1925. pp. 84. (*Recd*. 16/6/25.) From the Publisher: M. Edzo Venema.

MENSCHUTKIN, BORIS N. A short course of chemistry for technical colleges and universities. Leningrad 1925. pp. 128. [In Russian.] (*Recd*. 12/8/25.) From the Author.

—— M. W. Lomonossow. Moscow 1925. pp. 104. ill. [In Russian.] (*Recd*. 12/8/25.) From the Author.

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PLIMMER, ROBERT HENRY ADERS, and PLIMMER, VIOLET G. Food and health. London 1925. pp. vi + 64. ill. 3*s*. 6*d*. net. (*Recd*. 15/10/25.) From the Publishers: Messrs. Longmans, Green & Co.

R. STAZIONE SPERIMENTALE PER L'INDUSTRIA DELLE PELLI E DELLE MATERIE CONCIANTI NAPOLI-TORINO. Bolletino Ufficiale. Year I, etc. Torino 1923 +. (*Reference*.) From the Director.

RESEARCH ASSOCIATION OF BRITISH FLOUR-MILLERS. Bulletin. No. 1, etc. London 1924 +. (*Reference*.) From the Director.

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ROTHAMSTED EXPERIMENTAL STATION. Report 1923–24 with the supplement to the "Guide to the experimental plots" containing the yields per acre, etc. Harpenden 1925. pp. 130. ill. (*Reference*.) 2*s*. 6*d*. net. From the Director.

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SPROXTON, FOSTER. Cellulose ester varnishes. London 1925. pp. 178. ill. 15*s.* net. (*Recd.* 15/10/25.) From the Author.

THOMPSON, R. CAMPBELL. On the chemistry of the ancient Assyrians. London 1925. pp. 157 + 6 plates. [In mimeograph form.] 25*s.* net. (*Recd.* 7/9/25.) From the Author.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. II, part iii; Vol. III, part iii. Berlin 1925. pp. [384] + viii, [288]. ill. *M.* 14, *M.* 10. (*Recd.* 11/8/25.) From the Publishers: Herren Urban & Schwarzenberg.

ZSIGMONDY, RICHARD. Kolloidchemie. Ein Lehrbuch. 5th edition. I. Allgemeiner Teil. (Chemische Technologie in Einzeldarstellungen.) Leipzig 1925. pp. xii + 246. ill. *Gm.* 11. (*Recd.* 31/7/25.) From the Publisher: Herr Otto Spamer.

II. *By Purchase.*

ALLEN, HERBERT STANLEY. Photo-electricity. 2nd edition. London 1925. pp. xii + 320. ill. 18*s.* net. (*Recd.* 9/10/25.)

ALTERTHUM, HANS. Wolfram: Fortschritte in der Herstellung und Anwendung in den letzten Jahren. Braunschweig 1925. pp. viii + 112. *M.* 4.30. (*Recd.* 19/6/25.)

ARMSBY, HENRY PRENTISS, and MOULTON, C. ROBERT. The animal as a converter of matter and energy: a study of the rôle of live stock in food production. New York 1925. pp. 236. ill. 15*s.* net. (*Recd.* 14/10/25.)

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BAYLISS, SIR WILLIAM MADDOCK. The nature of enzyme action. 5th edition. London 1925. pp. viii + 200. ill. 9*s.* net. (*Recd.* 16/6/25.)

BECQUEREL, JEAN. La radioactivité et les transformations des éléments. Paris 1924. pp. 208. ill. 5 *fr.* (*Recd.* 22/6/25.)

BILLITER, JEAN. Technische Elektrochemie. 2nd edition of Die elektrochemischen Verfahren der chemischen Gross-Industrie. 2nd edition. Vols. I and II. Halle (Saale) 1923–24. pp. viii + 244, viii + 398. ill. (*Recd.* 19/6/25.)

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BROWNING, CARL HAMILTON. [Editor.] Immunochemical studies. London 1925. pp. xiv + 240. 12*s*. 6*d*. net. (*Recd.* 9/10/25.)

CHRISTIANSEN, WALTER G. Organic derivatives of antimony. New York 1925. pp. 230. 15*s*. net. (*Recd.* 9/10/25.)

CLÉMENT, LOUIS, and RIVIÈRE, C. Matières plastiques; soies artificielles. Paris 1924. pp. 528. ill. 55 *fr*. net. (*Recd.* 22/7/25.)

COUNCELL, R. W. Apologia alchymiæ: a re-statement of alchemy. London 1925. pp. xii + 88. 5*s*. net. (*Recd.* 16/6/25.)

CURIE, MADAME PIERRE. L'isotopie et les éléments isotopes. Paris 1924. pp. 210. ill. 22.50 *fr*. (*Recd.* 22/6/25.)

DIXON, WALTER ERNEST. A manual of pharmacology. 6th edition. London 1925. pp. xii + 478. ill. 18*s*. net. (*Recd.* 9/10/25.)

DODDS, EDWARD CHARLES, and DICKENS, FRANK. The chemical and physiological properties of the internal secretions. London 1925. pp. xiv + 214. ill. 8*s*. 6*d*. net. (*Recd.* 9/10/25.)

DUBOVITZ, HUGO. Chemische Betriebskontrolle in der Fettindustrie. Berlin 1925. pp. vi + 136. ill. *M*. 6.90. (*Recd.* 26/6/25.)

ELLIOT, CYRIL. Distillation in practice. London 1925. pp. 188. ill. 6*s*. net. (*Recd.* 14/10/25.)

FEUERFEST. Zeitschrift für Gewinnung, Bearbeitung, Prüfung und Verwendung feuerfester Stoffe. Year I, etc. Leipzig 1925 +. (*Reference.*)

GILLETT, HORACE WADSWORTH, and MACK, E. L. Molybdenum, cerium and related alloy steels. New York 1925. pp. 300. ill. 20*s*. net. (*Recd.* 12/6/25.)

GOODWIN, HAROLD. Autoclaves and high pressure work. London 1925. pp. 166. ill. 6*s*. net. (*Recd.* 14/10/25.)

GURWITSCH, LEO. Wissenschaftliche Grundlagen der Erdölverarbeitung. 2nd edition. Berlin 1924. pp. vi + 400. ill. *M*. 18 net. (*Recd.* 22/7/25.)

HAMILTON, ALICE. Industrial poisons in the United States. New York 1925. pp. xii + 590. 21*s*. net. (*Recd.* 9/10/25.)

HISTORY OF THE GREAT WAR. Medical Services. Vol. II. Including . . . gas warfare, and gas poisoning in tanks and mines. Edited by SIR WILLIAM GRANT MACPHERSON [and others]. London 1923. pp. viii + 622. ill. 25*s*. net. (*Recd.* 20/6/25.)

HOUBEN, JOSEF. Die Methoden der organischen Chemie. 3rd edition. Vol. I. Allgemeiner Teil. Leipzig 1925. pp. xxviii + 1340. ill. (*Reference.*) *M*. 75.

KERSHAW, G. BERTRAM. Sewage purification and disposal. 2nd

edition. Cambridge 1925. pp. xii + 364. ill. 18*s*. net. (*Recd.* 9/10/25.)

KERSHAW, JOHN BAKER CANNINGTON. Fuel economy and smoke prevention: being the 3rd edition of "Smoke prevention and fuel economy" by W. H. BOOTH and J. B. C. KERSHAW. London 1925. pp. xiv + 268. ill. 16*s*. net. (*Recd.* 9/10/25.)

LANGTON, HAROLD MCKEE. Blacks and pitches. London 1925. pp. 179. ill. 15*s*. net. (*Recd.* 14/10/25).

LE BLANC, MAX. Lehrbuch der Elektrochemie. 11th and 12th edition. Leipzig 1925. pp. viii + 391. ill. *M*. 13. (*Recd.* 22/6/25.)

LEWIS, WILLIAM CUDMORE MCCULLAGH. A system of physical chemistry. 4th edition. Vol. II. Thermodynamics. London 1925. pp. viii + 490. ill. 15*s*. net. (*Recd.* 26/6/25.)

MCKEE, RALPH H. [and others]. Shale oil. New York 1925. pp. 326. ill. 22*s*. 6*d*. net. (*Recd.* 9/10/25.)

NAMETKIN, S. Die Umlagerung alizyklischer Kerne ineinander. (Sammlung, Vol. XXVIII.) Stuttgart 1925.

PATTEN, NATHAN VAN. Bibliography of the corrosion of metals and its prevention. Kingston, Canada 1924. pp. iv + 186. (*Reference.*) 20*s*. net.

POGGENDORFF, JOHANN CHRISTIAN. Biographisch-literarisches Handwörterbuch. Vol. V. 1904 to 1922. Edited by P. WEINMEISTER. Part i. Leipzig 1925. pp. iv + 696. (*Reference.*) *M*. 60.

PRINGSHEIM, HANS, with the collaboration of JESAIA LEIBOWITZ. Zuckerchemie. Leipzig 1925. pp. xii + 322. *M*. 18. (*Recd.* 19/6/25.)

SMITH, SYDNEY. Forensic medicine: a text-book for students and practitioners. London 1925. pp. xiv + 498. ill. (*Reference.*) 21*s*. net.

TAMMANN, GUSTAV. A text-book of metallography: chemistry and physics of the metals and their alloys. Translated from the 3rd German edition . . . by REGINALD SCOTT DEAN and LESLIE GERALD SWENSON. New York 1925. pp. ii + 388. ill. 26*s*. net. (*Recd.* 16/6/25.)

[UNITED STATES] NATIONAL RESEARCH COUNCIL. *Division of Engineering and Industrial Research.* Marine structures, their deterioration and preservation: report of the Committee on Marine Piling Investigations. By WILLIAM G. ATWOOD and A. A. JOHNSON [and others]. Washington, D.C. 1924. pp. viii + 534. ill. 31*s*. 6*d*. net. (*Recd.* 12/6/25.)

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III. *Pamphlets.*

(a) *From Professor P. Phillips Bedson.*

AUSTIN, LEONARD. Demonstration of rescue-apparatus, Felling, August 31st, 1907. (From the *Trans. Inst. Mining Engineers*, 1908.) ill.

FERNANDES, FRANCIS VITO. The Indian school of Chemistry. The researches of Professor Ray and his pupils at Presidency College. (From the *Presidency College Magazine*, 1915, **1**.)

FRENCH COMMISSION ON THE USE OF EXPLOSIVES IN THE PRESENCE OF FIRE-DAMP IN MINES. Report. Translated by W. J. BIRD and M. WALTON BROWN. 3 parts. Newcastle-upon-Tyne 1890–91. pp. 164. ill.

MOREWOOD, A. PALMER. Shaw's gas tester, for detecting the presence of small percentages of gas in colliery workings. London 1896. pp. 18. ill.

NORTH OF ENGLAND INSTITUTE OF MINING AND MECHANICAL ENGINEERS. Report of the Committee appointed to enquire into the explosion of an air receiver at Ryhope Colliery. (From the *Trans. N. England Inst. Min. & Mech. Eng.*, 1888, **37**.) ill.

SMYTHE, JOHN ARMSTRONG. Two newly-discovered whin-dykes on the coast of Northumberland. (From the *Trans. Nat. Hist. Soc. Northumberland*, 1914, N.S. **4**).

—— On nitrosopinene. London 1898. pp. 19.

TROBRIDGE, FREDERICK GEORGE. Über die Ester- und Amid-Sauren der Itaconsäure. Beuel a. Rh. 1910. pp. 36.

(b) *Miscellaneous.*

ANDERSON, L. A. P., HOWARD, ALBERT, and SIMONSEN, JOHN LIONEL. Studies on lathyrism. I. (From the *Indian J. Med. Research*, 1925, **12**.)

GORTNER, ROSS AIKEN, and HOFFMAN, WALTER FRED. Quantitative estimation of chlorides and sulphates in expressed plant tissue fluids. (From the *Bot. Gaz.*, 1924, **77**.)

HENDRICK, JAMES. Some characters of Scottish soils. (From the *Trans. Highland & Agric. Soc. of Scotland*, 1925.)

MASON, FREDERICK ALFRED. An introduction to the literature of chemistry for senior students and research chemists. Oxford 1925. pp. 42.

MILLER, LEWIS B. Adsorption by aluminium hydrate considered as a solid solution phenomenon. (From the *U.S. Public Health Reports*, 1924, **39**.)

MINES DEPARTMENT. *Safety in Mines Research Board.* Second Annual report, 1923, etc. London 1924 +.

—— Paper No. 7. Explosives in Mines Research Committee. Second report 1924, etc. London 1925 +.

—— Paper No. 8. The ignition of fire-damp. By HUBERT FRANK COWARD and RICHARD VERNON WHEELER. London 1925. pp. 25. ill.

—— Paper No. 9. The lag on ignition of firedamp. By C. A. NAYLOR and RICHARD VERNON WHEELER. London 1925. pp. 16. ill.

—— Paper No. 10. Firedamp explosions within closed vessels. The effects of turbulence. By G. B. MAXWELL and RICHARD VERNON WHEELER. London 1925. pp. 12. ill.

MINISTRY OF HEALTH. Final Report of the Departmental Committee on the use of preservatives and colouring matters in food. London 1924. pp. 84.

MONIER-WILLIAMS, GORDON WICKHAM. The solubility of glazes and enamels used in cooking utensils. (*Ministry of Health Reports on Public Health and Medical Subjects.* No. 29.) London 1925. pp. iv + 17.

NATIONAL ASSOCIATION OF MASTER BAKERS, CONFECTIONERS AND CATERERS. Reports on research at the National Bakery School (Borough Polytechnic Institute), London, conducted by CHARLES DORÉE and JOHN KIRKLAND. (From the *Nat. Assoc. Review*, 1925.)

NATIONAL PHYSICAL LABORATORY. *Metrology Department.* Verification of weights: testing of balances: determination of densities. 1925. pp. 28.

PERKIN, FREDERICK MOLLWO. Recent progress in the peat problem. Paper read before the British Association at Southampton on August 27th, 1925. London 1925. pp. 24. ill.

PUIG, P. IGNACIO. Teoria de las valencias positivas y negativas. Barcelona 1924. pp. 31. ill.

PUIGGARI, HUGO. Fenómenos de transporte eléctrico en un hidrosol de oxido férrico. Trabajo presentado al 1er Congreso Sudamericano de Quimica. Buenos Aires 1924. pp. 11.

RADIUM. Le vingt-cinquième anniversaire de la découverte du radium (1898–1923). [Paris n.d.] pp. 86.

RAU, MADYAR GOPAL. The constituents of some Indian essential oils. Part XVI. (From the *Indian Forest Records*, 1924, **11**.)

RAU, MADYAR GOPAL and SIMONSEN, JOHN LIONEL. The constituents of some Indian essential oils. Part XVII. (From the *Indian Forest Records*, 1925, **11**.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, November 5th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
John Young Buchanan	June 21st, 1877.	Oct. 16th.
Harold James Cross	Feb. 15th, 1917.	Oct. 17th.
Francis Jones.....	Dec. 4th, 1873.	Oct. 22nd.
Charles Etty Potter	Dec. 5th, 1912.	Sept. 13th.

The PRESIDENT announced that Professors C. S. Gibson, G. T. Morgan, J. F. Thorpe, and W. P. Wynne, have been appointed by the Council to represent the Society on the Bureau of Chemical Abstracts, and that Professors T. M. Lowry, J. W. McBain, and J. C. Phillip will represent the Society on the Editorial Board of the Journal of Physical Chemistry, together with Professor F. G Donnan, appointed by the Faraday Society.

Certificates were read for the first time in favour of :

Harold Frederic Betts, B.Sc., 17, The Broadway, Broadstairs.
Edward Britnell, B.Sc., 9, Osterley Avenue, Isleworth.
Reginald John Bromfield, 141, Constantine Road, N.W. 3.
Francis Hereward Burstall, B.Sc., 12, Adelaide Road, Teddington.
Archer John William Butterfield, 163, Northumberland Park, N. 17.
John William Corran, B.Sc., Ph.D., A.I.C., Research Laboratory, Carrow Works, Norwich.
John Harold Cottier, 52, Aspen Grove, Lodge Lane, Liverpool.
John Horsfall Dyde, 18, Dean Road, Scarborough.
George Malcolm Dyson, B.A., B.Sc., Ph.D., 36, Hillsborough Road, E. Dulwich, S.E. 22.
Alfred Eccles, B.Sc., 18, Cambrian Terrace, Holbeck, Leeds.
George Albert Elliott, M.Sc., 263, Kennington Road, S.E. 11.
Eric Bertram Evans, B.Sc., 2, Boxmoor Terrace, Southchurch, Southend.
Elinor Katharine Ewbank, B.A., 22, Park Crescent, Oxford.

Elizabeth Monica Openshaw Farrow, M.A., 37, Chalfont Road, Oxford.
Oliver Free, B.A., The Lodge, Mansfield College, Oxford.
William Marshall Freeman, 1, Temple Gardens, Temple, E.C. 4.
Eva Florence Gee, The Station, L.N.E.R., Howsham, Lincoln.
George Vincent Hall, B.Sc., 6, Borough Road, Bridlington.
William Rowan Hare, 220, Eastfield, Peterborough.
Walter Healey, 28, Gooder Lane, Brighouse.
Thomas Henderson, M.C., M.A., B.Sc., Guildford Grammar School, West Australia.
Syed Husain, M.Sc., 112, Gower Street, W.C. 1.
Gilbert Jessop, M.Sc., Ph.D., 453, Glossop Road, Sheffield.
Brian Charles Lavers Kemp, B.A., Wellington College, Berks.
Banarsi Das Laroia, B.A., B.Sc., 3, Oxford Road, Teddington.
John Joseph Lennon, M.Sc., 6, Bartlemas Road, Oxford.
Ivan Roy McHaffie, B.A., M.Sc., 37, King Henry's Road, N.W. 3.
Neil McLean, M.A., B.Sc., 127, Blenheim Place, Aberdeen.
Leslie George Manchester, B.Sc., 557, Green Lanes, Hornsey, N. 8.
William Alfred Nottage Markwell, 26, Huntsmoor Road, S.W. 18.
Charles Henry Lawrence Miller, 50, Rowden Road, Beckenham.
Horace Winston Palmer, B.Sc., 15, Hollingdean Terrace, Brighton.
Austin McDowell Patterson, Antioch College, Yellow Springs, Ohio, U.S.A.
Ernest Phillis, B.Sc., 22, Fairford Terrace, Dewsbury Road, Leeds.
Jonathan Pollitt, B.A., 17, Caversham Avenue, Palmers Green, N. 13.
Charles Raymond Porter, M.Sc., A.I.C., 126, Linden Road, Bournville, Birmingham.
Evan Emrys Price, B.Sc., Rock House, Heathfield, Swansea.
Rose Rachel Sass, B.Sc., Newnham College, Cambridge.
Albert Sciver, B.Sc., A.I.C., 84, Vineyard Hill, Wimbledon Park, S.W. 19.
Frederick Francis Percival Smith, B.A., B.Sc., Peterhouse, Cambridge.
Robert Frederick Smith, 254, Higham Hill Road, Walthamstow, E. 17.
William Ernest Soper, B.Sc., 50, Aislibie Road, Lee, S.E. 12.
Herbert Kenneth Southern, B.Sc., Government Laboratory, Strand, W.C. 2.
Frank Harland Swire, 152, Queen's Road, Halifax.
Harold James Tattersall, B.Sc., Ph.D., 141, Thorold Road, Ilford.
Elvera Annie Tricker, 319, Norwich Road, Ipswich.
Norman Leopold Tyler, 9, St. Paul's Gardens, Spennymoor.
Herbert Ward Vernon, B.Sc. 245, Albert Road, N. 22.
Ewart Harrod Williams, B.Sc., A.I.C., 31, Thornsbeach Road, Catford, S.E. 6.
Gwyn Williams, B.Sc., Cae Ffynnon, Llandudno Junction.
John Laurence Wiltshire, B.Sc., 36, Fordel Road, Catford, S.E. 6.
Wilfred Fisher Wyatt, M.Sc., North Anston, Nr. Sheffield.

The following were formally admitted Fellows of the Chemical Society: W. J. V. Ward, H. F. Halliwell, R. J. W. Le Fèvre, I. J. Faulkner, J. Thurgood, and T. W. Jones.

The following papers were read:

"Further studies on a new chlorinating agent. Preparation of polychloro-derivatives of toluene." By O. Silberrad.

"The configuration of the ammonium ion." By W. H. Mills and E. H. Warren.

The following paper was taken as read :

" Ring-chain tautomerism. Part XV. The phenol-succineins and -glutareins." By S. DUTT.

Ordinary Scientific Meeting, Thursday, November 19th, 1925 at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., Vice-President in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
John Lloyd T. Jones	Feb. 7th, 1901.	Nov. 12th.
Frank George Pope	Feb. 18th, 1909.	Oct. 29th.
Robert Llewellyn Taylor	Jan. 15th, 1874.	Nov. 8th.

The CHAIRMAN announced that :

1. The Council has decided that the next Annual General Meeting and Dinner to take place on Thursday, March 25th, 1926, shall be held in Manchester. A local Sub-Committee has been appointed to make arrangements and full particulars will be announced later.

2. An Informal Meeting will be held in the Rooms of the Society on Thursday, December 17th, immediately after the conclusion of the formal business of the Ordinary Scientific Meeting at 8 p.m. Light refreshments will be provided, and smoking will be permitted, except on the Library Floor. The Council will welcome assistance from Fellows who can add to the interest of the Meeting by showing experiments or exhibiting apparatus, and those able to do so are requested to communicate with the Assistant Secretary not later than Monday, December 7th.

The following were formally admitted Fellows of the Chemical Society : Cyril C. Harris, John S. Carter, and T. H. Clare.

Certificates were read for the first time in favour of :

William Blakey, jun., B.A., 14, Marshall Road, Cambridge.
Herbert Clayton, M.A., B.Sc., The Dyson Perrins Laboratory, South Parks Road, Oxford.
John Charles Forsyth, 62, Worcester Street, Christchurch, New Zealand.
Ankarath Sankunni Mannadi Nayar, M.B., B.S., Ph.D., The Medical College, Madras.
William Bennett Price, B.Sc., The Laurels, Woolwich Road, Belvedere.
Madhavlal Sukhlal Shah, M.Sc., 22, Oxford Road, Putney, S.W. 15.
George Ernest Thompson, 7, Campbell Road, Bow, E. 3.
Bernard William Town, B.Sc., A.R.C.S., 79, The Grove, Hammersmith, W. 6.
Victor Martin Trikojus, B.Sc., Queen's College, Oxford.
Henry Woolf, P.O. Box 14, Broken Hill, Northern Rhodesia.

The following Certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2):

Edgar Calvin Le Roy Miller, M.D., Medical College of Virginia, Richmond Va., U.S.A.

The following papers were read:

"The constitution of the metallic ozonides." By E. C. C. Baly and R. W. Riding.

"Studies of dynamic isomerism. Part XX. Amphoteric solvents as catalysts for the mutarotation of the sugars." By T. M. Lowry and I. J. Faulkner.

"Studies of valency. Part V. Absorption spectra of halogen and sulphonic derivatives of camphor. Origin of the ketonic absorption band." By T. M. Lowry and G. Owen.

"Studies of valency. Part VI. General and selective absorption of halogen derivatives of methane. The origin of general absorption." By T. M. Lowry and R. R. Sass.

The following paper was taken as read:

"Studies of valency. Part VII. Surface polarity and the reaction of ethylene and chlorine. The effect of the adsorbed water layer." By R. G. W. Norrish and G. G. Jones.

List of papers, or abstracts thereof, received between October 16th and November 19th, 1925. (This list does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"Polymerisation of β-glucosan. The constitution of synthetic dextrins." By J. C. Irvine and J. W. H. Oldham.

"The action of mercurous nitrate on chloroauric acid." By W. B. Pollard.

"The freezing of inorganic hydrogels." By J. R. I. Hepburn.

"The bromination of some 5-substituted 1-phenylbenzthiazoles." By R. F. Hunter.

"Studies on the dependence of optical rotatory power on chemical constitution. Part VI. Rotatory powers of phenyl, *o*-, *m*-, *p*-tolyl and β-naphthyl derivatives of *d*-camphorimide and *d*-camphoramic acid." By B. K. Singh and A. N. Puri.

"Transformations of the sugar nitrates." By J. W. H. Oldham.

"Studies in colour and constitution. Part I. The positional bathochromic influence of the methylthiol group, alone, and in conjunction with the methoxy-group." By H. H. Hodgson and F. W. Handley.

"The photochemical oxidation of hydriodic acid in ultra-violet light. Part I." By T. MOORE.

"Ring-chain tautomerism. Part XVII. Instances showing how glutaric derivatives can simulate succinic compounds." By S. DUTT.

"A theory of colour on the basis of molecular strain. The effect of chromophoric superposition." By S. DUTT.

"The influence of the intensity of illumination on the velocity of photochemical changes." By F. BRIERS, D. L. CHAPMAN, and E. WALTERS.

"The salting-out effect. The influence of electrolytes on the solubility of iodine in water." J. S. CARTER.

"Germanium. Part II. Germanium tetrachloride and its ammonia compounds." By W. PUGH and J. S. THOMAS.

"The action of alcoholic soda and potash upon chloronitrobenzene." By D. H. RICHARDSON.

"The partial pressures of aqueous ethyl alcohol." By H. J. E. DOBSON.

"A comparison of some of the physical properties of the alkali cyanates and azides." By J. A. CRANSTON and A. Y. LIVINGSTONE.

"Reactions for nitrites." By B. C. MCEWEN.

"Lead dihydride and lead tetrahydride." By E. J. WEEKS.

"Some reactions of organic thiosulphates." By H. B. FOOTNER and S. SMILES.

"Air oxidation of titanous and vanadous sulphates." By A. S. RUSSELL.

"Complex formation in lead nitrate solutions. Part II. The quaternary system potassium nitrate–lead nitrate–barium nitrate–water." By S. GLASSTONE and E. J. RIGGS.

"Polymerisation of acetone by calcium carbide." By T. HOPKINS.

"Action of zinc alkyl halides on nitric esters." By T. HOPKINS.

"Observations on the Claisen reaction." By G. T. MORGAN and E. HOLMES.

"The specific heats of hydrocyanic acid. A reply." By E. H. INGOLD.

"The relation of homogeneous to catalysed reactions. The catalytic decomposition of hydrogen iodide on the surface of platinum." By C. N. HINSHELWOOD and R. E. BURK.

"The action of hydrogen fluoride on compounds of selenium and tellurium. Part II. Tellurium dioxide." By E. B. R. PRIDEAUX and J. O'N. MILLOTT.

"Halogenation of 2 : 6-dimethylbenzbisthiazole and of 2 : 4-diphenyl-3 : 5-diphenyliminotetrahydro-1 : 2 : 4-thiodiazole." By R. F. HUNTER.

"The reaction between hydroxylamine and ferric chloride." By A. D. MITCHELL.

"The equilibria underlying the soap-boiling processes. The system potassium oleate–potassium chloride–water." By J. W. MCBAIN and W. J. ELFORD.

"The solubility of sodium iodide in ethyl alcohol." By F. E. KING and J. R. PARTINGTON.

"Iodination in the carbazole series." By S. H. TUCKER.

"The chemistry of the caryophyllene series. Part I." G. G. HENDERSON, J. M. ROBERTSON, and (in part) C. A. KERR.

"On the Budde effect in bromine. Part I. The photoactive constituent in wet bromine." By B. LEWIS and E. K. RIDEAL.

"On the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and dry bromine." By B. LEWIS and E. K. RIDEAL.

"The constitution of the benzene nucleus." By B. C. MCEWEN.

"Keto-enol isomerism of ethylenebisacetylacetone." By G. T. MORGAN and C. J. A. TAYLOR.

"A buffer mixture for the alkaline range of hydrogen-ion concentration determinations." By W. R. G. ATKINS and C. F. A. PANTIN.

"The influence of carbon rings on the velocity of reactions involving their side-chains. Part I. The hydrolysis of cyclic and open-chain malonic esters." By R. GANE and C. K. INGOLD.

"The condensations of 3-bromo-, and 3-nitro-*p*-dimethylaminobenzaldehydes with ethyl acetoacetate and ammonia." By L. E. HINKEL and W. R. MADEL.

"The replacement of calcium carbonate by iron pyrites in nature." By C. O. HARVEY.

"A revision of the structural formula of glucose." By W. CHARLTON, W. N. HAWORTH, and S. PEAT.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, DECEMBER 3RD, 1925.

ANDREW, ROBERT LESLIE, Dominion Laboratory, Wellington, New Zealand. British (by birth). Analyst. Nineteen years' experience in Dominion Laboratory, N.Z., now senior assistant in charge of Food and Drugs work. Published work: "The Colorimetric Estimation of Lead in Cream of Tartar," *Analyst*, 1924, p. 129. "The Cryoscopic Method for the Detection of Added Water in Milk" (appendix to 50th Annual Report, Dominion Laboratory). (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

BAISSAC, LOUIS, Curepipe Road, Mauritius (Indian Ocean). British. Sugar Technologist, Department of Agriculture, Réduit, Mauritius. Lecturer

in Sugar Technology, College of Agriculture, Réduit, Mauritius. (*Signed by*) James P. Ogilvie, H. Tempany, W. H. Edwards.

BARKER, WILLIAM FRANCIS, Rhodes University College, Grahamstown, S. Africa. Professor of Chemistry. Ph.D. (Liverpool). (*Signed by*) I. M. Heilbron, E. C. C. Baly, R. A. Morton.

BASDEN, RALPH, 11, Ada St., Hamilton, Newcastle, N.S.W. Teacher of Chemistry. I have been engaged for four years as Teacher of Science at Sydney Grammar School; two years Teacher of Organic and Physical Chemistry at Newcastle Technical College, and four years in Manufacturing and Analytical Chemistry. (*Signed by*) A. R. Penfold, Robt. Grant, Fred J. Berry, Richard W. Challinor.

BELL, FRANK, 11, Edwy Parade, Gloucester. British. Student. Research student at Battersea Polytechnic. (*Signed by*) J. Kenyon, F. C. Ray, Henry Phillips, A. Houssa, Harold Hunter, P. W. B. Harrison, S. Greenberg.

BENNETT, ARTHUR NEVILLE COPNALL, 27, Dale Rd., Luton. British. Research Chemist to B. Laporte, Ltd., Luton. B.Sc. (Hons.) London. Have done research under Prof. Donnan at University College, and hope to publish shortly. (*Signed by*) W. E. Garner, D. McKie, Thomas Iredale.

BETTS, HAROLD FREDERICK, 17, The Broadway, Broadstairs, Kent. British. Research Student, East London College (Univ. of London). B.Sc. (Lond.), 2nd Class Hons. Chemistry. (*Signed by*) J. R. Partington, D. C. Jones, E. E. Turner.

BIRD, JOHN CECIL, 72, Dyne Rd., Kilburn, London, N.W. 6. British. Research and Works Chemist. B.Sc. (London), A.I.C., Associate of Univ. College of Nottingham. Science Master, Grammar School, Daventry. Chemist to Messrs. L. B. Holliday & Co., Ltd., Huddersfield. Chief Chemist and Works Manager to J. W. Drysdale & Co., London. Chemist to Messrs. Intermediates and Explosives, Ltd. (Bolckow, Vaughan & Co.), Co. Durham. Chemist to Messrs. Crookes Laboratories (British Colloids, Ltd., London). Investigation with Prof. H. H. Hodgson, M.A., into Absorption Spectra of Standard Dyestuffs (Huddersfield). (*Signed by*) Herbert Henry Hodgson, F. S. Kipping, E. R. Trotman.

BIRKETT, LIONEL CHRISTOPHER WILLIAM, Moor House, North Rd., Spennymoor, Co. Durham. British. Analytical Chemist on Coke Oven and Bye-products Plant. 5½ years' experience in Ironworks and Coke Oven laboratories. B.Sc. (3rd Class Hons.) after 3 years' study at Armstrong College, Newcastle-on-Tyne. (*Signed by*) W. N. Haworth, G. C. Leitch, H. V. A. Briscoe.

BOYD, JAMES, P.O. Box 1162, Johannesburg, S. Africa. British. Chief Examiner of Mine Air, Chamber of Mines, Johannesburg (and Assistant to General Manager, Chamber of Mines). F.I.C., A.R.T.C. (Glasgow). Assistant to Professor of Chemistry, Royal Technical College, Glasgow, 1908–11. Chemist, Goldfields Lab., Transvaal, 1912–13. Chief Examiner of Mine Air, Chamber of Mines, Johannesburg, 1914 to date. Author of various reports on Dust in Mine Air and Methods of investigating same (published in "Chamber of Mines Annual Reports," and for circulation to the mines of the Rand). Student, Royal Technical College, Glasgow, 1904–08. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson.

BRADHURST, FRANK SYMONDS, Bondi, Sydney, and c/o Holbrooks Ltd., Danks St., Waterloo, Sydney. Chief Chemist and Factory Manager. Matriculated from Sydney High School at Leaving Certificate Examination; obtained Scholarship available at the Sydney Technical College. Here I obtained the Honours Diploma with College Medal for year in Organic Chemistry, thereby becoming an Associate of the Sydney Technical College (A.S.T.C. Chem.).

Associate of the Australian Chemical Institute (A.A.C.I.). Chemist at Stedman-Hendersons, Ltd., Sweet Manufacturers, for 2½ years, then at Holbrooks (Australasia), Ltd., of Sydney, for 3 years, where I now hold the above position. I desire admission to the Chemical Society in order to keep in touch with modern research in the field of Food Analysis, and Food Manufacture. (*Signed by*) Richard W. Challinor, Fred J. Berry, Robert Grant, Arthur R. Penfold, S. E. Sibley.

BRITNELL, EDWARD, 9, Osterley Av., Isleworth, Middlesex. English. Chemist. B.Sc. (Honours Chemistry), London, July 1925. Assistant for 3 years to G. N. Huntly, 325, Kennington Rd., S.E. Assistant for 1½ years to G. T. Holloway & Co., 13, Emmett St., Limehouse. (*Signed by*) William G. Wagner, G. Nevill Huntly, Herbert F. Stephenson.

BROMFIELD, REGINALD JOHN, 141, Constantine Rd., Hampstead, N.W. 3. English. Assistant to Biochemist, The Hospital for Sick Children, Great Ormond St., W.C. For three years laboratory assistant at University College, London, under Prof. F. G. Donnan and Prof. N. Collie. For one year Acting Biochemist to Children's Hospital, Gt. Ormond St. For past two years Biochemical assistant, Hospital for Sick Children, Great Ormond St. Desire to become a member in order to receive the Journal and to keep in touch with current chemical literature, together with access to Library. (*Signed by*) J. N. Collie, Henry Terrey, Fred J. Kettel, J. Wicliffe Peck.

BURSTALL, FRANCIS HEREWARD, 12, Adelaide Road, Teddington, Middlesex. British. Research Chemist. D.S.I.R. Chemical Research Laboratory, Teddington. 1st Class Honours B.Sc., Birmingham University. (*Signed by*) G. T. Morgan, E. Holmes, C. E. Wood.

BUTTERFIELD, ARCHER JOHN WILLIAM, 163, Northumberland Park, Tottenham, N. 17. English. Articled Pupil in Engineering. Is desirous of keeping in touch with progress in the Science of Chemistry by attending the meetings and receiving the publications of the Society. (*Signed by*) W. J. A. Butterfield, Ernest M. Hawkins, E. R. Bolton.

CARLILE, JOHN HILDRED GEORGE, 29, Orlando Rd., Clapham, S.W. 4. British. Chemical Research Student, Royal College of Science. A.R.C.Sc., B.Sc. (*Signed by*) H. J. T. Ellingham, James C. Philip, H. F. Harwood.

CHALK, LESLIE JAMES, 14, Shrubbery Rd., Southall, Middx. Student (East London College). B.Sc., 1st Class Hons. in Chemistry. J. R. Partington, E. E. Turner, Elwyn Roberts.

CHARAN, RAMA, Allahabad, India. Indian (British). Glass Technologist, Govt. of India State Technical Scholar, B.Sc. from Allahabad University, 1922. Subjects: Maths., Physics, Chemistry, and English. B.Sc. Tech. from Sheffield University, 1924. Subjects: Glass Technology, Fuel, Refractory Materials, Geology and Mineralogy of Glassmaking Materials. For one year after graduation did research work on glasses containing more than one alkaline oxide and silica-lime. (*Signed by*) W. E. S. Turner, C. J. Peddle, F. G. Tryhorn.

CORRAN, JOHN WILLIAM, Research Laboratory, Carrow Works, Norwich. British. Physical and Biochemist. B.Sc. (Liv.), 1st Class Hons. Chem., 1921; Ph.D. (Liv.), 1923; A.I.C. Two years Research Physical Chemistry under Prof. W. C. M. Lewis; two years as physical and biochemist to Liverpool Cancer Research Committee. Publications: *J. Amer. Chem. Soc.*, 1922, **44**, 1673; 1923, **45**, 1627. *Biochem. J.*, 1924, **18**, 1358, 1364. (*Signed by*) W. C. M. Lewis, E. C. C. Baly, E. Morrison, Leslie J. Harris.

COTTIER, JOHN HAROLD, 52, Aspen Grove, Lodge Lane, Liverpool. British. Certificated School-teacher; formerly a student of Sheffield University. I

wish to obtain the Fellowship of the Society in order to receive the Journal and Abstracts, and thus keep in touch with advances in Chemistry. (*Signed by*) W. P. Wynne, F. G. Tryhorn, E. G. Turner, D. M. Bennett.

CROWTHER, EDWARD MORTIMER, Rothamsted Exptl. Station, and Bourtree, 24, Clarence Road, Harpenden, Herts. British. Assistant Physical Chemist and "Empire Cotton Growing Corporation," Soil Physicist, Rothamsted Exptl. Station. D.Sc. (Leeds), F.I.C., A.Inst.P. Publications on Physical Chemistry of Soils. *Journ. Agric. Sci.*, 1925, **15**, 201–255, 300–302, 303–306; *Trans. Faraday Soc.*, 1922, **17**, 317–321. Conjointly: *Journ. Agric. Sci.*, 1924, **14**, 221–231; 1925, **15**, 68–88; *Proc. Royal Soc.*, 1925, **106A**, 33–51, 215–222, 233–242; *Annals of Applied Biology*, 1925, **12**, 152–190. (*Signed by*) E. J. Russell, H. J. Page, C. T. Gimingham.

DICKINSON, FRANK EDWIN, Research Establishment, Sutton Oak, St. Helens, Lancs. British. A/g Superintendent, The Research Establishment, Sutton Oak, St. Helens, Lancs. Actively engaged in Chemical Industry as Analytical and Research Chemist and as Assistant Manager and Manager of Chemical Works for past fourteen years. Educated at King Edward's School, Stratford-on-Avon, and University of Birmingham. No papers published as all work of secret nature or commercial value. (*Signed by*) J. Davidson Pratt, E. Wheeler, Francis H. Carr.

DOLPHIN, JOSEPH RAYMOND, Chemical Department, University Rd., Edgbaston, Birmingham. British. Research Student. Pass B.Sc. Birmingham, 1st Class, 1923; Honours B.Sc. Birmingham, 1st Class, 1924. Research Student under Professor Morgan, O.B.E., D.Sc., F.R.S., from 1924–25 to become Research Chemist at J. A. Crabtree & Co., Ltd., Walsall, in Sept. 1925. (*Signed by*) G. T. Morgan, C. E. Wood, E. Ashley Cooper.

DONOVAN, WILLIAM, Dominion Laboratory, Wellington, New Zealand. British. Analyst, Dominion Laboratory, N.Z. M.Sc. (New Zealand University). Twenty years' experience in analytical work; now Assistant Dominion Analyst. Published work includes "Corrosion of Muntz Metal in Sea Water," *J.S.C.I.*, XLIII, 13, 72T; "Estimation of Nitrogen in Coal," *The Analyst*, Feb. 1924. (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

DUNN, JOHN STANLEY, 39, Victoria Park, Cambridge. British. Chemist. M.A. (Cantab.), Ph.D. (London), A.I.C. Late Research Chemist, Calico Printers Assocn., Manchester; now Research Chemist, British Non-Ferrous Metals Res. Assocn. With Dr. E. K. Rideal: *T.*, 1923, **123**, 1242; *T.*, 1924, **125**, 676. (*Signed by*) R. G. W. Norrish, Eric K. Rideal, H. McCombie.

DYDE, JOHN HORSFALL, 18, Dean Rd., Scarborough. British. Student at the University, Leeds, who intends to pursue post-graduate work in Biochemistry. Final year B.Sc. (Honours Chemistry). (*Signed by*) C. K. Ingold, B. Topley, H. M. Dawson.

DYSON, GEORGE MALCOLM, 36, Hillsborough Road, E. Dulwich, London, S.E. 22. British. Research Chemist. B.A. (Oxon.), B.Sc., Ph.D. (London). Research in Organic Chemistry, including work on the Reactions of Thiocarbonyl Chloride with Amino-compounds, Phenols, etc. *J.C.S.*, Trans., Sept., 1924, **125**, 1702; "The Reactions of Thiocarbonyl Chloride. Pt. I." (*Signed by*) D. L. Chapman, H. J. George, L. Rubenstein.

ECCLES, ALFRED, 18, Cambrian Terrace, Holbeck, Leeds. British. Research Student (University of Leeds). B.Sc., 1st Class Hons. (Pure Chemistry), 1925. (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman, J. W. Baker.

EDWARDS, EDWIN FRANCIS, Kogarah, Sydney, N.S.W., c/o Holbrooks (Australasia), Limited, Waterloo, Sydney. Works Chemist and Assistant

Factory Manager. Matriculated from High School at Leaving Certificate Examination, and gained Scholarship to Sydney Technical College. Attended the above College for five years—thereby completing the Diploma Course—and was subsequently granted the Associateship of the College, and the Diploma in Organic Chemistry. I am also an Associate of the Australian Chemical Institute. I was Assistant Chemist at the Woolwich Chemical Co., Sydney, for a period of two years, and Analyst at H.M. Customs, Sydney, for twelve months. At present I hold the above-mentioned position on the Staff of Holbrooks (Australasia), Limited, of Sydney. I desire admission to the Chemical Society in order to keep in touch with modern chemical literature and progress. (*Signed by*) Richard W. Challinor, Fred J. Berry, Robert Grant, Arthur R. Penfold, S. E. Sibley.

EDWARDS, JOHN MOELWYN, 92, Jamaica Rd., Rotherhithe, S.E. 16. British. Chemist and Pharmacist and Optician. (1) Early education at the Meirioneth County Grammar School. (2) Three years student of Chemistry at the Festiniog Higher Grade School. (3) Studied Analytical Chemistry and Physics under Mr. J. Thomas, B.Sc., at Muter's School of Chemistry. (4) Passed the Qualifying Examination of the Pharmaceutical Society of Great Britain in 1905. (5) Four years Sight Testing Optician with Mr. Hugh Jones, F.S.M.C., D.B.O.A. Am particularly anxious to keep in touch with Analytical work. (*Signed by*) Frank B. Arnold, John J. Laws, Percy Barrs.

ELLIOTT, GEORGE ALBERT, 263, Kennington Road, London, S.E. 11. British. Ramsay Memorial Fellow. M.Sc. (Lond.). (*Signed by*) L. F. Gilbert, S. Barratt, W. E. Garner.

EVANS, ERIC BERTRAM, 2, Boxmoor Terrace, Southchurch, Southend, Essex. English. Student. For two years a student at East London College; at present engaged in research there. Awarded 2nd Class in B.Sc. Hons. Lond., 1925. (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

EWBANK, (Miss) ELINOR KATHARINE, 22, Park Crescent, Oxford. British. Engaged in original research. Took 1st Class in Honours, School of Chemistry, Oxford, 1903. E. C. C. Baly and E. K. E., **87**, 1347; **87**, 1355. N. V. Sidgwick and E. K. E., **119**, 486; **121**, 1844; **125**, 2268. (*Signed by*) W. H. Perkin, N. V. Sidgwick, D. Ll. Hammick.

FARROW, (Miss) ELIZABETH MONICA OPENSHAW, 37, Chalfont Rd., Oxford. British. Demonstrator in Old Chemistry Dept., Oxford. Lecturer in Chemistry to 5 Women's Societies. M.A. (Oxon.) (*Signed by*) W. H. Perkin, N. V. Sidgwick, B. Lambert, M. P. Applebey, Allan F. Walden, E. G. J. Hartley, Frederick Soddy, J. Masson Gulland, S. G. P. Plant.

FREE, OLIVER, The Lodge, Mansfield College, Oxford. British. Demonstrator of Inorganic Chemistry. B.A., 2nd Class Honours. Research Student in Physical Chemistry (Radioactivity). (*Signed by*) M. P. Applebey, Frederick Soddy, B. Lambert, N. V. Sidgwick, A. F. Walden.

FREEMAN, WILLIAM MARSHALL, 16, Oakwood Avenue, Beckenham, Kent. British. Of the Honourable Society of the Middle Temple, Barrister-at-Law, Recorder of Stamford, and formerly Member of the Pharmaceutical Society of Gt. Britain. Author of "The Patents and Designs Act 1907, with Appendix on Chemical Patents." Occasional contributor to legal and other journals on Food and Drugs legislation, etc. Interested particularly in the promotion of the study of chemico-legal science especially with reference to the administration of the criminal law. (*Signed by*) Ernest C. Bennison, H. Berry, Harry Silvester.

GEE, EVA FLORENCE, The Station, L.N.E.R., Howsham, Lincoln. British.

Student of Chemistry at Bedford College. (*Signed by*) J. F. Spencer, H. Crompton, J. Stewart.

GEMMELL, JAMES WALTER SHANKS, Helen's Villa, Fleming Place, St. Andrews. British. Research Chemist. B.Sc. (Hons.) St. Andrews; now employed in Research Dept., Jute Industries, Ltd., Dundee, and desirous of keeping in touch with recent developments in chemical science. (*Signed by*) A. Killen Macbeth, James Craik, John Pryde.

GLOVER, FRANCIS REGINALD, 98/100, St. Peter's Street, Nottingham. British. Managing Director, Cooke & Glover, Engineers, Ltd., Engineers and Consulting Chemists, Nottingham, M.I.H.V.E., A.M.I.S.E. (*Signed by*) E. B. R. Prideaux, J. B. Firth, B. D. Shaw.

GOUDIELOCK, WILLIAM BOUCH O'BRIEN, 28, Fairfield Lane, Barrow-in-Furness. British. Chief Analyst, Vickers Ltd., Barrow-in-Furness. Full Technological Certificate, City and Guilds Institute, in Chemistry, Metallurgy, and Iron and Steel. Pupil in Vickers' Lab. under H. B. Weeks, F.I.C., for 5 years. Chief Laboratory Assistant for 8 years. Chief Analyst ever since. Lecturer for 2 years to Vickers' Engineering Apprentices on Chemical and Metallurgical Subjects in Connection with Firm's Scheme for Higher Education of Apprentices. Lecturer to Barrow Engineer's Assoc., Jan. 1920 and Jan. 1923. I am desirous of keeping in close touch with modern developments in Scientific Chemistry. (*Signed by*) H. B. Weeks, A. H. Mundey, W. J. Davison.

GRIGG, FELIX JOHN THEODORE, Christchurch (N.Z.). British. Government Analyst, Government Buildings, Christchurch, N.Z. M.Sc. (N.Z.) with Honours in Chemistry. A.I.C. (Great Britain). Seven years' experience in analytical work. Now Government Analyst at Christchurch (N.Z.). Published work: "Geochemistry of the Thermal Lakes, North Island, N.Z." (*N.Z. Journal of Science and Technology*, 1922, Volume 5, page 156). (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

HALL, GEORGE VINCENT, 6, Borough Road, Bridlington, Yorks. British. Student. Bachelor of Science, University of Leeds, June 1925. (*Signed by*) C. K. Ingold, H. M. Dawson, W. Lowson, P. K. Dutt.

HALL, JOHN, 202, Burton Rd., Derby. British. Chemist. M.Sc. (Leeds), A.I.C. Three years in Lab. of Sir W. G. Armstrong-Whitworth & Co.; two years in Lab. Dyehouse and Colour Plant of British Celanese. *J.C.S.*, **123**, 2029–2037. (*Signed by*) A. G. Perkin, G. Reeves, W. P. Skertchly.

HARE, WILLIAM ROWAN, 220, Eastfield, Peterborough. British. Student of Chemistry in the University of Oxford. Desirous of receiving literature (*Signed by*) D. Ll. Hammick, S. G. P. Plant, E. Hope.

HEALEY, WALTER, 28, Gooder Lane, Brighouse. English. Student, University of Leeds. Chemical Student who hopes to take up research. (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman.

HENDERSON, THOMAS, M.C., M.A., B.Sc., Toronhill Schoolhouse, Dunfermline. Scottish. Demonstrator in Chemistry (Inorganic), University of Leeds. M.A., B.Sc., St. Andrews, 1921. Holding a grant from the Dept. of Scientific and Industrial Research, carried on research work at St. Andrews University, under direction of Sir James C. Irvine, and have held the appointment noted above since October 1922. Vol. **121**, 1922, Trans., p. 892; Vol. **123**, 1923, Trans., p. 1130. (*Signed by*) R. Whytlaw-Gray, H. S. Patterson, B. Topley, W. Lowson, J. C. Irvine, Ettie S. Steele.

HIRST, HERBERT SIM, Trinity College, Cambridge. British. Research Assistant to Dr. E. K. Rideal, under Department of Scientific and Industrial Research Regulations. First class honours graduate in Physics and Chemistry

of St. Andrews University, with two years' research experience in Cambridge. "The Thermal Decomposition of Nitrogen Pentoxide," 1925, **127**, 657. (*Signed by*) Eric K. Rideal, W. H. Mills, Ulick R. Evans.

HUSAIN, SYED, 112, Gower St., London, W.C. 1. Indian. Student. M.Sc. (Aligarh Muslim University, India). (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

IWADARE, TORU, c/o Banyu Pharmaceutical Co., Ltd., 174, Shimomeguro, Tokyo, Japan. Japanese Proper. Became Chief Chemist and Managing Director of Banyu Pharmaceutical Co., Ltd., in September 1915. Have two years' experience as Assistant of the Chemical Dept. of the Tokyo Imperial University, and ten years' experience as Chief Chemist and Managing Director of Banyu Pharmaceutical Co., Ltd. Graduate, College of Science (Chemistry), Tokyo Imperial University, 1913. (*Signed by*) Joji Sakurai, T. Takamatsu, Y. Asahina.

JAYEWARDENE, DAVID CHRISTOPHER MENDIS, Fern Bank, Moratuwa, Ceylon. Sinhalese, British. Science Master, Prince of Wales' College, Moratuwa. (1) Science Master, St. John's College, Panadura, Ceylon (1918 and 1919). (2) Asst. Chemist, Butter Substitutes Supplies, Ltd., Colombo (1920). (3) Science Master, Prince of Wales' College, Moratuwa (since 1921). (*Signed by*) W. N. Rae, J. P. C. Chandrasena, K. V. Rau.

JESSOP, GILBERT, 453, Glossop Rd., Sheffield. British. Research Chemist. M.Sc., Ph.D. (Sheffield). Three years' Research in Physical Chemistry. Papers in the *Proc. Roy. Soc.*, 1925, **98B**, 206 (with Mr. N. K. Adam), and in the *J.C.S.* (with Mr. F. G. Tryhorn), 1925, **127**, 1320; (with Mr. N. K. Adam), 1925, **127**, 1863. (*Signed by*) W. P. Wynne, F. G. Tryhorn, N. K. Adam.

JOHNSON, CHARLES BENJAMIN, 134, Preston New Road, Blackburn. British. Minister of Religion (Fellow of Royal Astronomical Society). I desire to keep abreast, by means of the Society's Publications, of advance in General and Physical Chemistry. (*Signed by*) G. W. F. Holroyd, J. Hindle, Robert H. Pickard.

JONES, WALTER IDRIS, 7, Manor Street, Cambridge. Welsh. Research Student. Gonville and Caius College, Cambridge. Ph.D. (Cantab.), B.Sc. (Wales), etc. *Trans. Chem. Soc.*, 1923, **123**, 2688; 1924, **125**, 2590. (*Signed by*) Hamilton McCombie, John Dexter, Harold A. Scarborough.

KEENAN, HENRY WILFRID, 80, Upper Richmond Road, East Sheen, S.W. 14. British. Works Chemist. Practical experience in various branches of Analytical and Manufacturing Chemistry founded on a three years' Systematic Apprenticeship (with evening studies) under Dr. Julius Holzapfel and Dr. P. E. Bowles, F.I.C., by whom indentures are signed. Invented processes (including design and erection of plant for large scale production) dealing with (*a*) Paint and Varnish Industry, (*b*) Celluloid Industry, (*c*) Oils, and operated successfully. (*Signed by*) Charles Dorée, Francis Arnall, J. C. Crocker.

KEMP, BRIAN CHARLES LAVERS, Wellington College, Berks. British. Schoolmaster. Chemistry Master (VIth Form) at Wellington College; B.A. (Oxon.). 1922–23, research work on derivatives of Dianisoyl Methane. (*Signed by*) G. Watson Gray, D. Ll. Hammick, B. Lambert.

KING, CHARLES, F.S.A. (Scot.), 21, Newton Place, Glasgow. British. Electro-therapeutist. Fellow of the Society of Science, Lond. Applicant is in practice as Electro-therapeutist, and is desirous of keeping in touch with current chemical progress. (*Signed by*) G. G. Henderson, J. Roberts, Archd. N. Currie.

KOCH, FREDERICK KARL VICTOR, 9, Crossfield Road, Hampstead, N.W. 3.

English. Research in Physical Chemistry, Imperial College of Science and Technology. B.Sc. (1st Class), A.R.C.S. (2nd Class). (*Signed by*) James C. Philip, H. J. T. Ellingham, H. F. Harwood.

LANGFORD, CHARLES DUDLEY, 43, Ashbourne Av., Temple Fortune, London, N.W. 11. British. Research Student (Organic Chemistry), Royal College of Science. A.R.C.S., B.Sc. Honours (passed 1925, to be awarded 1926 owing to regulations). (*Signed by*) G. A. R. Kon, R. W. West, E. H. Farmer.

LAROIA, BANARSI DAS, Pindi Street, Ludhiana, Punjab, India. Indian. Student. B.Sc. (Hons.) Punjab University (India), B.A. (Hons.) Oxford University. At present student of Imperial College of Science and Technology (for Ph.D.). (*Signed by*) E. H. Farmer, G. A. R. Kon, M. A. Whiteley.

LASZLO, HENRY GUINNESS DE, 3, Fitzjohn's Avenue, Hampstead, N.W. 3. British. Research Chemist. B.A. Hons. (Cantab.), Ph.D. (Zurich). (*Signed by*) M. A. Whiteley, G. Ingle Finch, Samuel Smiles.

LEATHERBARROW, BERTRAM GREY, Hill Crest, Station Rd., Brimington, Chesterfield. British. Senior Assistant Teacher, Brimington Central School. Intermediate B.Sc. Two years subsequent graduation courses. Headmaster, Brimington Central Evening School, teaching all the Technical Courses. Student, Liverpool University 1919–1923. (*Signed by*) E. C. C. Baly, W. C. McC. Lewis, I. M. Heilbron, H. J. Stern.

LENHER, SAM, 15, Gordon Street, London, W.C. 1. American. Research Student at the Ramsay Laboratory, University College, London. Graduate of the University of Wisconsin (B.A. Degree), 1924. Internal student for the Ph.D. degree, University College, London, one year. McHaffie and Lenher, *J.C.S.*, 1925, **127**, 1559—1572. (*Signed by*) F. G. Donnan, W. E. Garner, J. A. Currie.

LENNON, JOHN JOSEPH, 6, Bartlemas Road, Oxford. Irish. Research Student. M.Sc., National University of Ireland, 1924, 1851 Scholar. Paper in collaboration with Hugh Ryan, D.Sc., *Proc. Royal Irish Acad.*, xxxvii, B, p. 27. (*Signed by*) W. H. Perkin, Francis Lions, R. D. Haworth, John Rankin.

MACARTNEY, WILLIAM, c/o Grattan & Co., Ltd., Belfast. British. Pharmaceutical Chemist. Chief Chemist of Messrs. Grattan & Co., Ltd., Wholesale Manufacturing Chemists and Aerated Water Manufacturers. Member of the Pharmaceutical Society of Ireland. Vice-President North Irish Pharmaceutical Society, Vice-President Ulster Drug Trade Association. No published papers in the *Journal of the Chemical Society*. In order to keep in touch with current advances in Chemistry. (*Signed by*) Henry Wren, Chas. J. Still, A. W. Stewart, Theo. Harper.

MCHAFFIE, IVAN ROY, 37, King Henry's Rd., London, N.W. 3. Canadian. Research Student, University College, London. B.A., M.Sc. University of Manitoba, Canada. "The Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum," *J.C.S.*, 1925, **127**, 1559–1572. (*Signed by*) F. G. Donnan, W. E. Garner, S. Barratt.

MCLEAN, NEIL, M.A., B.Sc., 127, Blenheim Place, Aberdeen. British. Station Director of the British Broadcasting Station at Aberdeen. Applicant is a Master of Arts and Bachelor of Science of Glasgow University, and is much interested in chemical science and desirous of having the best available literature on this subject for the purposes of his work. (*Signed by*) J. F. Tocher, G. G. Henderson, Archd. N. Currie.

MANCHESTER, LESLIE GEORGE, 557, Green Lanes, Hornsey, N. 8. British. Student. Two years a student at East London College; now engaged in

research work at same college; awarded 2nd Class in B.Sc. Hons. Lond. 1925. (*Signed by*) J. R. Partington, E. E. Turner, R. J. W. Le Fèvre.

MARKWELL, WILLIAM ALFRED NOTTAGE, 26, Huntsmoor Road, S.W. 18. English. Chemist. Desire to receive the *Journal* and to keep in touch with the progress of Chemical Science. (*Signed by*) E. W. Lucas, S. Greenberg, F. C. Ray, J. L. White, Henry Phillips.

MARTIN, WILLIAM FRANCIS, 27, Shandon Crescent, Edinburgh. British. Work's Chemist, in the employment of Messrs. T. & H. Smith, Ltd., Blandfield Chemical Works, Edinburgh. Fellow of Institute of Chemistry (F.I.C.), Member of Pharmaceutical Soc. of Gt. Britain (M.P.S.). (*Signed by*) James Walker, Alexander J. Dey, James Watt.

MILLER, CHARLES HENRY LAWRENCE, 50, Rowden Rd., Beckenham, Kent. British. Student (B.Sc. Honours Chemistry) at East London College. At present doing research work. Desirous of keeping in touch with modern Chemical Research. (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones, W. H. Patterson.

MOORE, ARTHUR, Highfield, Oakworth, Keighley, Yorks. British. Student (Chemistry). 3rd Year (final) Hons. Chemistry, Royal Coll. of Science, London, S.W. 7. (*Signed by*) H. L. Riley, H. F. Harwood, H. D. Murray.

MORRISON, ALEXANDER JOHN, Sydney, N.S.W. Assistant Superintendent of Testing and Inspection, Public Works Dept., Sydney. *Training:* Student for 3 years (night course) in the Chemical and Assay Laboratory of the late William Grosse, Mining Engineer and Metallurgist. *Sydney Technical College:* 4 years' course practical chemistry; 3 years' course theoretical chemistry; 2 years' course organic chemistry. Engaged on special investigation in connection with fixed oils and alloys. *Original Papers:* (With F. R. Morrison), "Examination of the fixed oil of the Queensland Nut," read before the Sydney Technical College Chemical Society (Vol. 1, pages 84—88). "Testing of Sand for Use in Portland Cement Mixtures," Paper read before the Sydney Technical College Chemical Society 1914 (Vol. 1, pages 17—26). "Permeability of Concrete" (with the late B. J. Smart, B.Sc. (London), Paper read before the Engineering Association of New South Wales (Vol. xxxiii, Part 2, page 1). Have been engaged in the chemical and mechanical testing of all classes of structural materials in the Testing Laboratory, Public Works Department, New South Wales, for the past 27 years. These materials include Portland cement, steel, alloys, asphaltum, tars, paints, oils, etc. Representative of the Australian Chem. Institute on the Engineering Standardisation Committee dealing with the drawing up of a Standard Specification for Portland Cement for the Commonwealth of Australia. (*Signed by*) A. R. Penfold, R. Grant, Richard W. Challinor, Fred J. Berry, George Z. Du Pain.

MORRISON, FRANK RICHARD, Brae Street, Waverley, Sydney, N.S.W. Australia. Asst. Economic Chemist, Technological Museum, Sydney. Diploma in Chemistry of Sydney Technical College, 1921. Associate of Australian Chemical Institute since 1920. Member of Royal Society of N.S.W. since 1921. Member of Sydney Technical College Chemical Society since 1913, and Joint Hon. Secretary since 1921. *Positions held:* One year in laboratory of Sydney Technical College; three years in laboratory of Metropolitan Board of Water Supply and Sewerage, Sydney; nine years in present position at Technological Museum, Sydney. *Original papers:* "The Occurrence of Rutin in the leaves of the *Boronia* (N. O. Rutaceæ)" (read before the Royal Society of N.S.W., 2nd November, 1921); "The

essential oil of *Kunzea corifolia*" (read before the Royal Society of N.S.W., 1st November, 1922); "A Chemical examination of the seeds of the 'Bunya Bunya' (*Araucaria Bidwilli*, Hooker)" (read before the Royal Society of N.S.W., 3rd December, 1924). *Conjointly with Mr. A. R. Penfold, F.A.C.I., F.C.S.* "Preliminary note on a new stearoptene (probably a phenol ether) occurring in some essential oils of the Myrtaceæ" (read before the Royal Society of N.S.W., 5th July, 1922); "The essential oil of *Eriostemon Crowei* (*Crowea saligna*) and the presence of a new phenol ether" (read before the Royal Society of N.S.W., 6th December, 1922); "Preliminary note on the electrolytic reduction of Piperitone" (read before the Royal Society of N.S.W., 5th September, 1923); "Notes on *Eucalyptus piperita* and its essential oils, with special reference to their Piperitone content" (read before the Royal Society of N.S.W., 2nd July, 1924). *Conjointly with Mr. A. Morrison:* "The chemical examination of the fixed oil of the Queensland Nut (*Macadamia ternifolia*)" (read before the Sydney Technical College Chemical Society, 24th June, 1923). (*Signed by*) A. R. Penfold, R. Grant, Richard W. Challinor, Fred J. Berry, George Z. Du Pain.

MURGATROYD, JOHN BLACKBURN, 90, St. George's Square, Westminster, S.W. 1. British. Demonstrator, Imperial College of Science and Technology, South Kensington. Taking up Research at the above College. (*Signed by*) H. B. Baker, J. N. Sugden, Leslie S. Theobald.

NANAVATI, CHITSUKHLAL HIRALAL, 80, Esplanade Road, Fort, Bombay. Hindoo. L.T.C., Analytical Chemist. Graduate of The Victoria Jubilee Technical Institute, Bombay; in Chemistry with special subject of Foods, Drugs and General Analysis; in Second Class with the title of Licentiate of Technical Chemistry, of the year 1921. Worked as Analytical Chemist with Messrs. Hughes & Davies and Messrs. Killick, Nixon & Co.; at present practising as Analytical Chemist. (*Signed by*) S. J. Shàh, Kapilram H. Vakil, R. G. Saraiya.

NICHOLSON, HENRY, "Aberlady," Osborne Rd., Stockton-on-Tees. English. Chemistry Master in Boys Secondary School, Stockton-on-Tees, since Nov. 1905. B.Sc. Durham University, 1904. M.Sc. for Research on the influence of the acetyl group as a protective agent in the oxidation of α-acetylnaphthylamine, 1907. (*Signed by*) J. G. Taylor, J. A. Smythe, W. M. Madgin.

O'MEARA, ANNA MARIA, 83, Elsham Road, Holland Park, Kensington, W. 14. Irish. Pharmacist. M.P.S. (London). Was for 4 years trained under John Armstedt Ray, M.A., Ph.C., Trinity Coll., Dublin, at his Laboratory in 23, Nassau Street, but never took any Analytical Examination. Was 3 years Pharmacist at Bolingbroke Hospital, Wandsworth Common, S.W. 11; was 1 year at Willesden General Hospital as Pharmacist, and occasionally have worked at the M.A.B. Homerton and Park Royal, Hither Green. At present am pharmacist at the Women's Hospital, Soho Sq., and I take Students for both the qualifying and Apothecaries' Hall Exam. and train them for same. (*Signed by*) H. Lucas, A. Thomas, S. Greenberg.

PALMER, HORACE WINSTON, 15, Hollingdean Terrace, Brighton. British. Research Student, East London College. B.Sc. London, Hons. I, Chemistry. (*Signed by*) J. R. Partington, D. C. Jones, W. H. Patterson.

PARKER, NORMAN FREDERICK, 45, Sellons Avenue, Harlesden, N.W. 10. British (English). Chemical Engineer. B.A. Cambridge; Associate of Institute of Chemistry; 1st Class, Natural Science Tripos, Part II (Chemistry), 1923. (*Signed by*) W. J. Pope, C. T. Heycock, W. H. Mills.

PATTERSON, AUSTIN MCDOWELL, Antioch College, Yellow Springs, Ohio,

U.S.A. United States. Professor of Chemistry, Antioch College, U.S.A. Formerly Editor of *Chemical Abstracts*. (*Signed by*) C. S. Gibson, T. Slater Price, John Greenaway.

PHILLIS, ERNEST, 22, Fairford Terrace, Dewsbury Rd., Leeds. British. Research Student, Leeds University. B.Sc., 1st Class Hons. in Pure Chemistry, 1925. (*Signed by*) J. B. Cohen, C. K. Ingold, P. K. Dutt, J. W. Baker.

POLLITT, JONATHAN, 17, Caversham Avenue, Palmers Green, N. 13. English. Chemistry Master, Hornsey County School, 1905– . B.A. (N.U.I.) Chemistry, Physics, Maths. Student (Chemistry) Birkbeck College since 1908. (*Signed by*) George Senter, Samuel Sugden, B. R. Heasman, F. J. Thorneycroft, A. M. Ward, Wm. W. Myddleton.

PORTER, CHARLES RAYMOND, 126, Linden Road, Bournville, Birmingham. English. Chemistry research assistant. M.Sc., A.I.C. Three years research assistant in Chemistry Department, University of Birmingham; part author of *Berichte*, 1925, **58**, 333, and *J.C.S.*, 1924, **125**, 731 and 1269. (*Signed by*) J. D. Main Smith, W. J. Hickinbottom, W. N. Haworth.

PRICE, EVAN EMRYS, Rock House, Heathfield, Swansea, Glam. British. Science Teacher, The College, Penarth, S. Wales. Graduate in Chemistry of University of Wales. Studied at University College, Swansea, 1920—1924. (*Signed by*) J. E. Coates, Leonard E. Hinkel, E. Stanley Hiscocks.

PRING, MARJORIE ELLEN, 66, St. Augustine's Avenue, S. Croydon, Surrey. British. Research Student at Bedford College for Women, Regent's Park. B.Sc., 1st Class Hons. in Chemistry, London University. (*Signed by*) J. F. Spencer, H. Crompton, M. S. Crewdson.

RÂY, JNANENDRA NATH, Calcutta. Indian. Lecturer, Calcutta University, M.Sc. (Cal.). Research Student, Manchester Univ. "Synthesis of oxyberberine" (joint author), *J.*, 1925, **127**, 740; "Synthesis in the Thianthren series," *J.*, 1921, **119**, 1959; "Catalytic action of Iodine in sulphonation," *J.*, 1920, **117**, 1405; joint author, "Modification and extension of Friedel & Crafts' reaction," *J.*, 1920, **117**, 1335. (*Signed by*) Robert Robinson, Arthur Lapworth, Henry Stephen, Wilson Baker.

ROBERTS, HERBERT CHARLES, 15, Estcourt Terrace, Headingley, Leeds. British. Chemist Director, Taylor's Drug Co., Ltd., P.O. Box 141, Burley Hill, Leeds. 20 years Analytical Chemist to above Co. Since 1908 Chemist Director and Superintendent under the Pharmacy Act to above Co. (*Signed by*) John Rennie, F. C. Savage, F. Pilkington Sargeant.

SANDERSON, PHYLLIS MARY, 7, Cresswell Place, S.W. 10. British. Research (Biochemical). I desire to become a member of this Society for the purpose of keeping in touch with current scientific investigations. (*Signed by*) F. G. Donnan, W. E. Garner, Henry Terrey.

SASS, ROSE RACHEL, Newnham College, Cambridge. British. Research Student. B.Sc. Hons. of the University of the Witwatersrand, Johannesburg, S. Africa. Demonstrator for 3 years. Now a research student in the Laboratory of Physical Chemistry, Cambridge University. (*Signed by*) T. M. Lowry, Eric K. Rideal, I. J. Faulkner.

SAXON, ROBERT, Westfield Terrace, Baildon, Yorks. British. Schoolmaster. Teacher of Chemistry at the Belle Vue Secondary School for 17 years. Teacher of Steam and Heat Engines, which included the Thermal Chemistry of Carbon and Hydrogen combustion and tests for SH_2, NH_3, etc., in Coal and Producer Gas for 15 years in the Belle Vue Technical School (evening). Eleven years Head Master present School, The Forster School for Boys, Bradford, under the Bradford Authority; entrance to school only by

Scholarship Examination. Bachelor of Science, Victoria Univ., Manchester, 1896. Studies under Prof. Tilden, Royal Coll. of Science, London, 1900, and Prof. Watts, Geology, 1901 (Vacation Course). (*Signed by*) Barker North, Robt. D. Abell, T. W. Price.

SCIVER, ALBERT, 84, Vineyard Hill, Wimbledon Park, S.W. 19. English. Analytical and Consulting Chemist and Bacteriologist. B.Sc. (First Class Honours, University College, London), A.I.C. Assistant to Drs. S. and E. K. Rideal, 28, Victoria St., S.W. 1. Lecturer on Bacteriology applied to Chemistry at Battersea Polytechnic. (*Signed by*) F. G. Donnan, Eric K. Rideal, W. E. Garner.

SCOTT, GEORGE BATY, 37, Woodbridge Road, Knowle, Bristol. British. Organic and Inorganic Chemistry Student for two years at Central Polytechnic Institute, after passing the Qualifying Examination of Pharmaceutical Society, 1896. For some years have been closely associated with British Fine Chemicals, embracing Dye Intermediates, Research Chemicals, Saccharin and by-products. Wishful to have access to Society's Library and Publications, thus keeping up to date with the latest advances in Chemistry. (*Signed by*) J. Wicliffe Peck, D. Hughes, T. O. Kent, W. D. Wallace, Archibald Macpherson.

SCAMMELL, RUPERT BOSWOOD, c/o F. H. Faulding & Co., Ltd., Castlereagh St., Redfern, Sydney, N.S.W. British. Manufacturing Chemist. Bachelor of Science (Sydney). Six years' experience in Manufacturing Chemistry with the above firm. I desire to keep in touch with modern chemical literature for research purposes. (*Signed by*) J. Kenner, George Harker, J. C. Earl.

SHIN, UPO, B.A.S., Agricultural Farm, Mandalay. Burman. Officiating Agricultural Chemist, Burma, Mandalay. Published as Memoirs of the Department of Agriculture in India on "The Phosphate Requirements of some Lower Burma Paddy Soils." (*Signed by*) Maung Ba, Maung Ba San, Maung Tun Tin.

SINGH, DALIP, near Tehsil, P.O. Lahore, India. Indian. Research Student, Cambridge University. Ph.D. Cambridge. (*Signed by*) W. J. Pope, W. H. Mills, Eric K. Rideal.

SMITH, FREDERICK FRANCIS PERCIVAL, Peterhouse, Cambridge. British. Research Student in the Cambridge Univ. Laboratories. 1st Class Nat. Sci. Tripos, Parts I and II. 1st Class London Ext. B.Sc. Hons. (in Chemistry). (*Signed by*) Hamilton McCombie, Harold A. Scarborough, W. A. Waters.

SMITH, ROBERT FREDERICK, 254, Higham Hill Road, Walthamstow, E. 17. British. Student of Chemistry at East London College. Desirous of keeping in touch with Modern Research. (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

SOPER, WILLIAM ERNEST, 50, Aislibie Road, Lee, London, S.E. 12. British. Research Student at East London College. B.Sc. (Lond.). (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

SOUTHERN, HERBERT KENNETH, Glenariff, Whaley Bridge, Nr. Stockport, Cheshire, also Government Laboratory, Strand, W.C. 2. British. Temporary Assistant Chemist, Government Laboratory. B.Sc. (Hons. Chem.) after 3 years and M.Sc. after a further year's research work in physical chemistry at Manchester University. Assistant Demonstrator in chemistry for 1 year at Manchester University. Six months as chemist with paint and enamel firm; 4 months at Government Laboratory. (*Signed by*) Robert Robertson, J. J. Fox, Geo. Stubbs, T. W. Harrison.

SPEIGHT, ERIC ALFRED, 61, Arthur Road, Wimbledon Park, S.W. 19.

British. Research worker in Organic Chemistry. Associateship of the Royal College of Science. B.Sc. (Lond.), Diploma of Imperial College, all in Chemistry. Have been engaged in study of Chemistry for 6 years, the last two being research. Published paper in Oct. 1924 *J.C.S.* on formation of Hydrindone derivatives. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, Arnold Stevenson.

SWIRE, FRANK HARLAND, 152, Queen's Road, Halifax, Yorks. British. Pharmacist. "Minor" Qualification of the Pharmaceutical Society. Member of the Pharmaceutical Society of Gt. Britain. Late Student in Chemistry at the Halifax Technical College and at The School of Pharmacy, Bloomsbury Sq., London, W.C. 1. (*Signed by*) T. E. Wallis, F. Browne, W. J. Stansfield.

TATTERSALL, HAROLD JAMES, B.Sc., Ph.D., 141, Thorold Road, Ilford, London, E. British. Research Chemist. Graduate of St. Andrews University. B.Sc., Ph.D. Research work carried out at University College, Dundee. Presently engaged in research photographic chemistry. Publishing under authorship McKenzie and Tattersall, probably in November 1925. (*Signed by*) Alex. McKenzie, O. Rhys Howell, R. Roger, John Foggie.

THORPE, WILLIAM VEALE, 270, Balham High Road, London, S.W. British. Research Student, Medical Research Council, Mount Vernon, Hampstead, N.W. 3. B.A. (Cambridge Natural Science Tripos, Parts I and II). One year's research at Mount Vernon. (*Signed by*) W. J. Pope, Jocelyn Thorpe, Hamilton McCombie, W. H. Mills.

TOWLER, WILLIAM MILBURN, 28, Denton Ave., Roundhay, Leeds. British. Student. B.Sc. Hons. Chemistry, Leeds University. (*Signed by*) H. M. Dawson, P. K. Dutt, H. Holness.

TRAILL, DAVID, 58, Chalmers St., Dunfermline, Scottish. Research Student. B.Sc. (1st Cl. Hons. Chemistry, St. Andrews), 1923. Research in Organic Chemistry, 1923–1925. Macbeth and Traill, *T.*, 1925, **127**, 892; and 1118. (*Signed by*) A. Killen Macbeth, Irvine Masson, James Craik.

TRICKER, ELVERA ANNIE, 319, Norwich Rd., Ipswich. British. Student of Chemistry at Bedford College. (*Signed by*) J. F. Spencer, H. Crompton, J. Stewart.

TURNER, DONALD MORRISON, 40–42, Lexington St., W. 1. British. Representative of Mead Johnson & Co., Food Specialists. M.Am.Chem.Soc. Ten years Asst. Analyst, Govt. Laboratory, Newfoundland. Desire to receive the publications of the Society and keep in touch with modern work. (*Signed by*) D. James Davies, G. S. W. Marlow, F. S. Aumonier.

TURNER, GEOFFREY, 85, Winchester Avenue, Leicester. English. Research Student, attending Loughborough College, Leics. B.Sc. (2nd Class Honours, London); Diploma of Loughborough College (Honours). (*Signed by*) A. Bramley, A. T. Eggington, G. Lawton.

TYLER, NORMAN LEOPOLD, 9, St. Paul's Gardens, Spennymoor, Co. Durham. British. Chief Chemist and Manager of Messrs. Intermediates and Explosives, Ltd., Dean and Chapter Colliery, Ferryhill, Co. Durham. City and Guilds and South Kensington Examinations, Inorganic and Organic. South Staffs. Scholarship Metallurgy., Iron and Steel. Secretary of N.E. Section of the British Association of Chemists. Fourteen years with Messrs. Chance and Hunt, Ltd., Oldbury and Wednesbury. Chemist in Charge of several plants for eight years. (*Signed by*) S. I. Levy, L. R. B. Pearce, W. A. S. Calder.

VERNON, HERBERT WARD, 245, Albert Rd., London, N. 22. British. Research Chemist. B.Sc. in Hons. Chemistry of Victoria University, Manchester. Held post as Research Chemist for last nine years. (*Signed by*) Percy C. C. Isherwood, B. H. Bowles, R. E. Brett.

WEBB, FREDERICK HENRY, "St. Malo," Jameson Road, Harpenden. British. Manufacturing Chemist and Optician. (1) Early Education at the Dunstable Grammar School. (2) Studied Analytical Chemistry under J. B. Hoblyn, B.Sc., F.I.C. (3) Studied Chemistry and Physics at the London School of Chemistry under Henry Wootton, B.Sc. (4) Passed the Qualifying Examination of the Pharmaceutical Society in 1910. (5) Passed the Qualifying Examination as a Fellow of the National Association of Opticians in 1923. Particularly interested in Analytical and Scientific work. (*Signed by*) Frank B. Arnold, J. J. Laws, Percy Barrs.

WILLIAMS, EWART HARROD, 31, Thornsbeach Road, Catford, S.E. 6. British. Chemist, Government Laboratory, Clement's Inn Passage, W.C. B.Sc. (Hons. Lond.), A.C.G.F.C., A.I.C. Research work at Finsbury Technical College with Prof. A. J. Hale, and at the Government Laboratory with Dr. J. J. Fox. I desire to keep in touch with modern developments in Pure and Applied Chemistry, through the Society's Journal, and by attending the Scientific Meetings of the Society. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox, A. G. Francis.

WILLIAMS, GWYN, Cae Ffynnon, Llandudno Junction, North Wales. Welsh. Research Student in Chemistry at University College of North Wales, Bangor. 1924, B.Sc. (Wales) with 1st Class Hons. in Chemistry. 1924–5, Research Student at University College, Bangor. (*Signed by*) Kennedy Orton, F. G. Soper, H. B. Watson.

WILLIAMS, HUGH AMPHLETT, 249, Kennington Rd., S.E. 11. English. Student. Student of the Institute of Chemistry, desiring the use of the Library and the Periodicals. (*Signed by*) George A. Stokes, Ernest W. Wright, A. J. Hale, H. M. Atkinson.

WILLIAMS, ROBERT HARDING, 131, Anlaby Road, Hull. British. Chemist (Pharmaceutical), practising as a Chemist at above address. (Leeds University Matric.). Two years at Swansea Municipal College (3rd year Medical Student). M.P.S. (1907). One year Hull Technical College. Was 2 years as Chemist in Middlesbro' (Analytical), and have been in business at above address nearly 4 years. Have been doing analytical work for a number of years. (*Signed by*) Harry Thompson, Thos. A. Nightscales, Edward Chapman.

WILTSHIRE, JOHN LAURENCE, 36, Fordel Road, Catford, London, S.E. 6. English. Assistant Works Chemist to Messrs. Burt, Boulton, and Haywood, Coal Tar Distillers, London. B.Sc. London, 2nd Class Honours in Chemistry (1925). Three years' experience with consulting analyst (Mr. F. W. Harbord). Now occupied as above and in pure chemical research under Mr. E. de B. Barnett at the Sir John Cass Technical Institute, London. (*Signed by*) E. de Barry Barnett, Marcus A. Matthews, James W. Cook.

WOLFE, JOHN JAMES BENJAMIN, 24, Greyhound Road, Hammersmith, W. 6. English. Student (Research), East London College. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones.

WRIGHT, GORDON MITCHELL, University Chemical Labs., Cambridge. British. Research Chemist. M.A. (Cantab.), B.Sc. (Glasgow). (*Signed by*) Hamilton McCombie, A. C. P. Lunn, Harold A. Scarborough.

WYATT, WILFRED FISHER, North Anston, Nr. Sheffield. British. Demonstrator in Chemistry, the University of Sheffield. B.Sc. Hons. Chemistry, 1923, Sheffield University; M.Sc., 1924, Sheffield University. (*Signed by*) W. P. Wynne, F. G. Tryhorn, G. M. Bennett, Arthur W. Chapman.

ZIMMERMANN, JOHN FREDERICK, 17, Stile Hall Gardens, Chiswick, W. 4. British. Research Chemist. Diploma of Engineer Chemist, Zurich Poly-

technicum. 2½ Years as Assistant to Dr. Tcherniac. (*Signed by*) J. Tcherniac, A. G. Bloxam, C. S. Gibson.

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From the Publishers: Herren Urban & Schwarzenburg.

BARBAUDY, JEAN. Contribution a l'étude de la distillation des mélanges ternaires hétérogènes. Paris 1925. pp. iv + 156. ill. (*Recd.* 11/11/25.) From the Author.

EUCKEN, ARNOLD. Fundamentals of physical chemistry. Translated and adapted from the 2nd German edition by ERIC R. JETTE and VICTOR K. LAMER. New York 1925. pp. xxiv + 700. ill. 27*s.* 6*d.* net. (*Recd.* 12/11/25.)

From the Publishers: The McGraw-Hill Publishing Co.

JOURNAL OF THE CHEMICAL INDUSTRY. Vol. I, etc. Moscow 1924 +. [In Russian.] (*Reference.*) From Dr. M. Nierenstein.

KOPACZEWSKI, W. Introduction a l'étude des colloïdes: état colloïdal et ses applications. Paris [1925]. pp. viii + 226. ill. 16 *fr.* (*Recd.* 2/11/25.)

From the Publishers: MM. Gauthier-Villars et Cie.

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UNITED STATES. *Department of Agriculture.* Department Bulletin No. 1323. Citrus pectin. By HOMER D. POORE. Washington 1925. pp. 19.

—— *Department of Commerce.* Bureau of Standards. Technologic Paper No. 273. Performance tests of a liquid laundry soap used with textile materials. By F. R. MCGOWAN, F. W. SMITHER, and CHARLES W. SCHOFFSTALL. Washington 1924. pp. 26. ill.

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WORLEY, FREDERICK PALLISER. A new view of atomic structure and the relationship of the chemical elements. (From the *Rept. Austral. Assoc. Adv. Sci.*, 1923, **16**.) ill.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Informal Lecture, Thursday, November 26th, 1925, at 6 p.m., Dr. N. V. SIDGWICK, M.A., F.R.S., Vice-President, in the Chair.

The CHAIRMAN mentioned that this was the first of the Informal Lectures to be given by the Society, and then called upon Professor R. Robinson, D.Sc., F.R.S., to deliver his Lecture entitled: "Recent Research on the Structural Relationships of some Plant Products."

At the conclusion of the Lecture a Vote of Thanks to the Lecturer was proposed by Professor T. M. Lowry, seconded by Dr. R. H. Pichard, and carried with acclamation, Professor Robinson making due acknowledgment.

Ordinary Scientific Meeting, Thursday, December 3rd, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
James Kerr Erskine	Dec. 5th, 1889.	April, 1925.
Robert Walter Oddy	May 15th, 1890.	Nov. 24th, 1925.
William Robert Lang	March 4th, 1897.	Nov. 20th, 1925.

Certificates were read for the first time in favour of:

Dattatraya Vishwanath Bal, Rothamsted Experimental Station, Harpenden.
Bernard Meredith Brown, B.Sc., F.I.C., Hill Close, Croham Manor Road, S. Croydon.
Frederick Leslie Clark, 170, Barnsley Road, Sheffield.
Reginald Clifford Fawcett, B.Sc., The Cottage, Pentre, Wrexham.
Ko Ko Gyi, Agricultural College, Mandalay.
Tom Heap, B.Sc., Birch Mount, Church Road, New Mills, Stockport.
Stanley Barker Johnson, c/o Colombo Gas & Water Co., Ltd., Colombo, Ceylon.
Leonard George Jupp, B.Sc., A.R.C.S., 6, Chesham Road, Kemp Town, Brighton.
Horace Alfred Mayes, B.Sc., The Cottage, Sewage Works, Vicarage Lane, East Ham, E. 6.

Henry Geoffrey Ordish, B.A., Chilcombe, Milton Road, Harpenden.
Arnold Piukus, 238, Amhurst Road, Stoke Newington, N. 16.
Clifford Burrough Purves, B.Sc., Edenbank, Cupar.
Suresh Chandra Ray, P.O. Alambazar, Ray Villa, Calcutta.
Edna Clark Smith, B.Sc., 9, Gilston Road, S.W. 10.
Sidney David Sutton, 2, Glasshouse Street, W. 1.
Raymond Taylor, M.A., B.Sc., St. Brelades, Woodside Road, Parkstone.
Richard Victor Thomas, B.A., 17, Pretoria Road, Cambridge.
Henry Wilkins, B.Sc., 13, Kinfauns Road, Goodmayes.
Reginald Frank Wright, A.R.C.S., Fairhazel, Avondale Road, Hove.

Messrs. E. Horton and W. B. Saville were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Robert Leslie Andrew.
Louis Baissac.
William Francis Barker, Ph.D.
Ralph Basden.
Frank Bell.
Arthur Neville Copnall Bennett, B.Sc.
Harold Frederick Betts, B.Sc.
John Cecil Bird, B.Sc., A.I.C.
Lionel Christopher William Birkett, B.Sc.
James Boyd, F.I.C.
Frank Symonds Bradhurst.
Edward Britnell, B.Sc.
Reginald John Bromfield.
Francis Hereward Burstall, B.Sc.
Archer John William Butterfield.
John Hildred George Carlile, B.Sc., A.R.C.S.
Leslie James Chalk, B.Sc.
Rama Charan, B.Sc., B.Sc.Tech.
John William Corran, B.Sc., Ph.D., A.I.C.
John Harold Cottier.
Edward Mortimer Crowther, D.Sc., F.I.C.
Bertram Cuthbert.
Frank Edwin Dickinson.
Joseph Raymond Dolphin, B.Sc.
William Donovan, M.Sc.
John Stanley Dunn, M.A., Ph.D., A.I.C.
John Horsfall Dyde.
George Malcolm Dyson, B.A., B.Sc., Ph.D.
Alfred Eccles, B.Sc.
Edwin Francis Edwards.
John Moelwyn Edwards.
George Albert Elliott, M.Sc.
Eric Bertram Evans, B.Sc.
Elinor Katharine Ewbank, B.A.
Elizabeth Monica Openshaw Farrow, M.A.
Oliver Free, B.A.
William Marshall Freeman.
Eva Florence Gee.
James Walter Shanks Gemmell, B.Sc.
Francis Reginald Glover.
William Bouch O'Brien Goudielock.
Felix John Theodore Grigg, M.Sc., A.I.C.
George Vincent Hall, B.Sc.
John Hall, M.Sc., A.I.C.
William Rowan Hare.
Walter Healey.
Thomas Henderson, M.C., M.A., B.Sc.
Herbert Sim Hirst.
Syed Husain, M.Sc.
Toru Iwadare.
David Christopher Mendis Jayewardene.
Gilbert Jessop, M.Sc., Ph.D.
Charles Benjamin Johnson.
Walter Idris Jones, B.Sc., Ph.D.
Henry Wilfrid Keenan.
Brian Charles Lavers Kemp, B.A.
Charles King.
Frederick Karl Victor Koch, B.Sc., A.R.C.S.
Charles Dudley Langford, B.Sc., A.R.C.S.
Banarsi Das Laroia, B.A., B.Sc.
Henry Guinness de Laszlo, B.A., Ph.D.
Bertram Grey Leatherbarrow.
Sam Lenher, B.A.
John Joseph Lennon, M.Sc.

William Macartney.
Ivan Roy McHaffie, B.A., M.Sc.
Neil McLean, M.A., B.Sc.
Leslie George Manchester, B.Sc.
William Alfred Nottage Markwell.
William Francis Martin, F.I.C.
Charles Henry Lawrence Miller, B.Sc.
Edgar Calvin le Roy Miller, M.D.
Arthur Moore.
Alexander John Morrison.
Frank Richard Morrison.
John Blackburn Murgatroyd.
Chitsukhlal Hiralal Nanavati.
Henry Nicholson, M.Sc.
Anna Maria O'Meara.
Horace Winston Palmer, B.Sc.
Norman Frederick Parker, B.A., A.I.C.
Austin McDowell Patterson.
Ernest Phillis, B.Sc.
Jonathan Pollitt, B.A.
Charles Raymond Porter, M.Sc., A.I.C.
Evan Emrys Price, B.Sc.
Marjorie Ellen Pring, B.Sc.
Jnanendra Nath Rây, M.Sc.
Herbert Charles Roberts.
Phyllis Mary Sanderson.
Rose Rachel Sass, B.Sc.
Robert Saxon, B.Sc.
Rupert Boswood Scammell, B.Sc.
Albert Sciver, B.Sc., A.I.C.
George Baty Scott.
Upo Shin.
Albert Louis Auguste Sigot.
Dalip Singh, Ph.D.
Frederick Francis Percival Smith, B.A., B.Sc.
Robert Frederick Smith.
William Ernest Soper, B.Sc.
Herbert Kenneth Southern, M.Sc.
Eric Alfred Speight, B.Sc.
Frank Harland Swire.
Harold James Tattersall, B.Sc., Ph.D.
William Veale Thorpe, B.A.
William Milburn Towler, B.Sc.
David, Traill, B.Sc.
Elvera Annie Tricker.
Donald Morrison Turner.
Geoffrey Turner, B.Sc.
Norman Leopold Tyler.
Herbert Ward Vernon, B.Sc.
Frederick Henry Webb.
Ewart Harrod Williams, B.Sc., A.I.C.
Gwyn Williams, B.Sc.
Hugh Amphlett Williams.
Robert Harding Williams.
John Laurence Wiltshire, B.Sc.
John James Benjamin Wolfe.
Gordon Mitchell Wright, M.A., B.Sc.
Wilfred Fisher Wyatt, M.Sc.
John Frederick Zimmermann.

The following papers were read:

"On the Budde effect in bromine. Part I. The photoactive constituent in wet bromine." By B. Lewis and E. K. Rideal.

"On the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and dry bromine." By B. Lewis and E. K. Rideal.

"The influence of carbon rings on the velocity of reactions involving their side-chains. Part I. The hydrolysis of cyclic and open-chain malonic esters." By R. Gane and C. K. Ingold.

"The density of boric oxide glass and the suspected variation in the atomic weight of boron." By H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson.

Ordinary Scientific Meeting, Thursday, December 17th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	*Died.*
George Frederick William Blackburn	May 15th, 1913.	Nov. 23rd.
Edmund Knecht	Dec. 1st, 1910.	Dec. 8th.
James Grant	Feb. 6th, 1890	Dec. 7th.

The PRESIDENT announced that:

1. A Special Lecture will be delivered by Professor J. Barcroft, F.R.S., entitled "Hæmoglobin" on Thursday, February 11th, 1926, at 8 p.m. The Lecture will be held in the Chemistry Theatre of the University College, Gower Street, W.C. 1, by the kind permission of the College Authorities.

2. British Chemical Abstracts "A," Pure Chemistry for 1926, printed on one side of the paper only, and gummed or ungummed, will be obtainable by Fellows at the price of £3 0*s*. 0*d*., post free. Application should be made to the Assistant Secretary, Mr. S. E. Carr, as soon as possible.

The following were formally admitted Fellows of the Chemical Society: Thomas M. Sharp, Arthur Moor, Cecil J. May, J. F. Zimmermann, F. Bell, C. D. Langford,and J. M. Edwards.

Certificates were read for the first time in favour of:

Edwin Melhuish Bailey, Almond Hill, Pumpherston, Midcalder.
Carl Howard Collie, B.A., New College, Oxford.
William Eric Downey, Ph.D., Imperial College of Science and Technology, S. Kensington, S.W. 7.
Andor Fodor, Ph.D., Hebrew University, Jerusalem.
Herbert Harris, B.Sc., Ph.D., A.R.C.S., 1, Royal York Villas, Clifton, Bristol.
Ralph Harry Klein, A.I.C., 11, Park Place Villas, Maida Hill, W. 2.
Montague Alexander Phillips, A.I.C., 31, Cator Street, S.E. 15.
Devasikhamani Sunderavelu Pillai, 37, Hill Street, Stoke-on-Trent.
Charles Aylmore Ray, B.A., 47, Somerford Grove, Tottenham, N. 17.
Ivy Winifred Elizabeth Rogers, 8, St. Lawrence Road, W. 10.
Ronald Stanley Russell, B.A., 47, Redington Road, Hampstead, N.W. 3.
Robert John Schaffer, B.A., B.Sc., 3, Hambalt Road, S.W. 4.
Charles Richard Noël Strouts, B.A., B.Sc., A.I.C., Westminster Bank, Kew Gardens, Surrey.
Frank Sherwood Taylor, M.A., B.Sc., 21, Shortlands Road, Shortlands, Kent.
Claude Stanley Watson-Will, Musgrave Road, Indooroopilly, Brisbane.
Idris Williams, B.A., 19, Silver Street, Cambridge.

The meeting was then adjourned, and the Informal Meeting declared open.

The Council has made the following Grants from the Research Fund:

	£	s.	d.
Preparation and investigation of rare earth carbides. N. L. Anfilogoff	10	0	0
Preparation of phenanthrenes from stilbenes. J. N. Ashley ...	5	0	0
Investigation of certain binary and ternary systems. C. R. Bailey	5	0	0
Synthesis of genistein. W. Baker	15	0	0
Studies in the anthracene series (*contd.*). E. de B. Barnett ...	5	0	0
(*a*) Studies in aliphatic and cyclic sulphides			
(*b*) Reactivity of some quinoxaline bases. G. M. Bennett ...	5	0	0
Study of the mutual solubility relations of certain binary liquid systems. H. F. Betts	3	0	0
The dynamic isomerism of menthyl–cotarnine and of assymmetrical xanthydrols. B. C. Chatterjee	12	0	0
Thiocyano- and selenocyano-groups in the aromatic nucleus. F. Challenger	5	0	0
Preparation and study of certain polyhydroxy derivatives of diphenic acid. G. H. Christie	5	0	0
Synthesis of substituted tri- and tetra-methylene ring derivatives from compounds obtained by condensation of malonic ester with aldehydes. H. Clayton	5	0	0
Anthranyl ketones. J. W. Cook	5	0	0
Addition of bivalent carbon compounds to bodies of the diazomethane class. K. Cooper	5	0	0
Stability of Schiff's bases. P. K. Dutt	5	0	0
Conversion of asymmetric bromo compounds into the corresponding sulphonic acids. E. B. Evans	5	0	0
Influence of the benzoyl group on the mobility of the three-carbon tautomeric system. M. D. Farrow	10	0	0
Studies in the catalytic activity of charcoal. J. B. Firth ...	10	0	0
Solubility relationships of alums and pseudo alums. S. Glasstone	3	0	0
Study of alkylene thiosulphates and of alkylene disulphonic acids. J. Goodspeed	5	0	0
Quasi-aromatic structure (*contd.*). F. R. Goss	5	0	0
Properties of conjugated compounds. A. T. Healey	6	0	0
Periodic chemical reactions. E. S. Hedges	15	0	0
Substitution in the aromatic nucleus. W. J. Hickinbottom ...	4	0	0
Photochemical combination of hydrogen with other gases. H. S. Hirst	7	0	0
(*a*) Synthetical experiments in the anthocyanidin series ...			
(*b*) Synthesis of indole derivatives. H. R. Ing	10	0	0
Conditions of equilibrium between alkali and alkaline earth halides and the alcohols (*contd.*). W. J. Jones	8	0	0
The chemistry of the three-carbon system. L. G. Jupp ...	8	0	0
(*a*) Reaction with ammonia of various unsaturated cyano esters (*b*) Methylation and ethylation products of various unsaturated cyano amides. (Miss) W. Kilroy	5	0	0
Lactone formation from the $\alpha\alpha'$- $\beta\beta'$-dibromo adipic acids. C. D. Langford	6	0	0
Properties of conjugated compounds. B. D. Laroia	6	0	0
Substituted diphenyl compounds. R. J. W. Le Fèvre	5	0	0

	£	s.	d.
Condition of formation and stability of carbon rings. J. J. Lennon	8	0	0
Action of nitric acid on unsaturated hydrocarbons. (Miss) P. V. McKie	10	0	0
Synthesis of (*a*) Degradation product of brucine, and (*b*) Harmaline and some of its derivatives. R. H. F. Manske ...	10	0	0
The effect of bulky groups on the mobility of the 3-carbon system. C. J. May	5	0	0
Researches on thallium compounds (*contd.*). R. C. Menzies ...	8	0	0
Three carbon tautomerism. B. T. Narayanan	6	0	0
Kinetics of the induction period of the hydrogen-chlorine reaction with ultra-violet light. R. G. W. Norrish	10	0	0
Action of ozone on dry iodine. H. W. Palmer	5	0	0
Nitration of substituted phthalides. J. N. Rây	7	0	0
Reactions between 1 : 3-diketones and amino and amido bodies. E. Roberts	5	0	0
Investigation of certain sesquiterpenes. J. M. Robertson ...	5	0	0
Properties of unsaturated cyclic ketones. J. Ross	5	0	0
The direct introduction of substituents into a mono-substituted diphenyl. H. A. Scarborough	5	0	0
Preparation and properties of various types of halogenated naphthalene derivatives. J. B. Shoesmith	10	0	0
Researches on sulphuryl chloride and chlorination. O. Silberrad	5	0	0
Influence of substituents on the stability of certain spiro and associated ring systems. S. S. G. Sircar	6	0	0
The basic salts, salts of mixed acids, and complex salts of metals of the 3rd and 8th periodic groups. J. D. Main Smith ...	12	0	0
Nitration studies of tertiary aromatic amines. J. M. Smith ...	5	0	0
Condensation reactions with certain β-halogenated acids. M. G. Thomson	5	0	0
Introduction of the methylene-dioxy group and of similar groups into the aromatic nucleus. V. M. Trikojus	8	0	0
Conversion of substituted aromatic amines into quinolines. E. E. Turner	5	0	0
Effect of polar substituents on the Walden inversion among benzene derivatives. E. E. Turner	5	0	0
The chemistry of molybdenum. W. Wardlaw	5	0	0
Reaction of halogens with aliphatic acids, anhydrides, and allied substances. H. B. Watson	5	0	0
(*a*) Spatial structure of *cyclo*paraffins			
(*b*) Constitution of the mono-chloro- and mono-bromo-methyl succinic acids. W. A. Wightman	5	0	0
(*a*) The migratory aptitudes of methoxy-phenyl groups			
(*b*) Experiments upon phthalophenone derivatives, etc. E. W. Wignall	10	0	0
Structural mobility in dihydromuconic systems. R. F. Wright .	5	0	0
Total	£388	0	0

List of papers, or abstracts thereof, received between November 20th and December 17th, 1925. (This list does not include titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"The mechanism of the formation of *o*- and *m*-hydroxybenzaldehydes from the nitration product of benzaldehyde." By H. H. HODGSON and H. G. BEARD.

"The constitution of the normal monosaccharides. Part III. Rhamnose." By E. L. HIRST and A. K. MACBETH.

"Resolution of *dl*-dicentrine." By R. D. HAWORTH, W. H. PERKIN, and J. RANKIN.

"Synthetical experiments in the *iso*quinoline group. Part VI. A synthesis of derivatives of paraberine." By R. CAMPBELL, R. D. HAWORTH, and W. H. PERKIN.

"The action of alkaline arsenites on some halogenated organic compounds." By I. E. BALABAN.

"The equivalent conductivity of solutions of sodium hydroxide and the mobility of the hydroxyl ion." By H. R. RAIKES, A. F. YORKE, and F. K. EWART.

"An investigation of the zirconium in Colorado pitchblende." By O. FREE.

"Some products from the resins of *Xanthorrhœa, Hastilis, X. Arborea*, and *X. Reflexa*." By H.H. FINLAYSON.

"The nitration of β-naphthoic acid and some new amino- and nitronaphthoic acids." By H. A. HARRISON and F. A. ROYLE.

"Preparation of *p*-bromophenylhydroxylamine by the emulsification process. A modification." By R. D. HAWORTH and A. LAPWORTH.

"Optical activity and the polarity of substituent groups. Part III. Menthyl acetophenone-*o*-carboxylate." By H. G. RULE and J. SMITH.

"The crystal structure of catechol." By W. A. CASPARI.

"The chlorination and bromination of 4-aminodiphenyl." By H. A. SCARBOROUGH and W. A. WATERS.

"Studies of dynamic isomerism. Part XXI. The velocity of mutarotation of glucose and of tetramethylglucose in aqueous alcohols." By E. M. RICHARDS and T. M. LOWRY.

"Studies of dynamic isomerism. Part XXII. The velocity of mutarotation of glucose and of tetra-acetylglucose in aqueous acetone." By G. G. JONES and T. M. LOWRY.

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